MATS UNIVERSITY

NAAC GRADE A+ ACCREDITED UNIVERSITY

MATS CENTRE FOR OPEN & DISTANCE EDUCATION

Inorganic Chemistry II

Master of Science

Semester - 2

SELF LEARNING MATERIAL

CC 07

INORGANIC CHEMISTRY II

MATS University

INORGANIC CHEMISTRY

CODE: ODL/MSS/MSCCH/201

S.No	Module No	Unit No	Page-no
01	Module 01	**THEORIES OF METAL COMPLEXES**	1-73
	Unit 01	Introduction to Metal Complex Theories	1-14
	Unit 02	Valence Bond Theory (VBT)	14-33
	Unit 03	Ligand Field Theory (LFT)	23-33
02	Module 02	**SPECTRAL & MAGNETIC CHARACTERISTICS OF METAL COMPLEXES**	34-178
	Unit 04	Introduction to Spectral & Magnetic Characteristics	34-46
	Unit 05	Electronic Transitions in Metal Complexes	46-59
	Unit 08	Effects on Spectra	59-72
	Unit 09	Magnetic Characteristics of Metal Complexes	73-90
	Unit 10	Advanced Magnetic Concepts	90-110
03	Module 03	**REACTION MECHANISMS OF TRANSITION METAL COMPLEXES – PART I**	111-150
	Unit 11	Introduction to Reaction Mechanisms	111-123
	Unit 12	Energy Profile of Reactions	123-128
	Unit 13	Kinetics of Octahedral Substitutions	128-137
	Unit 14	Anation Reactions	137-150
04	Module 04	**REACTION MECHANISMS OF TRANSITION METAL COMPLEXES – PART II**	150-159
	Unit 15	Substitution Reactions in Square Planar Complexes	150-159
	Unit 16	Redox Reactions in Metal Complexes	159- 167
	Unit 17	Outer-Sphere & Inner-Sphere Reactions	167-180
05	Module 05	**METAL & COMPLEXES**	181-216
	Unit 18	Introduction to Metal ð Complexes	181-196
	Unit 19	Metal Carbonyl Complexes	196-203
	Unit 20	Transition Metal-Nitrosyl Complexes	203-211
	Unit 21	Dinitrogen & Dioxygen Complexes	211-216
		REFERENCES	217-218

COURSE DEVELOPMENT EXPERT COMMITTEE

1. Prof. (Dr.) Ashish Saraf, HoD, School of Sciences, MATS University, Raipur, Chhattisgarh
2. Prof. (Dr.) Vishwaprakash Roy, School of Sciences, MATS University, Raipur, Chhattisgarh
3. Dr. Prashant Mundeja, Professor, School of Sciences, MATS University, Raipur, Chhattisgarh
4. Dr. Sandhyarani Panda, Professor, School of Sciences, MATS University, Raipur, Chhattisgarh
5. Mr. Y. C. Rao, Company Secretary, Godavari Group, Raipur, Chhattisgarh COURSE COORDINATOR

Dr. Nitin Kumar Jaiswal, Professor, School of Sciences, MATS University, Raipur, Chhattisgarh

COURSE /BLOCK PREPARATION

Dr. Radha Krishnan, Associate Professor, School of Sciences, MATS University, Raipur, Chhattisgarh

March, 2025

First Edition: 2025 ISBN:978-93-49916-55-5

@MATS Centre for Distance and Online Education, MATS University, Village- Gullu, Aarang, Raipur- (Chhattisgarh)

Printed & Published on behalf of MATS University, Village-Gullu, Aarang, Raipur by Mr. MeghanadhuduKatabathuni, Facilities & Operations, MATS University, Raipur (C.G.)

Printed at: The Digital Press, Krishna Complex, Raipur-492001(Chhattisgarh)

Acknowledgements:

The material (pictures and passages) we have used is purely for educational purposes. Every effort has been made to trace the copyright holders of material reproduced in this book. Should any infringement have occurred, the publishers and editors apologize and will be pleased to make the necessary corrections in future editions of this book.

MODULE INTRODUCTION

Course has five modules. Each module is divided into individual units. Under this theme we have covered the following topics:

S.No	Unit No	Module No
01	**Module 01**	**THEORIES OF METAL COMPLEXES**
	Unit 01	Introduction to Metal Complex Theories
	Unit 02	Valence Bond Theory (VBT)
	Unit 03	Ligand Field Theory (LFT)
	Unit 04	Ligand Field Stabilization Energy (LFSE)
	Unit 05	Factors Affecting the Splitting Parameter (Ä)
02	**Module 02**	**SPECTRAL & MAGNETIC CHARACTERISTICS OF METAL COMPLEXES**
	Unit 06	Introduction to Spectral & Magnetic Characteristics
	Unit 07	Electronic Transitions in Metal Complexes
	Unit 08	Effects on Spectra
	Unit 09	Magnetic Characteristics of Metal Complexes
	Unit 10	Advanced Magnetic Concepts
03	**Module 03**	**REACTION MECHANISMS OF TRANSITION METAL COMPLEXES – PART I**
	Unit 11	Introduction to Reaction Mechanisms
	Unit 12	Energy Profile of Reactions
	Unit 13	Kinetics of Octahedral Substitutions
	Unit 14	Anation Reactions
04	**Module 04**	**REACTION MECHANISMS OF TRANSITION METAL COMPLEXES – PART II**
	Unit 15	Substitution Reactions in Square Planar Complexes
	Unit 16	Redox Reactions in Metal Complexes
	Unit 17	Outer-Sphere & Inner-Sphere Reactions
05	**Module 05**	**METAL & COMPLEXES**
	Unit 18	Introduction to Metal ð Complexes
	Unit 19	Metal Carbonyl Complexes
	Unit 20	Transition Metal-Nitrosyl Complexes
	Unit 21	Dinitrogen & Dioxygen Complexes

These themes of the Book discuss about Theories of metal Complexes and spectral & Magnetic characteristics of Metal complexes. The reaction mechanisms of transition metal complexes have been covered broadly in two Units. The structure of metal complexes with multiple application are also highlighted in the last Unit. This book is designed to help you think about the topic of the particular find relatively easy. This will reinforce your earlier learning.

MODULE- I

THEORIES OF METAL COMPLEXES

OBJECTIVE

- The principal aims of this chapter are:
- To delineate metal complexes & comprehend their importance in coordination chemistry as well as in diverse industrial, biological, & catalytic applications.
- To examine the theoretical frameworks employed to characterize metal complexes, encompassing their foundational concepts, assumptions, & constraints.
- To elucidate Valence Bond Theory (VBT) & its use in comprehending the bonding & geometry of coordination compounds, as well as its limits in precisely predicting magnetic & spectral characteristics.

Unit 1 Introduction to Metal Complex Theories

Metal complexes, or coordination compounds, constitute a rich & important domain of inorganic chemistry that connects basic theoretical principles with a multitude of practical applications. These exceptional, official deals contain a steel (or metallic ion) with attached molecules or ions, known as the ligands. Metal complexes have been studied extensively for over a century, leading to the development of a range of theoretical frameworks to explain their structure, bonding, stability & other chemistries. These theories not only forms the basis for appreciate and comprehend ing the general inherent nature of interactions between metal & the ligands but also guide multiple industrial yields in the span of several fields of science.

Definition of Metal Complexes

When a central metal atom or ion coordinates with one or more the ligands, a metal complex is formed, which results in a unique chemical entity with characteristics that differ from the metal & the the ligands independently. The ligands can either be neutral molecules, such as ammonia or water, or negatively charged ions, such as chloride or cyanide, which donate electron pairs in a coordinate covalent bond with the central metal. The the ligands are binding to the metal (as electron pair acceptors) in a process called coordination, resulting in a structure in which the metal acts as a Lewis acid & the ligands as Lewis bases (electron pair donor).

The nomenclature of metal complexes adheres to specific regulations established by the International Union of Pure & Applied Chemistry (IUPAC). These nomenclature conventions classify the core metal, the types of the ligands, & elemental types, & may also encompass structural data such as geometric isomerism & oxidation states. Significance of standardized nomenclature in coordination chemistry

Core Principles in Coordination Chemistry

At a fundamental level, metal complex formation is a Lewis acid-base interaction in which the metal center is an electron pair acceptor (Lewis acid), & the ligands are electron pair donors (Lewis bases).. For example, hard metal ions (Na^+, Mg^{2+}, Al^{3+}) possessing high charge density & low polarizability have a stronger interaction with hard bases, such as F^-, OH^-, & H_2O, which are characterized by small & highly electronegative donor atoms. This principle predicts the stability of different metal-ligand combinations, & accounts for many trends in coordination chemistry.

The chelate effect is the increased stability that arises when bidentate (or polydentate) the ligands (the ligands that bind through more than one donor atom) are used in place of monodentate the ligands. Perhaps the most significant aspect of this increased stability originates from beneficial entropy differences since, after the metal ion has formed a complex with the chelating the ligands, there are far fewer independent particles in solution.

Stereochemical aspects are central to the chemistry of metal complexes. These electronic & steric factors are the driving forces behind the preference of certain geometric arrangement by different coordination numbers. For example, four-coordinate complexes usually have tetrahedral or square planar structures, & six-coordinate complexes tend to have octahedral shapes.

Another important concept is isomerism in metal complexes, which can take on different forms:

- Structural isomers differ in the connectivity of the atoms in the molecule.
- Stereoisomers same bonds different spatial arrangements
- Geometric isomers (like cis & trans forms) differ in the relative positions of the ligands
- The thing which is called as optical isomer are the non-superimposable mirror images.
- Linkage isomerism occurs when the atom of an ambidentate ligand that is binding to the metal is different.

• Coordination isomers involve the transfer of the ligands between the different metal centers within polynuclear complexes

The 18-electron rule can be a useful tool in predicting the stability of a complex, especially for transition metals. Similar to the octet rule in main group chemistry, this principle states that stable complexes typically possess a total of 18 valence electrons (the total from the metal's d electrons & the total donated by the ligands).

Valence Bond Theory (VBT) is one of the earliest quantum mechanical descriptions of bonding in metal complexes. Based chiefly on work done by Linus Pauling in the 1930s, this theory sought to extrapolate the notion of orbital hybridization—previously useful for rationalizing molecular shapes in organic substances—to coordination chemistry. VBT states that when a metal binds with a ligand to form a complex, its atomic orbitals hybridize to form a new set of equivalent orbitals that are directly pointing towards the the ligands.. For example, when a tetrahedral complex is formed, the metal has sp^3 hybridization, whereas d^2sp^3 hybridization is generally involved in the formation of an octahedral complex (in case of transition metals).

One of the major advantages of VBT is its ability to explain the magnetic behavior of the coordination compounds. The theory differentiates between two types of complexes:

• Outer orbital (high-spin) complexes where the hybridization involves outer d orbitals (4d or 5d) resulting in more unpaired electrons

• Low-spin (inner orbital) complexes, with inner d-orbital (3d) hybridization, producing fewer unpaired electrons

This explains the fact that many transition metal complexes correlate the observed magnetic moments & show that two complexes of the same metal behave differently depending on the nature of the ligands., VBT explains the bonding in octahedral complex $[Co(NH_3)_6]^{3+}$, where the Co^{3+} ion (d^6) uses d^2sp^3 hybridization with only two 3d orbital participating in hybridization & four 3d orbital containing 6 d-electrons in pairs. The inner orbital complex is diamagnetic, as would be expected from experiment.

Theory has a hard time explaining:

• Colors of transition metal complexes due to electronic transition between split d orbitals

• The relative strengths of the different metal–ligand bonds & how these change across the spectrochemical series

• The exact energetics of the complex formation, for example the stabilization energies of specific geometric disposition

Notes

- Complexes & especially the fine structure seen in electronic spectra: detailed spectroscopic characteristics

Crystal Field Theory: Fundamentals and Applications

Crystal Field Theory (CFT), introduced in the 1930s by physicists Hans Bethe & John Van Vleck, represented an important shift in the treatment of metal complexes compared to previous methods. Driven partly by the increasing complexity of metal complexes & their structures, CFT departed from Valence Bond Theory, which had an emphasis on covalent bonding & orbital overlap, & adopted an approach that was predominantly electrostatic, largely interpreting the interaction between a metal ion & its the ligands as arising from the repulsion between the the ligands' electron pairs & the electrons in the metal's d orbitals. CFT assumes that the ligands, treated as point negative charges or dipoles, break the spherical symmetry of the electrical field of the isolated metal ion. This perturbation leads to the common splitting of the degenerates d orbitals of the transition metal into the subsets with the particular energies. The exact splitting pattern for this depends on how the the ligands are arranged geometrically around the metal center.

For tetrahedral complexes the pattern is inverted with the e set at lower energy than the t_2 set. The number of the ligands is also fewer & they do not align as directly with the d orbitals, but consequently the splitting is only about 4/9th the size of that seen in octahedral complexes. In the case of square planar complexes, which are widely observed for d^8 trace metals like Pt(II), they do show a more complex splitting pattern, which causes all 5 d orbitals to obtain different energies. This unique architecture assists to explain why this geometry is common for specific electronics configurations. The complex then looks colored, & the measured color is the complementary color to what was absorbed. This elegantly explains why the same metal can exhibit different colors in different complexes due to different the ligands causing differing magnitudes of d-orbital splitting.

Crystal Field Theory (CFT) led to the generation of the spectrochemical series, a hierarchy of the ligands based on their effective d-orbital splitting. Strong-field the ligands (e.g. CO, CN^-) lead to large splitting & weak-field the ligands (e.g. I^-, Br^-) give rise to small splitting. This series enables the prediction & explanation of the spectroscopic characteristics of a range of complexes. In particular, a high-spin & low-spin concept of transition metal complexes is used in CFT to account for magnetism. An example of a high-spin species is [Ti(H2O)6]+3.209209209210 Death by Pynthesis (orbital pairing energy developing an energetic shortage of one-electron notations for those of Delta (Δ) < P in LotM correct picture 14 mm parentheses)! In contrast, in high-spin complexes, when $\Delta < P$ electrons pair only after all other orbitals (or lower-energy orbitals) are occupied, resulting in a high-spin state with a larger number of unpaired electrons. This framework can successfully account for variable spin states of some complexes of Fe^{2+}, Co^{2+}, & Ni^{2+} based on the the ligands. CFT has also been used to explain the thermodynamic stability of transition metal complexes in terms of Crystal Field Stabilization Energy (CFSE), another success of CFT. This energy is the extra stability provided for a complex by reversibly filling lower-energy d orbitals preferentially. The CFSE also varies systematically across the transition series & overlaps with experimental quantities such as hydration enthalpies, lattice energies & stability constants.

Notes

Ligand Field Theory: Concepts evolved from Crystal Field Theory

Ligand Field Theory (LFT) developed in the 1950s as an attempt to provide a more advanced treatment for the metal complexes, partly sidestepping some of the limitations of CFT without doing away with the general terminology. Originally developed in the early 1950s by Carl Ballhausen, John Griffith, & Leslie Orgel, ligand field theory (LFT) is a hybrid between the molecular orbital treatment & the crystal field view, incorporating molecular orbital character into the crystal field model. The key insight that forms the basis of LFT is that metal-ligand bonding must include a substantial covalent contribution rather than proceeding purely on an electrostatic basis. This appreciate and comprehend ing was pivotal at describing various complex behavior which were hard to comprehend with pureCFT, especially for those paramount π-acceptor & π-donor the ligands such as carbonyl (CO) or cyanide (CN^-) complexes. In LFT, the splitting of d orbitals arises due to both electrostatic repulsions (as in CFT) & orbital interaction (between metal & the ligands). The theory makes a distinction between two classes of interaction between orbitals:

- σ-bonding (head-on overlap between metal and ligand orbitals)
- π (pi)-bonding, i.e. sideways overlap of appropriate orbitals

This distinction enables the LFT to account for the spectrochemical series on a more fundamental basis. Strong-field the ligands such as CO & CN^- are high in the series because they donate electron density through σ-bonds and accept electron density from filled metal d orbitals through π-back-bonding. This π-acceptor behavior gives rise to an effective splitting of the d orbitals that exceeds expectations based only on electrostatic arguments. On the other hand, the ligands with filled p orbitals, like halide or oxide ions, are able to undergo π-donation to the metal, reducing the energy gap between t_2g & eg orbitals in octahedral complexes. Therefore, this π-donor nature explains their lower position in the spectrochemical series, such as these the ligands.

Notes

LFT more accurately describes bonding in square planar complexes, especially common for d^8 metals such as Pt(II) & Pd(II). This combines with consideration of strong σ & π interactions along both diagonal axes xy to rationalize the stability of this geometry for these charge configurations; no doubt explains the remarkable stability of complexes such as cisplatin $[Pt(NH_3)_2Cl_2]$! One other aspect regarding the merits of LFT is its ability to accommodate charge transfer bands in the absorption spectra. Although d-d transition (between split d orbitals) give rise to relatively weak absorption bands, charge transfer transitions, where the electron is promoted between mostly metal based & mostly ligand based molecular orbitals, can be much stronger. LFT distinguishes between:

- Metal-to-Ligand Charge Transfer (MLCT) is typical in complexes with π-acceptor the ligands
- Ligand-to-Metal Charge Transfer (LMCT), typically found in complexes with a more easily oxidized the ligands or high-redox-state metals

These charge transfer transitions are responsible for the sharp spectroscopic characteristics and color of complexes such as $[Fe(CN)_6]^{3-}$ (LMCT) & $[Ru(bpy)_3]^{2+}$ (MLCT). Gaining an appreciate and comprehend ing of these phenomena has been key for applications from photochemistry to materials science. For spin pairing, LFT offers more refined reasoning as it points a finger on orbital interactions. It is capable of explaining various phenomena, such as the temperature-dependent spin crossover phenomenon in which some complexes have their spin states converted between high-spin & low-spin states as external pressure or light irradiation is applied. The role of group theory in the context of LFT has allowed for detailed interpretation of electronic spectra. Using intuition based on symmetry characteristics of metal complexes, researchers can discern which electronic transitions are allowed or forbidden by selection rules, providing the basis for assigning experimental spectral bands & obtaining detailed insights into bonding & electronic structure.

While this leads to order of magnitudes improvement over CFT, Ligand Field Theory is still semi-empirical as it often needs experimental data to find the key parameters, where the latter can not be calculated from quantum mechanics first principles. Such a limitation has become less of an issue with the advent of computational techniques that permit the calculation of ligand field parameters from quantum mechanical calculations.

Instead LFT has modern applications not only to these types of coordination compounds, but also:

- Bioinorganic chemistry elucidating the action of metalloenzymes & metalloproteins
- Material science, assisting in the design of coordination polymers & metal-organic frameworks
- Photochemistry, used in the design of photosensitizers & light-harvesting complexes
- Catalysis, appreciate and comprehend ing reaction mechanisms and catalyst optimization

Ligand Field Theory continues to find application today, illustrating how theoretical models in chemistry do not grow obsolete but are refined & complement each other over time. LFT is an example of a hybrid model that, by leveraging the conceptual clarity of Crystal Field Theory & the more detailed bonding description of Molecular Orbital Theory, achieves the best of both worlds: intuitive conceptualization & quantitative detail.

Metal Complexes — Molecular Orbital Theory

Molecular Orbital Theory (MOT) represents the most comprehensive methodology for understanding bonding in metal complexes, wherein the complete coordination molecule is analyzed inside a singular quantum mechanical framework. Molecular Orbital Theory (MOT) distinguishes itself from Valence Bond Theory and Crystal Field Theory by considering all valence orbitals of the complex, rather than solely those of the metal, thereby providing a more comprehensive understanding of the electronic structure through the formation of molecular orbitals that are delocalized across the entire complex. The MOT principle posits that atoms, including metals and ligands, amalgamate their orbitals to create molecular orbitals that exhibit bonding, antibonding, and non-bonding characteristics. The quantity of molecular orbitals produced corresponds to the amount of atomic orbitals utilized for bonding. Electrons are subsequently allocated to these molecular orbitals in accordance with the Aufbau principle, Pauli exclusion principle, and Hund's rule.

For a standard octahedral complex ML_6, the molecular orbital diagram is constructed by analyzing the interactions between the metal's valence orbitals (often ns, np, and (n-1)d) and the six ligand group orbitals, which are linear combinations of individual ligand orbitals with the appropriate symmetry. This results in the creation of:

- Bonding molecular orbitals, mainly ligand-based but with some metal character
- Primarily metal-based but with some ligand character antibonding molecular orbitals

Notes

- Non-bonding molecular orbitals, which can be purely metal-based (e.g., t_2g orbitals in octahedral complexes lacking π-bonding) or ligand-based

$dz2, dx2\ y2$ –	–	eg
s	–	$a1g$
px, py, pz	–	$t1u$
dxy, dxz, dyz	–	$t2g$

The orbitals own their respective symmetry characteristics, which determine what interaction can occur. In an octahedral complex, the metal eg orbitals (dx^2-y^2 & dz^2) interact strongly with ligand group orbitals of the same symmetry to form σ bonds, while the metal t2g orbitals (dxy, dxz, & dyz) may interact with ligand orbitals of appropriate symmetry to form π bonds if such orbitals are available. MOT naturally captures the π-bonding effects that are of great importance for the characteristics of the complexes. There are two disambiguated kinds of π interactions:

- π-backbonding (or π-backdonation): electrons from filled d orbitals on a metal are donated to empty π* antibonding orbitals on the ligands such as CO or CN^-ℓ

- π-donation methods, in which orbitals filled with electrons at the ligands (-OH^-, Cl^-, etc.) are contributed to empty d orbitals of the metal

These π interactions explain possessions which simpler theories cannot successfully explain, including the very high strength of metal-carbonyl bonds compared to what that would be expected, the trans influence in square planar complexes, & the unique varieties of organometallic compounds. The molecular orbital treatment is especially useful to describe electronic spectra of coordination compounds. MOT, as opposed to CFT, is not limited to d-d transitions, making it useful for examining any potential electronic transitions, including:

- d-d transitions (between the molecular orbitals primarily composed of metal d orbitals)

- Charge transfer transitions (between the molecular orbitals of primarily metal character & the molecular orbitals of primarily ligand character)

• Intraligand (between molecular orbitals localized largely on the the ligands) transitions

Notes

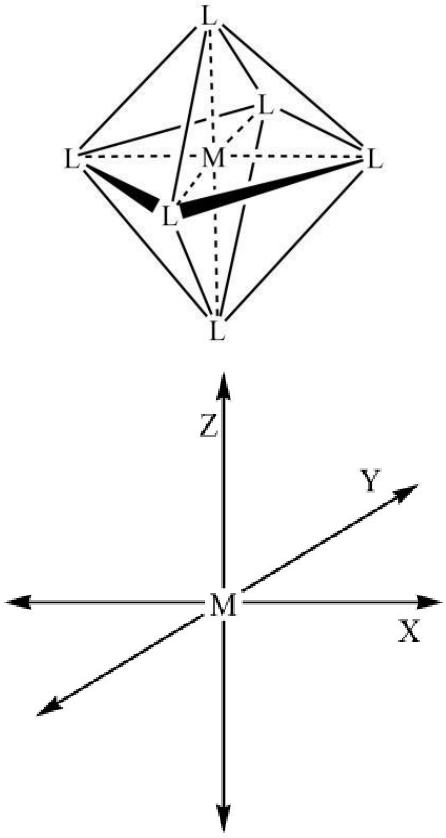


Figure - The octahedral coordination and corresponding σ-basis set for ligand orbitals in octahedral complexes.

The further development of MOT for coordination compounds is a part of the general trend in theoretical chemistry to more integrated & deep-rooted theories. By taking into consideration all electronic interactions in metal complexes, MOT provides the most comprehensive picture of their structure, bonding, & characteristics, creating a solid basis for both fundamental research & practical use in this broad & significant field of chemistry.

MOT constructs molecular orbitals extending over the entire complex & provides the most thorough account of bonding. This means that all kinds of orbital interactions, including the tiny π-backbonding that largely affect the characteristics of the complex, are automatically

Notes

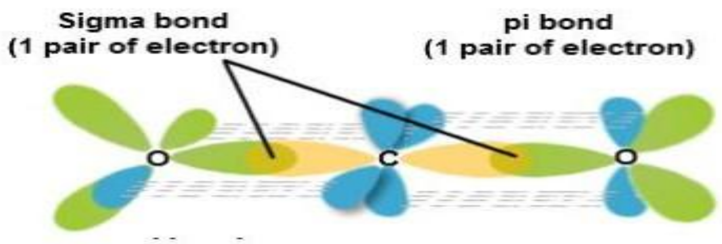
taken into account. Describing Characteristics: For example, VBT provides a model that correlates structural characteristics (i.e., coordination geometries) with the directional character of hybridized orbitals. But CFT, LFT & MOT gives us more & better appreciate and comprehend ing on the reason why specific geometries preferred for electron configurations, producing patterns such as the predominance of square planar complexes for d^8 metals.

Unit 2 Valence Bond Theory (VBT)

Basic Principles & Assumptions

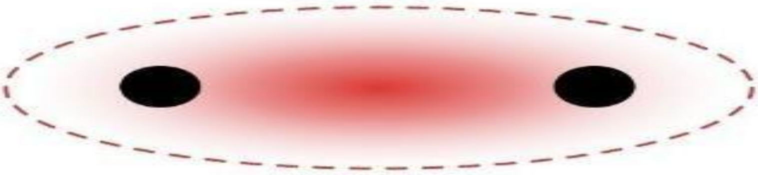
Valence Bond Theory was formulated in the early 20th century as a preliminary quantum mechanical model for chemical bonding. Valence Bond Theory (VBT), initially formulated in the late 1920s and early 1930s by Linus Pauling and colleagues, adopts an alternative perspective on molecule structure, emphasizing the overlap of atomic orbitals to create localized interactions between atoms. The application of quantum mechanics to elucidate Lewis structures changed chemistry. VBT relies on several foundational assumptions. Initially, it posits that a chemical bond occurs when the atomic orbitals of two atoms intersect, allowing their electrons to pair and generate a zone of heightened electron density between the nuclei. The electrons are organized into pairs with opposite spins, adhering to the Pauli Exclusion Principle, hence reducing electrostatic repulsion. Increased orbital overlap results in a stronger relationship. With the advancement of valence bond theory (VBT), the notion of hybridization was introduced, specifically the mathematical amalgamation of atomic orbitals to form hybrid orbitals that had distinct energy, shape, and orientation. The nature of a bond: The bonding process elucidates how different atoms, such as carbon, can form several equivalent bonds while possessing a limited number of valence electrons in the appropriate orbitals. For instance, carbon, possessing a ground state electronic structure of ($1s^2$ $2s^2$ $2p^2$), appears counterintuitive in its ability to form four equivalent bonds, as evidenced empirically in methane. Carbon employs sp^3 hybridization, utilizing one s and three p orbitals to produce four equivalent hybrid orbitals oriented towards the vertices of a tetrahedron, accurately depicting the geometry of methane.

Notes

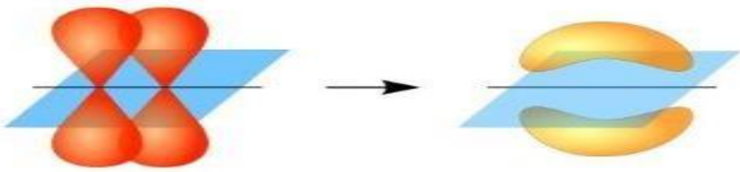


Formation of Sigma and Pi Bonds – Valence Bond Theory (VBT)

These hybridization schemes serve to effectively predict & thus account for the molecular geometries of millions of compounds, particularly organic compounds. In addition, another integral principle of VBT is resonance structures.. This part of VBT describes dipoles between molecules and a lot of physical characteristics of compounds. Sigma (σ) & pi (π) bonds, by the nature of their orbital overlap. Sigma bonds resulta from head-on overlap of atomic orbitals along the internuclear axis, while pi bonds form from parallel overlap of p orbitals that are perpendicular to the bond axis. This distinction accounts for rotational barriers and reactivity patterns in molecules with multiple bonds.



σ bond between two atoms: localization of electron density

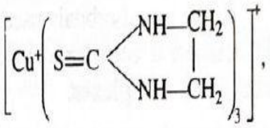


Two p-orbitals forming a π-bond.

Notes

Coordination Number	Type of Hybridisation	Distribution of Hybrid Orbitals in Space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

VBT can also describe color & spectroscopic characteristics of the formed coordination compounds. D-d electronic transitions explain the characteristic colors of transition metal complexes, according to the theory. These transitions happen between split d-orbitals where the energy differences are in the region of visible spectrum. Split nature & magnitude depends on the metal's oxidation state, the ligand field strength, the complex's geometry VBT specifically addresses these through its hybridization models. For hetero nuclear complexes with multiple types of the ligands, the trans effect — the fact that some the ligands can cause incoming the ligands to orient themselves trans to the original ligand during substitution reactions — is addressed by VBT. This phenomenon can be understood in the context of the way in which metal d-orbitals are populated in the presence of a given ligand & how the ligand can preferentially stabilize certain layers of the bond direction more strongly than others.

Coordination number of the central metal atom/ion	Type of hybridisation undergone by the central metal atom/ion	Geometry of the complex	Examples of complexes
2	$sp(4s, 4p_x)$	Linear or diagonal	$[CuCl_2]^-$, $[Cu(NH_3)_2]^+$ etc.
3	$sp^2(4s, 4p_x, 4p_y)$	Trigonal planar or equilateral triangular	 , $[Cu^+Cl(tu)_2]^0$ (distorted trigonal planar) etc.
4	$dsp^2(3d_{x^2-y^2}, 4s, 4p_x, 4p_y)$	Square planar	$[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$
4	$sp^2d(4s, 4p_x, 4p_y, 4d_{x^2-y^2})$	Square planar	$[Cu(NH_3)_4]^{2+}$ $[Pt(NH_3)_4]^{2+}$ etc.
4	$sp^3(4s, 4p_x, 4p_y, 4p_z)$	Tetrahedral	$[NiCl_4]^{2-}$, $[Cu(CN)_4]^{3-}$, $Ni(CO)_4$ etc.
5	$dsp^3(3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$	Trigonal bipyramidal	$Fe(CO)_5$, $[CuCl_5]^{3-}$, $[Ni^{2+}(triars)\ Br_2]^0$
5	$dsp^3(3d_{x^2-y^2}, 4s, 4p_x, 4p_y, 4p_z)$	Square pyramidal	$[Co^{2+}(triars)\ I_2]^0$, $[Ni(CN)_5]^{3-}$ etc.
6	$d^2sp^3(3d_{x^2-y^2}, 3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$	Inner-orbital octahedral	$[Ti(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$ etc.
6	$sp^3d^2(4s, 4p_x, 4p_y, 4p_z, 4d_{x^2-y^2}, 4d_{z^2})$	Outer-orbital octahedral	$[Fe^+(NO^+)(H_2O)_5]^{2+}$, $[CoF_6]^{3-}$ etc.

Notes

Table: Important types of hybridisation found in the first row transition metal complexes and the geometry of the complexes

Limitations of VBT

- VBT cannot account for the relative stabilities of different shapes and different coordination numbers in metal complexes, e.g., it cannot explain satisfactorily as to why Co(+2) (d^8 system) forms both octahedral and tetrahedral complexes while Ni(+2) (d^7 system) rarely forms tetrahedral complexes.
- VBT cannot explain as to why Cu(+2) forms only one distorted octahedral complex even when all the six ligands are identical.
- This theory cannot account for the relative rates of reactions of analogous metal complexes. e.g. [Mn(phen)3]2+ dissociates

Notes

instantaneously in acidic aqueous solution while $[Fe(phen)_3]^{2+}$dissociates at a slow rate.

- The classification of metal complexes on the basis of their magnetic behaviour into covalent (inner-orbital) and ionic (outer-orbital) complexes is not satisfactory and is often misleading.

- VBT fails to explain the finer details of magnetic properties including the magnitude of the orbital contribution to the magnetic moments, i.e. although both tetrahedral (sp^3 hybridisation) and outer-orbital octahedral (sp^2d^2 hybridisation) complexes of Co(+2) (d^7 system) have three unpaired electrons and are, therefore, expected to have μ value equal to 3.87 B.M.; the tetrahedral complexes generally have μ value in the range of 4.4 - 4.8 B.M., while the octahedral complexes have still higher value of μ in the range of 4.7 - 5.2 B.M. The increase in the value of μ is due to the orbital contribution. Similar is the case with tetrahedral and octahedral complexes of Ni(+2) (d^8 system). VBT cannot explain the increase in the value of μ.

- VBT cannot interpret the spectra (colour) of the complexes.

- This theory does not predict or explain the magnetic behaviours of complexes. This theory only predicts the number of unpaired electrons. Its prediction even for the number of unpaired electrons and their correlation with stereochemistry is misleading. VBT cannot explain the temperature dependent paramagnetism of the complexes.

- VBT cannot give any explanation for the order of reactivities of inner-orbital inert complexes of d^3, d^4, d^5 and d^6 ions of the observed differences in the energies of activation in a series of similar complexes.

- The magnetic moment values of the complexes of certain ions (e.g., Co^{2+}, Ni^{2+} etc.) are much higher than those expected by spin-only formula. VBT cannot explain the enhanced values of magnetic moments.

Unit 3 Ligand Field Theory (LFT)

Ligand Field Theory (LFT) is an enhancement of Crystal Field Theory (CFT) that offers a more thorough comprehension of transition metal complexes through the integration of molecular orbital concepts. In contrast to CFT, which regards ligands as simple point charges affecting the d-orbitals of the metal core, a fundamental element of LFT is the notion of molecular orbital overlap between the metal and ligand

Notes

orbitals. This hypothesis acknowledges that ligands contain electron-donating orbitals capable of interacting with the metal's d-orbitals, resulting in the creation of bonding, nonbonding, and antibonding molecular orbitals. The energy disparity among these orbitals affects the electronic transitions responsible for the distinctive hues of transition metal complexes. Furthermore, LFT elucidates the discrepancies in magnetic characteristics encountered in various coordination contexts by examining the degree of orbital interactions and electron delocalization.

Differential Splitting of d-Orbitals in Different Ligand Fields

An octahedral complex contains a central metal ion surrounded by six the ligands located at the corners of an octahedron. These the ligands approach along the ±x, ±y & ±z axes & therefore create a very symmetric environment that interacts differently with the five d-orbitals of the transition metal. In a free metal ion, the d-orbitals are degenerate (energetically equivalent). They split into two unique sets when subjected to an octahedral field however. eg set: Includes dx^2-y^2 & dz^2 orbitals, which extend along the directions toward the the ligands. These orbitals feel stronger repulsive interactions with the ligand electrons, so their energy is higher. t set: dxy, dxz, & dyz orbitals that point between the the ligands. Orbitals with lower energy experience weaker repulsive interactions.

Octahedral complexes have rich spectroscopic behavior. In the case of d^1 configurations, only one absorption band is obtained corresponding to the t2g → eg transition with energy equal to Δo. More complicated spectra are obtained in multi-electron systems due to interelectronic repulsions & selection rules.This tetragonal field degeneracy lowers the symmetry from cubic to tetragonal, where the axial the ligands (along the z-axis) are at different distances from the metal center than the equatorial the ligands (in the xy-plane). With this distortion, the degeneracy of the d-orbitals is further split:

- dz^2 (energy relies on axial ligand distance)
- dx2-y2 (distance to equatorial the ligands affects energy)

The t2g set splits into:

- And dxy (mainly sensitive to equatorial the ligands)
- One degenerate pair: dxz and dyz (touched by both axial & equatorial the ligands)
- (dx^2-y^2) (most energy, axial points of the ligands)
- dxy (in between the ligands in the xy-plane)
- dxz & dyz (degenerate pair)

Notes

- dz^2 (lowest for many cases)

Square planar geometry is especially favored for d^8 metal ions (for instance, Pt^{2+}, Pd^{2+}, Au^{3+}, & strong-field the ligands with Ni^{2+}) where the stabilization by placing eight electrons in all except the highest energy dx^2-y^2 orbital is quite large.. They also exhibit in their electronic spectra (especially those compounds with available d-electrons) several bands of absorption associated with the transitions between the d-orbitals (there are 5, but owing to the crystal field effect, their degeneracy can be destroyed) molecular orbital energy level diagram for σ-bonding in octahedral complexes can be shown as:

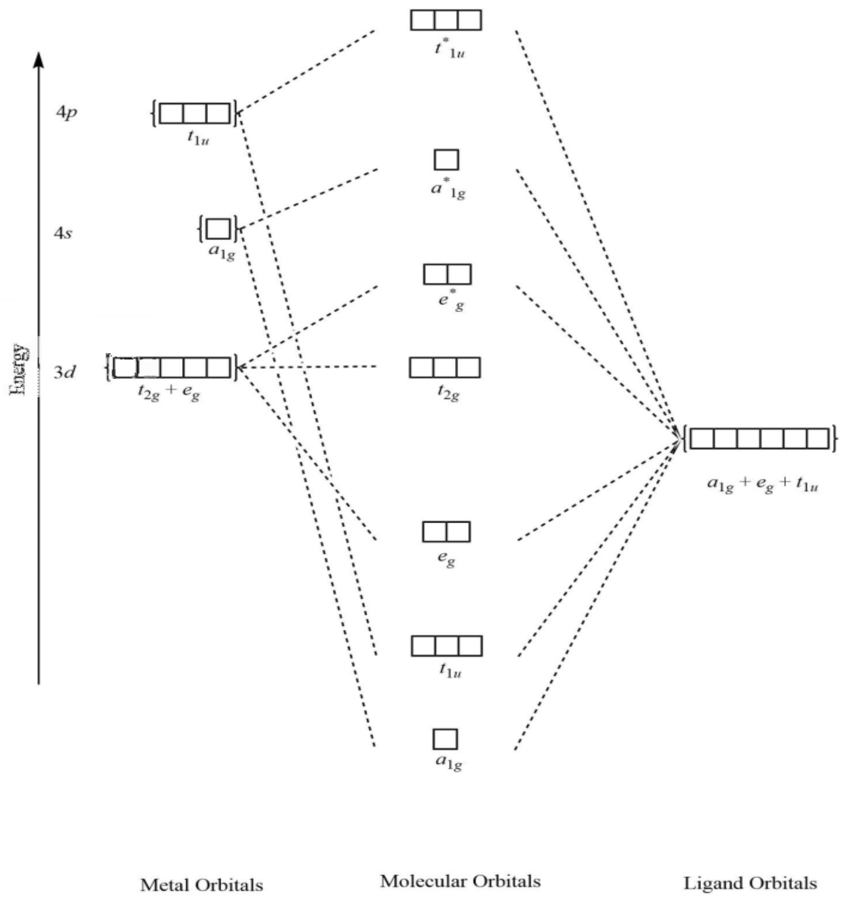


Figure - The formation of σ-molecular orbitals (bonding, antibonding and non-bonding) in octahedral complexes of transition metals.

Tetrahedral Field

The metal ion in tetrahedral complexes is surrounded by four the ligands at the opposite corners of a cube. In contrast to octahedral geometry, the the ligands do not approach along the coordinate axes, but rather along the body diagonals of a cube. Tetrahedral case: The d-orbital splitting in a tetrahedral field is inverted as compared to the octahedral case:

- t2 set: dxy, dxz, & dyz orbitals, of higher energy
- E set: Consists of dx^2-y^2 & dz^2 orbitals that is of low energy.

To denormalize, common tetragonal geometry includes:

- low spin d^0 configurations (MnO_4^-, for exemple)
- d^{10} configurations (e.g. $ZnCl_4^{2-}$)
- Weak-field the ligands in d^4-d^7 configurations

The symmetry designations of different metal orbitals taking part in this type of overlap can still be given as

s	–	*a*1
px, *p*y, *pz*	–	*t*2
dxy, *dxz*, *dyz*	–	*t*2
*dz*2, *dx*2 *y*2	–	*e*

–

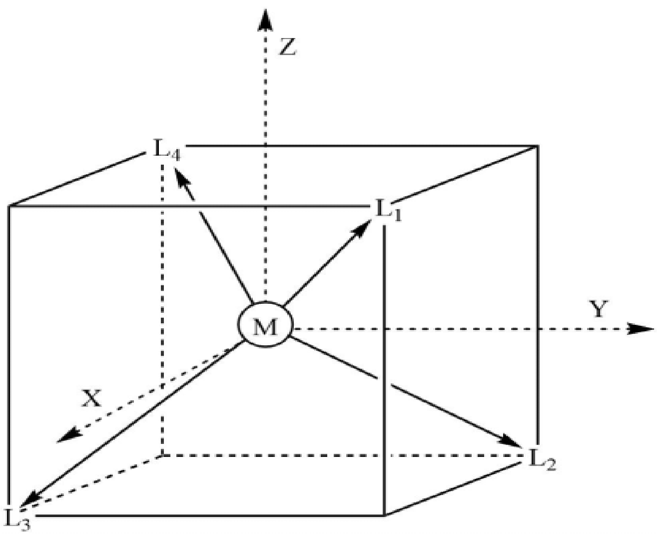


Figure The σ-basis set for ligand orbitals in tetrahedral complexes.

Molecular orbital energy level diagram for σ- bonding in tetrahedral complexes can be shown as:

Notes

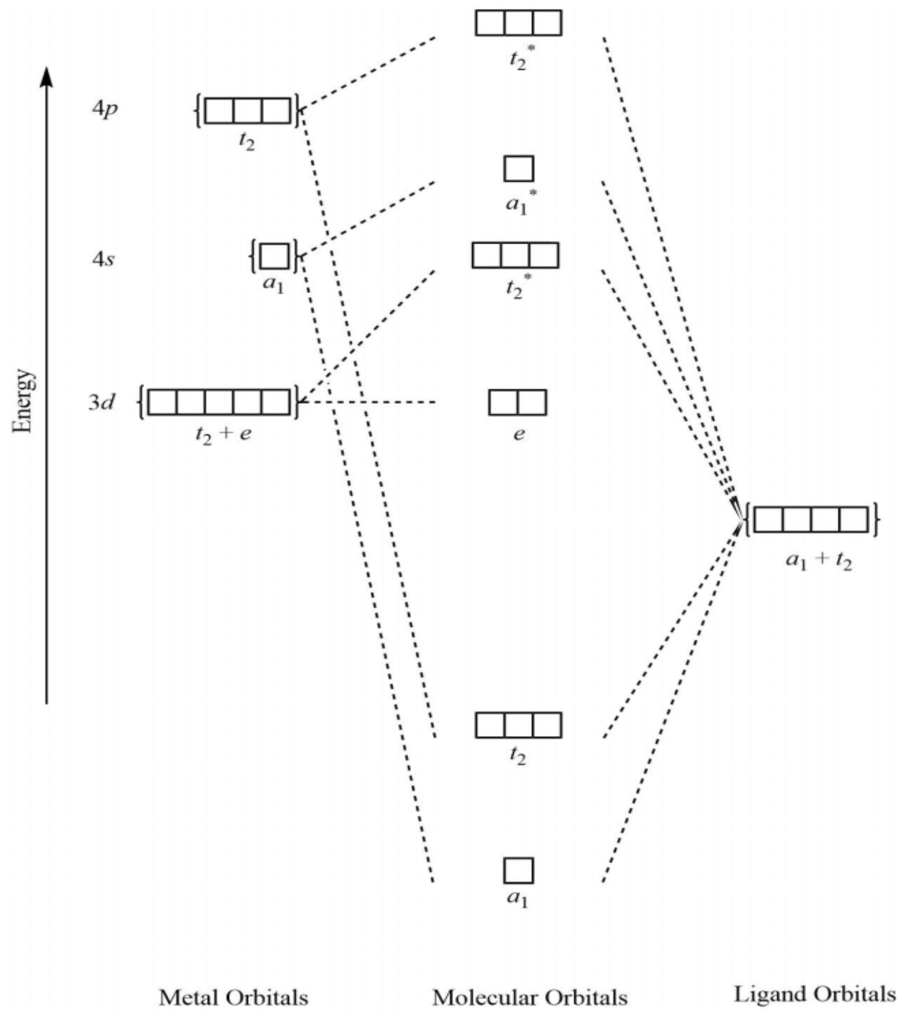


Figure - The formation of σ-molecular orbitals (bonding, antibonding and non-bonding) in tetrahedral complexes of transition metals.

The tetrahedral vacancies exhibit spectra results that more bands formed within bands when compared with octahedral spectra, indicating the intensity of absorption for tetrahedral complexes compared to octahdral complex.

Trigonal Bipyramidal and Square Pyramidal Fields

Trigonal bipyramidal & square pyramidal geometries are largely found in five-coordinate complexes,

This splitting is sensitive to distortions, & trigonal bipyramidal complexes readily interconvert with square pyramidal geometry.

The symmetry designations of different metal orbitals taking part in square-planar overlap are:

s – $a1g$

px, *py*	–	*eu*
*dz*2	–	*a*1*g*
*dx*2 *y*2 –	–	*b*1*g*
pz	–	*a*2*u*
dxy	–	*b*2*g*
dyz, *dxz*	–	*eg*

Notes

Five-coordinate complexes are often fluxional, rapidly transforming between trigonal bipyramidal & square pyramidal geometries. Such dynamic behavior can complicate spectroscopic characterization, which often requires low-temperature studies to "freeze out" individual conformations.

These two geometries are relatively common in:

Intermediates in substitution reactions

- Complexes with metals of d^5 microlations (e.g., Fe^{3+}, Mn^{2+})
- Complexes with sterics-heavy the ligands that preclude higher coordination numbers

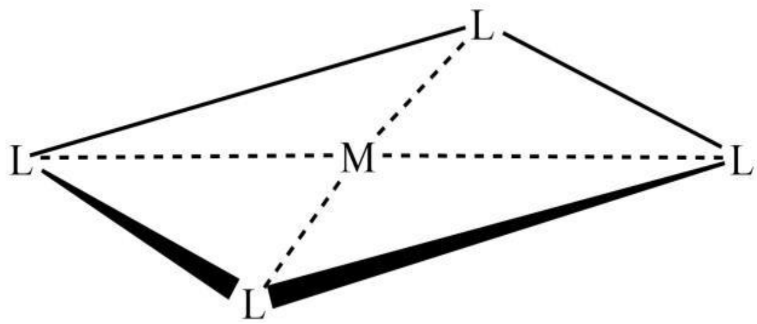


Figure -. The σ-basis set for ligand orbitals and corresponding coordination in square-planar complexes of transition metals.

The molecular orbital energy level diagram for σ-bonding in square-planar complexes can be shown as

Notes

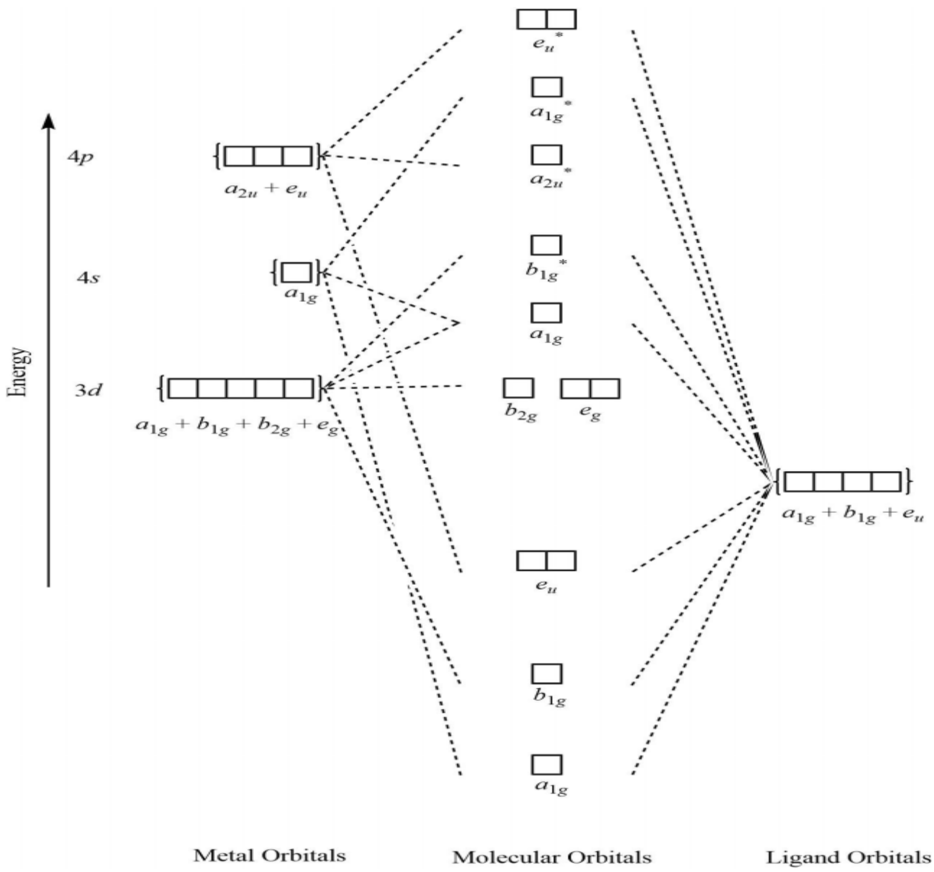


Figure -. The generation of σ-molecular orbitals in square-planar complexes.

The d-orbital splitting arrangements of five-coordinate complexes yield characteristic electronic spectra, although the appearance of the spectra is greatly influenced by distortions & fluxional behavior.

Jahn-Teller Effect

(15, 17, 31) Jahn-Teller effect represents an essential process in coordination chemistry, where specific electronic states spontaneously distort the coordination geometry, thus preventing orbital degeneracy & resulting in a more stable overall state. This effect is important & has a much stronger impact on the structure, spectroscopy & reactivity of transition metals complexes.

What Causes Distortion & What are the Types of Distortion

The Jahn-Teller theorem (1937) states that all non-linear molecular systems in degenerate electronic states will undergo a distortion that removes the degeneracy & lowers the total energy (Hermann, 1937; Edward, 1937). This message will impact most configurations with unbalanced occupancy of degenerate orbitals, in the setting of transition metal complexes. This is most strongly felt in octahedral complexes, where the following electronic configurations will apply:

- d^9 configurations (e.g. Cu^{2+}): Add one electron into the eg set for an asymmetric occupation.
- High-spin d^4 configurations (e.g., Cr^{2+}): 1 electron in the eg set.
- Low-spin d^7 cases (Co^{2+} for example): One hole in the eg set.

The degree of distortion goes in the following roughly order: $d^9 \gg$ high-spin $d^4 \gg$ low-spin d^7.

Degenerate occupation of t2g orbitals (d1, d2 low-spin, d5 low-spin) also gives rise to weak Jahn-Teller distortions (the second-order Jahn-Teller effect).

There are two main types of distortion that take place in octahedral complexes.

Tetragonal elongation: The most common distortion is where the metal-ligand bonds elongate along one axis, conventionally the z-axis. This causes the dz^2 orbital to become lower in energy than the dx^2-y^2 orbital, & causes a rise in energy of the dxy orbital in the t2g set, with a rise for dxz & dyz as well. Tetragonal compression: This is less common but also observed in some systems, it is characterized by contraction of metal-ligand bonds in the direction of one axis. This increases the energy of the dz^2 orbital compared to the dx^2-y^2 & makes corresponding changes in the t2g set. Energetic preference for elongation over compression in most cases is the result of subtle interplay between the electronic & nuclear repulsion terms. Jahn-Teller distortions (which in a very general sense describe the deformation of degenerated electron energy levels), while petite in one case, exhibit large amplitudes in another case.

- Strong effects (10^{-2} to 10^{-3} eV stabilization) are for eg degeneracy.
- Weak effects (10^{-4} to 10^{-5} eV stabilization) are for t2g degeneracy.

In the dynamic Jahn-Teller effect, the energy barrier between different distorted structural configurations is small & interconversion between several distorted geometries is rapid. This creates an average structure that can look undistorted in some experimental measurements.

All effects on spectra and structure

We can first explore some observable characteristics of transition metals complexes which are related to the Jahn-Teller effect:

X-ray crystallography: Structural distortions in Jahn-Teller active complexes. In Cu^{2+} octahedral complexes, the axial bonds are usually longer than equatorial bonds by 10–20%. These distortions can spread through crystal lattices, & in some cases lead to cooperative effects.

Notes

Electronic spectra: Jahn-Teller distortions break degeneracy of electronic states, giving rise to:

- Splitting of absorption bands that would be single in undistorted complexes.
- Vibronic coupling leads to broadening of spectral features
- Typical absorption patterns unique to the type & degree of distortion

In fact, Cu^{2+} complexes display a d-d spectrum with three bands instead of one, as would be expected for a normal octahedral complex.

- Vibrational spectra: Characteristic splitting in the regions of metal-ligand stretching evident in infrared & Raman spectroscopy spectra, attributed to loss of symmetry due to formation of complex.
- EPR spectra: Electron paramagnetic resonance spectroscopy is particularly sensitive to Jahn-Teller effects. The g tensor components in Cu^{2+} complexes are anisotropic reflecting the distorted environment.

which computing for crystal field stabilization energy: Jahn-Teller distortions have a substantial impact on the net stabilization energy of complexes, thus influencing thermodynamic characteristics including:

- Formation constants
- Redox potentials
- Reaction energetics

The Jahn-Teller effect plays a role in many chemical processes:

- Stereochemistry preferences: Some metal ions have a tendency to form distorted complexes (Cu^{2+} has a preference for elongation in octahedral or square planar geometries).
- Kinetics of ligand exchange: Longer bonds, particularly those along the distorted axis, are typically more labile, giving rise to diagnostic kinetic regimes.
- Cooperative phenomena in solid-state materials: Jahn-Teller distortions can crystallize into long-range order in extended lattices, leading to:
- Magnetic ordering
- Phase transitions
- Property of electric conductivity
- Catalytic activity: The electronic asymmetry and structural distortion can facilitate enhanced reactivity at certain coordination sites.

Rich & complex behavior results in transition metal systems from the interplay of the Jahn-Teller effect and other electronic factors (spin-orbit coupling, metal-ligand covalency). His work makes a significant contribution towards rational design of coordination compounds with tunable electronic, magnetic & catalytic characteristics.

Some examples of Jahn-Teller effect are:

- Copper (II) complexes: The prototypical Jahn-Teller active systems, featuring d^9 configuration, resulting in significant axial elongation. Axial Cu-O bonds in $[Cu(H_2O)_6]^{2+}$ are ~40% longer than equatorial ones.
- Manganese (III) complexes: In high-spin d^4 configuration, strong Jahn-Teller distortions play a role in determining manganese bioinorganic chemistry in the context of photosystem II.
- Chromium (II) complexes: High-spin d^4 configuration exhibits distortions that affect the air sensitivity & unique chemistry of Cr^{2+} compounds.
- Jahn-Teller Effects in Low-Spin Cobalt (II) Complexes: CCFT of Cobalt(II) (d7)-based complexes show that no Jahn-Teller effects are observed in the d7 configuration, though they will be very dependent on spin-orbit coupling effect

Unit 4 Ligand Field Stabilization Energy (LFSE)

Ligand field stabilization energy (LFSE) is one of the most basic ideas in coordination chemistry, & helps to provide a theoretical underpinning to the thermodynamic & structural characteristics of transition metal complexes. This energy term corresponds to the coordination of a central metal ion with its the ligands that causes the degeneracy of d-orbitals to split & leads to a net decrease of the energy of the complex. A huge energy term, associated with their larger numbers, deeper orbitals, & so on, which have far-reaching consequences for the stability, reactivity, & physical characteristics of coordination compounds as the fields dedicated to these phenomena are of paramount importance in explaining the reactivity of transition metals in these reactions. LFSE is a concept that arose from crystal field theory & was developed into more comprehensive ligand field theory based on molecular orbitals to explain metal-ligand interaction. The fundamental principle behind LFSE comes from the stabilization of electrons in lower-energy d-orbitals after they have been split by surrounding the ligands, & the energy benefit they provide. This stabilizing influence varies systematically across the transition series & is critically dependent on the metal ion electron configuration, the complex geometry, and the coordinating the ligands nature. It is not only of theoretical importance — the impact of LFSE reaches much,

Notes

much further. It rationalises many experimental observations in coordination chemistry, such as the Irving-Williams series of stability constants, the coordination geometry of certain metal ions & the deviations from trends in hydration enthalpies through first-row transition metals. The impact of LFSE explained in this article also deepens our comprehension of vital physical characteristics including color, magnetism & reactivity patterns of metal complexes, used in applications from catalysis to materials science.

Determining LFSE involves weighing factors such as the number & arrangement of d- electrons, the value of the crystal field splitting parameter, and the spatial arrangement of the ligands around the transition metal. Unique patterns of d-orbital splitting are observed for different coordination geometries, giving rise to characteristic LFSE values that compete for the stability of competing structural configurations. LFSE demonstrates the influence of this electronic phenomenon over all types of thermodynamics parameters (lattice energies, hydration enthalpies, formation constants) associated to coordination compounds. Here, we embark on a detailed dive into the world of ligand field stabilization energy, with an emphasis on both its theoretical background & practical calculation approaches, as well as highlighting the thermodynamic ramifications this concept holds in furthering our appreciate and comprehend ing of transition metal chemistry & its applications.

Factors Affecting the Splitting Parameter (Δ)

Nature of the Metal Ion

The nature of the central metal ion largely governs the extent of the crystal field splitting parameter. Such influence is realized through multiple mutually dependent characteristics of the electronic structure & the position of the metal in the periodic table. The valence shell can be defined through their principal quantum number which directly influences the splitting parameter. When we go down a group on the periodic table, we increase the principal quantum number & have more diffuse d-orbitals. These orbitals are more distant from the nucleus & interact less strongly with the ligand's orbitals. Thus, crystal field splitting usually decreases down a group. For example, under otherwise equivalent conditions (same the ligands & oxidation state), the splitting parameter follows the trend: 3d Cu^{2+} This is because the effective nuclear charge experienced by these d-electrons increases with atomic number as you go across the period. Due to increasing number of protons in the nucleus & electrons in the d-orbital effective nuclear charge increases making the d-orbitals more closely attached to nucleus better interacting with ligand field. The electronic character of the metal ion is another factor that influences the splitting parameter. In particular, the number of d-electrons affects the interactions between d-orbitals & the ligands. Peak 9: Mn^{2+}, [Ar] $4s^2$ $3d^5$ → Transition metals with a d^5 configuration (half-filled set of d-type orbitals) often exhibit less than expected crystal field splitting than would be expected if we just looked at where in the periodic table they are. Reduced splitting occurs because half-filled set of orbitals are more stable than the alternative; this arrangement results in maximum parallel spins per d-orbital, which maximizes exchange energy..

Notes

Oxidation State of the Metal

The oxidation state of the metal ion has a huge effect on the crystal field splitting parameter & is one of the most important factors controlling the electronic structure of coordination compounds. Higher oxidation states invariably yield larger splitting parameters, an observation that can be rationalized using a number of interrelated phenomena. First & foremost, oxidation state directly modifies the effective nuclear charge which the d-electrons are experiencing. Higher oxidation states imply increased removal of electrons from the metal, resulting in lower electron-electron repulsions, such that more electron density can be drawn into the nuclear region. This shrinkage of the d-orbitals allows for more overlap with ligand orbitals, which increases their interaction & leads to a higher genius of the crystal electric field splitting parameter. For instance, Fe^{3+} complexes typically have higher splittings than the respective Fe^{2+} complexes with identical the ligands. The effective nuclear charge increases for higher oxidation states, which leads to reducing the ionic radius of the metal ion. The smaller dimensions then reduce metal-ligand bond distances, which in turn increases the overlap of orbitals & increases the covalent bonding character. At elevated oxidation states, this leads to a stronger effective covalent interaction contributing significantly to the increased crystal field splitting found in high oxidation state complexes.

Ligand Nature (Spectrochemical Series)

The identity of the the ligands coordinating to a metal ion has perhaps the most direct & strongest effect on the crystal field splitting parameter. This effect is classified in the spectrochemical series, which orders

- I^- pairing energy: Low-spin complex Paramagnetism in complexes can occur in low-spin complexes (Δ > pairing energy) with minimum unpaired electrons & high-spin complexes (Δ Zn^{2+}. This unique stability is rationalized by Jahn-Teller distortion of octahedral Cu^{2+} complexes, which offers increased stabilization, when compared to the reduced Δ, for this configuration.

- Language of ResponseMechanisms & Kinetics: The relative value of Δ affects the transitional free energy (i.e., the activation energy) for ligand replacement reactions. The large Δ of spin

Notes

transitions for a dioxyhemoglobin in the framework of qualitative valence bond theory explain the kinetic inertness range found in arrays of metal-coordinating second & third-row transition metal complexes due to their high energy barrier for rearranging d electron configuration during ligand exchange. This property is of great importance in the design of stable catalysts and therapeutic agents.

- Redox Characteristics: The crystal field splitting impacts redox potentials by stabilizing some oxidation states more than others. For example, strong-field the ligands such as CN^- & CO stabilize lower oxidation states via π-backbonding, whereas weak-field the ligands stabilize higher oxidation states. This relationship is harnessed in the development of redox catalysts & electrochemical sensors.

Rational design of coordination compounds for various applications has been achieved by using the knowledge of what influences the parameters that govern the crystal field splitting:

- In catalysis, Δ can be fine-tuned allowing for the modulation of the electronic structure of metal centres thereby affecting substrate binding, activation & product selectivity. Different redox potentials of both the ligands & metals can lead to sequence-selective electron transfer reactions, resulting in catalytic activity, as is the case with the hydrogenation reactions catalyzed by Wilkinson's catalyst $[RhCl(PPh_3)_3]$, where high-field the ligands generate an electronic configuration suitable for oxidative addition of H_2.

- In medicine, platinum-based anticancer agents such as cisplatin $[Pt(NH_3)_2Cl_2]$ depend on the kinetic inertness imparted by Pt^{2+}'s large crystal field splitting to ensure that the drug has time to reach its biological target before it undergoes a ligand exchange. Likewise, gadolinium MRI contrast agents take advantage of the electronic nature governed by the crystal field splitting to modulate relaxivity.

- Spin-crossover complexes in material science can exist in either a high or low spin state but can undergo a reversible transition between the two states through temperature, pressure, or light, making them useful for applications in molecular switches, sensors, & data storage. Comparably, these materials exist at the boundary where Δ is at par with the energy for electron pairing, rendering them exquisitely vulnerable to external stimuli.

- In the field of environmental chemistry, the design of selective chelating agents for remediation of heavy metals is based on the principles of crystal field theory to ensure that high affinity & selectivity for target metal ions is achieved.

-ligand vibrational modes (Resonance Raman spectroscopy), allowing the extraction of information about strength of metal-ligand bonds & covalency relative to the crystal field splitting.

In general, the ligands that are non-innocent, meaning they can have more than one redox state & share electron density with the metal in non-trivial ways, do not follow the crystal field-theory model perfectly. The assignment of formal oxidation states is also obscure in the case of dithiolene, catecholate & nitrosyl the ligands & the resulting electronic structure is complex & would require advanced theoretical treatment. Crystal field splitting patterns are greatly affected by Jahn-Teller and pseudo-Jahn-Teller distortions that break degeneracy of the orbitals. Such effects dominate in d^9 (Cu^{2+}), high-spin d^4 (Cr^{2+}), & low-spin d^7 (Co^{2+}) octahedral complexes (among others), where they can elongate or compress along certain axes & modify the simplified octahedral splitting into a more complicated arrangement. The cooperative effects seen in polynuclear complexes & metal clusters whereby several metal centers interact via bridging the ligands or direct metal-metal bonds, leads to complex electronic structures where the crystal field splitting of one metal center gives rise to the crystal field splitting of neighboring centers, & is subsequently affected by them.

Metal Complexes: Practical Applications in Everyday Life

Metal complexes discreetly regulate several processes that sustain & improve our quality of life, frequently functioning unnoticed within the items & systems we encounter daily.. Contemporary water purification systems often utilize metal-based coagulants such as aluminum sulfate & iron chloride, which create coordination complexes with contaminants, leading to their aggregation & precipitation for removal via filtration, thereby enhancing drinking water safety for millions worldwide. The MRI contrast agents that transformed medical imaging & diagnostics operate via gadolinium complexes specifically engineered to improve tissue contrast while being non-toxic; these agents temporarily modify the magnetic characteristics of tissues through coordination interactions, uncovering physiological details that would otherwise be obscured & facilitating earlier, more precise disease detection

Theoretical Frameworks for Metal Complexes: Practical Applications

. 1. The smartphone in your pocket comprises various circuit components that depend on meticulously designed metal-organic compounds for semiconductor production; photoresists utilized in lithographic patterning frequently incorporate coordination complexes whose photochemical characteristics stem from energy levels anticipated by theoretical models, facilitating the creation of nanoscale electronic components that process information & connect individuals worldwide.

Notes

2. Water purification tablets employed by hikers & in emergencies frequently contain silver coordination compounds, whose antimicrobial efficacy stems from the interaction of silver ions with biological molecules; these portable purification solutions ensure safe drinking water in the absence of conventional treatment infrastructure.

3. Energy-efficient LED bulbs used in residential & commercial settings often utilize rare earth metal complexes as phosphors to transform primary emissions into warm white light, as elucidated by ligand field & molecular orbital theories; these lighting solutions consume considerably less electricity than incandescent counterparts, thereby decreasing energy expenses & environmental repercussions.

4. Metal-organic frameworks (MOFs) employed in advanced gas storage, separation, & catalysis applications exhibit remarkable characteristics due to the meticulously regulated coordination spheres surrounding metal centers, resulting in materials with unparalleled surface areas & selectivity that could potentially transform hydrogen storage for clean energy, carbon capture for climate change mitigation, & water harvesting in arid regions.

5. Biodegradable chelating agents, which substitute environmentally persistent compounds in cleaning products & industrial processes, were developed based on theoretical insights into coordination stability constants & metal-ligand interactions, resulting in effective cleaning agents & industrial processes with diminished environmental impact. Collectively, these applications illustrate the direct translation of theoretical frameworks in coordination chemistry into technologies that improve environmental sustainability, human health, energy efficiency, & the information processing skills that characterize modern society.

Valence Bond Theory: Practical Applications

Valence Bond Theory, despite its constraints, has offered significant insights that inform the creation of materials & compounds with particular magnetic, catalytic, & structural attributes found in everyday products & technology.

1. Dental amalgams, which have restored functionality to billions of teeth globally, comprise mercury-silver complexes whose structural integrity & durability are partially attributed to the hybridization states of the constituent metals, resulting in restorations that endure the demanding oral environment characterized by temperature fluctuations, mechanical stress, & chemical exposure.

2. Colorimetric water test kits utilized by homeowners & environmental monitors to identify metal contaminants such as lead, copper, or iron operate through coordination reactions that yield visible color changes when metal ions interact with specific the ligands in the test reagents;

Notes

3. . The precious metal catalysts employed in petroleum refining & pharmaceutical production rely on particular hybridization states to promote electron transfer & molecular activation, so ensuring the efficient generation of fuels & medications that support mobility & health.

4. The efficacy of numerous food packaging materials in resisting oxidative deterioration relies on metal-based oxygen scavengers, whose success stems from hybridization states that promote oxygen binding & removal, hence prolonging shelf life & minimizing food waste.

5. The vivid glazes on ceramic dishware frequently incorporate transition metal complexes, with color contingent upon the hybridization & electronic characteristics of elements such as copper, cobalt, or iron within the glassy matrix.

6. These ornamental finishes elevate functional items into aesthetic components of everyday life, illustrating the application of Valence Bond Theory in decorative arts & crafts that enrich domestic settings.

Ligand Field Theory: Practical Applications

Ligand Field Theory has transformed our comprehension of color, magnetism, & reactivity in coordination compounds, facilitating the advancement of materials & technologies that improve beauty, efficiency, & utility in several aspects of daily life.

1. The sunscreen safeguarding your skin from detrimental ultraviolet radiation probably comprises titanium dioxide or zinc oxide particles, whose electronic characteristics, shaped by ligand field effects, provide broad-spectrum UV protection while remaining transparent to visible light; this essential health protection technology illustrates how metal-ligand interactions directly aid in preventing skin cancer & premature aging.

2. The dynamic LCD screens that convey information across various devices, from wristwatches to televisions, employ color filters with metal complexes whose specific absorption characteristics, elucidated by ligand field splitting patterns, generate the red, green, & blue color components that amalgamate to produce full-color images; these display technologies have revolutionized access to information, entertainment, & communication by translating electronic signals into visible data through the principles of coordination chemistry.

3. The photochromic lenses in eyeglasses, which darken in sunlight & clear indoors, generally incorporate coordination complexes of silver, copper, or other transition metals within the lens material.

Notes

4. The contrast agents utilized in medical magnetic resonance imaging gain their efficacy from paramagnetic metal centers, with their magnetic characteristics influenced by ligand field effects; these diagnostic instruments improve the visualization of internal tissues, facilitating non-invasive identification of pathological conditions that may otherwise necessitate exploratory surgery.

5. Coordination compounds utilized in cancer chemotherapy, especially platinum complexes such as cisplatin & its derivatives, leverage ligand exchange kinetics influenced by ligand field effects to selectively attach to DNA in rapidly proliferating cells; these pharmaceutical agents have revolutionized cancer treatment outcomes despite their difficult side effect profiles.

6. The selectivity of ion-selective electrodes employed in water quality assessment, blood electrolyte analysis, & industrial process regulation arises from the preferential coordination of specific metal ions by meticulously engineered the ligands, resulting in sensors capable of differentiating chemically analogous species based on nuanced variations in coordination preferences. Collectively, these applications illustrate the practical implications of ligand field splitting theory, which governs the energetic configuration of d-orbitals in coordination compounds, directly influencing technologies that safeguard health, augment visual information presentation, facilitate medical diagnostics, & advance environmental sustainability across various facets of modern life.

Multiple-Choice Questions (MCQs)

1. Valence Bond Theory (VBT) explains the bonding in metal complexes using:

a) Molecular orbitals

b) Hybridization & overlapping of atomic orbitals

c) Electrostatic interactions only

d) Crystal field interactions

2. Which of the following is not a limitation of Valence Bond Theory (VBT)?

a) It does not explain the color of metal complexes

b) It cannot explain the magnetic characteristics of all complexes

c) It accurately predicts electronic spectra

d) It does not consider the ligand field effects

3. In an octahedral field, the d-orbitals split into:

a) t2gt_{2g}t2g (lower energy) & ege_geg (higher energy) levels

b) ege_geg (lower energy) & t2gt_{2g}t2g (higher energy) levels

c) dxy,dxz,dyzd_{xy}, d_{xz}, d_{yz}dxy,dxz,dyz (higher energy) & dz2,dx2−y2d_{z^2}, d_{x^2-y^2}dz2,dx2−y2 (lower energy)

d) Uniform energy levels

4. The Jahn-Teller Effect occurs primarily in:

a) High-spin d^6 octahedral complexes

b) Low-spin d^4 tetrahedral complexes

c) d^9 octahedral complexes

d) d^1 square planar complexes

5. The Ligand Field Stabilization Energy (LFSE) is dependent on:

a) The distribution of d-electrons in metal orbitals

b) The oxidation state of the metal

c) The nature of the ligand

d) All of the above

6. The Spectrochemical Series arranges the ligands based on their ability to:

a) Form covalent bonds

b) Increase the splitting parameter (Δ)

c) Decrease the oxidation state of metal ions

d) Enhance thermal stability

7. Which metal oxidation state generally results in a larger splitting energy (Δ)?

a) +1

b) +2

c) +3

d) +4

8. In Molecular Orbital Theory (MOT) for metal complexes, π bonding occurs due to:

a) Overlap of metal d-orbitals with ligand p- or π-orbitals

b) Purely ionic interactions

c) Weak van der Waals forces

Notes

d) Absence of hybridization

9. In MOT diagrams, π-acceptor the ligands (e.g., CO, CN^-) tend to:

a) Increase the metal-ligand bond strength

b) Decrease metal oxidation state

c) Act as weak-field the ligands

d) Reduce ligand field splitting

10. Which of the following correctly compares VBT, LFT, & MOT?

a) VBT explains color better than LFT

b) LFT is better than MOT in explaining bonding

c) MOT considers both σ & π bonding, unlike VBT & LFT

d) VBT & MOT predict paramagnetism more accurately than LFT

Short Answer Questions

1. Define metal complexes & explain why theoretical models are important in appreciate and comprehend ing them.

2. What are the main assumptions of Valence Bond Theory (VBT)?

3. How does Ligand Field Theory (LFT) explain d-orbital splitting in octahedral fields?

4. Explain the Jahn-Teller Effect with an example.

5. What is Ligand Field Stabilization Energy (LFSE), & why is it important?

6. How does the spectrochemical series affect ligand field splitting?

7. What factors influence the crystal field splitting parameter (Δ)?

8. Compare σ & π bonding in metal complexes based on Molecular Orbital Theory (MOT).

9. How does π bonding in metal complexes affect their stability?

10. List two advantages & two disadvantages of each metal complex theory (VBT, LFT, MOT).

Long Answer Questions

1. Explain the Valence Bond Theory (VBT) & discuss its strengths & limitations in explaining coordination complexes.

2. Describe the splitting of d-orbitals in various ligand fields (octahedral, tetrahedral, square planar) according to Ligand Field Theory (LFT).

3. Discuss the Jahn-Teller Effect, its origin, & how it influences molecular structure & spectra.

4. What is Ligand Field Stabilization Energy (LFSE)? Explain how LFSE affects the thermodynamics & stability of metal complexes.

5. Explain the factors affecting the splitting parameter (Δ), including metal ion characteristics, oxidation state, & ligand nature.

6. Describe Molecular Orbital Theory (MOT) for metal complexes, including group theory, σ & π bonding, & MO diagrams.

7. Compare & contrast Valence Bond Theory (VBT), Ligand Field Theory (LFT), & Molecular Orbital Theory (MOT) in terms of their applications & limitations.

8. Explain the Spectrochemical Series & how it helps predict the field strength of the ligands.

9. Discuss the role of π bonding in metal complexes & how it affects ligand field stabilization & spectroscopic characteristics.

10. How do theoretical models of metal complexes help in appreciate and comprehend ing their magnetic, electronic, & structural characteristics?

Notes

MODULE -2

SPECTRAL & MAGNETIC CHARACTERISTICS OF METAL COMPLEXES

Objectives

- To comprehend the spectral & magnetic characteristics of metal complexes & their importance in coordination chemistry.
- To comprehend the formulation & analysis of term symbols for d-ions, encompassing multiplicity & degeneracy.
- To investigate electronic transitions in metal complexes, emphasizing d-d transitions, selection criteria, Orgel diagrams, & Tanabe-Sugano diagrams.
- To investigate the impacts of Jahn-Teller distortion, spin-orbit coupling, & charge transfer on spectral characteristics.

Unit 4 Introduction to Spectral & Magnetic Characteristics

Electronic spectroscopy and magnetism, two fundamental physical phenomena that underlie the atomic & molecular structure of matter, have transformed our appreciate and comprehend ing of molecular systems. Characteristics of this kind, closely tied to the electronic structure of matter, serve as powerful analytical tools for scientists in fields ranging from chemistry & physics to materials science & astronomy. Electronic spectra are a type of spectrum resulting from the interaction of atoms or molecules with electromagnetic radiation, leading to transitions between energy levels. Under quantum mechanical principles, these transitions produce unique spectral patterns that act as identifiers for chemistry. Absorbing or emitting light at particular wavelengths provides valuable insight into electronic structure, bonding characteristics, & molecular dynamics. Magnetic characteristics arise likewise due to the intrinsic spin of electrons (along with their orbital motion) within atoms & molecules. Magnetic ordering behavior of materials i.e. diamagnetic/ paramagnetic/ ferromagnetic & antiferromagnetic provides a great deal of information about electronic distribution & structure arrangement at atomic scale.

Theoretical Background for Electronic Transitions

Electronic transitions are the basis of spectroscopic phenomena and result from the quantum mechanical behaviour of electrons in atoms & molecules. When electrons jump from one energy state to another, including when they discharge light, for example, these transitions are electromagnetically coupled, & they will either absorb or release electromagnetic radiation with energy equal to the difference between their energies. At the core of this mechanism is quantum theory, specifically Planck's & Einstein's realization that energy is quantized & light behaves like a wave & a particle simultaneously. The Bohr model was the first successful theoretical model describing electronic transitions in the hydrogen atom & modeled the energy levels as $E_n = -R_H/n^2$, with R_H the Rydberg constant & n the principal quantum number. Although this model described the hydrogen spectrum, more complex systems needed the solution to wave mechanics in the work of Erwin Schrödinger. The wave function of a quantum mechanical system is given by the Schrödinger equation ($\hat{H}\Psi = E\Psi$), in which the Hamiltonian operator ($\hat{H}$) contains terms for kinetic & potential energy.

Notes

With the Schrödinger equation being unsolvable, approximation methods become required for many-electron systems. One widely used approach is the Born-Oppenheimer approximation, which separates the nuclear & electronic degrees of freedom in a molecular system, thereby greatly simplifying the quantum mechanical treatment of molecules. The approximation can often be importantly justified owing to violent differences between the masses of nuclei & electrons, for which one can often treat electronic transitions separately from the nuclear motion. Selection rules for electronic transitions are connected to quantum mechanics, through the calculation of transition dipole moments. These rules specify the transitions that are "allowed" (high probability) & those that are "forbidden" (low or zero probability). The principal selection rules encompass:

Laporte rule, forbidding direct transitions between states of the same parity in centrosymmetric molecules.

Note: The spin selection rule ($\Delta S = 0$), i.e., total spin quantum number is conserved.

Due to conservation of angular momentum, there is an important selection rule for orbital angular momentum ($\Delta L = \pm 1$). Forbidden transitions occasionally happen through mechanisms that lift these selection rules, such as spin-orbit coupling, vibronic coupling, or magnetic dipole & electric quadrupole interactions. The intensity of electronic transitions is proportional to the square of the transition dipole moment, $\mu = \int \Psi_f^* \hat{\mu} \Psi_i \, d\tau$, with Ψ_i & Ψ_f being the wave functions of the initial & final electronic states, & $\hat{\mu}$ the electric dipole moment operator. This integral quantifies the overlap between states & gives, via Fermi's Golden Rule, the transition probability. The molecular orbital theory (Chapter 8) extends these concepts to molecules, describing electronic transitions between molecular orbitals (e.g., σ→σ, π→π, & n→π* transitions). The energies of such transitions are connected to the bonding features & are affected by conjugation, substituent effects, solvents, etc.

Notes

The time-dependent perturbation theory provides a rigorous treatment of the role played by electromagnetic radiation in inducing transitions between quantum states. It considers the electromagnetic field as a perturbation to the molecular Hamiltonian, & produces transition rates expressions that relate directly to experimentallyaccessible magnitudes, such as few-photon absorption coefficients or emission intensities. Modern theoretical descriptions commonly use density functional theory (DFT) & time-dependent DFT to estimate the energies & intensities of electronic transitions with great accuracy. These tools have become important to interpret experimental spectra & to predict the spectroscopic characteristics of new materials. Hence, the theoretical underpinnings of electronic transitions are a refined synthesis of quantum mechanics, electromagnetic theory, & computational methods. This framework not only accounts for observed spectroscopic phenomena, but also informs future design principles for molecules & materials with tunable optical characteristics for applications ranging from solar cells to fluorescent biomarkers.

Fundamental Aspects of Magnetism

The magnetic characteristics of materials come from the motion of electric charges (mostly electrons), which creates magnetic moments via two ways: by the orbital angular momentum (the movement of electrons in orbits around nuclei) & the intrinsic spin angular momentum. The total magnetic moment of an atom or molecule is expected to be given by the vector sum of these contributions, subject to the quantum mechanical rules that restrict angular momentum to discrete values. Magnetic susceptibility (χ) describes the characteristics of how a material interacts with external magnetic fields, as the extent of the induced magnetism (M) when exposed to an external magnetic field (H) can be expressed as: $M = \chi H$. Based on the susceptibility values & the mechanisms that lead to the magnetization of the material, materials can be broadly classified into several categories, including: Diamagnetic material has a negative susceptibility (χ 0) & thus generate magnetization that is parallel to the applied field. Parametricism arises when there are unpaired electrons with random orientations of magnetic moments (thermal action & Brown motion) but which become partly to some extent aligned in an external field. The susceptibility obeys the Curie law: $\chi = C/T$, where C is the Curie constant & T is the absolute temperature.

The ferromagnetic material is known to obtain a spontaneous magnetization in the absence of an external field & to have very high positive values of the susceptibility. This phenomenon occurs due to the strong exchange interactions that favor parallel alignment of neighboring magnetic moments and produce magnetic domains. Above the Curie temperature (TC), exchange interactions are overcome by thermal energy, & ferromagnetic materials exhibit paramagnetic behavior. Antiferromagnetic materials are characterized by magnetic moments that are configured in an anti-parallel manner, yielding a total net magnetization of zero despite strong internal order. Above the Néel temperature (TN), thermal fluctuations destroy this ordering, & the material becomes paramagnetic. Contrary to antiferromagnets, ferrimagnetic materials consist of opposing magnetic moments of unequal magnitudes leading to a net magnetization. This class of material inherits characteristics from both the ferromagnetic & antiferromagnetic systems & is well represented in ferrites which have wide commercial usage in electronic devices.

Notes

In solids, the predominant interactions leading to magnetic ordering are of a quantum mechanical nature — group exchanges resulting from Coulomb repulsion of electrons with the Pauli exclusion principle. $H = -2J\sum S_i S_j$ (J is the exchange integral & S_i & S_j are spin operators). J values that are positive promote ferromagnetic alignment, & negative J values favor antiferromagnetic ordering. Magnetic anisotropy, the directional dependence of magnetic characteristics, arises from its crystal structure (magnetocrystalline anisotropy), sample shape (shape anisotropy), & the presence of external stresses (magnetoelastic anisotropy). These interactions form preferred directions of magnetization known as "easy axes" & affect the macroscopic magnetic behavior. Through thermal fluctuations, temperature has a tremendous effect on magnetic characteristics. Critical temperatures (TC or TN) indicate phase transitions between ordered & disordered states, where a competition between exchange energy and thermal energy dictates magnetic ordering. Above these temperatures, all materials show Curie-Weiss behavior: $\chi = C/(T-\theta)$, where θ is the so-called Weiss constant.

Materials are influenced by external magnetic fields capable of aligning magnetic moments & causing domain wall motion in ferromagnetics & ferrimagnets. Such a process produces a typical sigmoidal magnetization curve (hysteresis loop), which allows determining important parameters like saturation magnetization, remanence & coercivity. appreciate and comprehend ing the basis of magnetic behaviour has led to technological innovations in data storage, sensing, energy conversion & medical imaging. Ongoing research of emergent phenomena including multiferroicity, topological magnetic states, & quantum magnetism, using large volumes of magnet materials, will not only broaden the horizon of magnetism, but, in particular, offer new scientific & technological applications.

Electromagnetic Spectrum and Its Regions

The electromagnetic spectrum is the range of all electromagnetic radiation frequencies, all waves emitted by the sun and all the

Notes

wavelengths needed by plants. This full continuum, ranging from low-energy radio waves to high-energy gamma rays, interacts differently with matter & gives us unique spectroscopic information. The lowest energy region of the spectrum is occupied by radio waves with wavelengths ranging from kilometers to centimeters. Despite their low energy, radio waves allow powerful analytical methods, including nuclear magnetic resonance (NMR) spectroscopy, which investigates the magnetic environment of atomic nuclei, and electron paramagnetic resonance (EPR), which investigates unpaired electrons. These techniques give detailed structural information of molecules in a non-destructive manner. Microwave radiation (centimeter to millimeter wavelengths) couples with rotational energy levels in molecules. Microwave spectroscopy is the most precise measurement of rotational transitions & thus provides very accurate molecular geometries & dipole moments. Moreover, microwave radiation in ferromagnetic resonance studies studies the driving of electron spin transitions that is used to explore & better appreciate and comprehend magnetic materials.

Infrared (IR) radiation (wavelengths from 700 nm to 1 mm) mainly gives rise to vibrational modes of molecules. The IR spectrum has different regions, far-IR (10-400 cm^{-1}), mid-IR (400-4000 cm^{-1}) & near-IR (4000-14000 cm^{-1}). Mid-IR spectra are particularly useful to obtain structures by identifying functional groups from their characteristic absorption bands, while far-IR spectra provide information about crystal lattice vibrations and metal–ligand vibrations. Near-infrared (Near-IR) spectroscopy is widely used for fast compositional analysis & process control. Visible light (400-700 nm) corresponds to electronic transitions in the atoms & molecules (usually valence electrons). Such transitions yield the colors that we see, & they are the basis of colorimetry, photometry, & many spectrophotometric techniques. What it tests: Conjugated systems, d-d transitions in transition metal complexes, charge transfer Ultraviolet (UV) radiation ranges from 10 to 400 nm and is classified into near-UV (400-200 nm) & vacuum-UV (200-10 nm). UV spectroscopy has mainly shown the electronic transitions of π-electrons, non-bonding electrons & charge transfer species. This approach is especially useful for the investigation of aromatic species, unsaturated systems, & biological compounds such as proteins & nucleic acids.

X-rays (0.01-10 nm) excite core (rather than valence) electrons, revealing atomic composition & structure. X-ray absorption spectroscopy, including XANES (X-ray Absorption Near Edge Structure) & EXAFS (Extended X-ray Absorption Fine Structure) probes electronic structure & local coordination environments [5]. X-ray diffraction (XRD) techniques yield atomic-resolution crystal structures, while X-ray photoelectron spectroscopy (XPS) provides valuable information on the elemental composition & oxidation states of surface species. Gamma rays (less than 0.01 nm), emitted from nuclear reactions, are the highest energy photons in the spectrum. Gamma rays are exploited in Mössbauer spectroscopy to probe nuclear energy levels influenced by chemical phase environments, in this way providing details about oxidation states, coordination numbers, & magnetic characteristics, most commonly for iron bearing compounds. Most regions of the electromagnetic spectrum are not distinctly separated & overlap one another in practice. Modern spectroscopic methods often amalgamate multiple domains or utilize couplings between such domains. As an example, Raman spectroscopy uses visible or near-IR radiation to indirectly excite vibrational transitions via inelastic scattering.

With the advent of tunable lasers, synchrotron radiation sources & free-electron lasers, the range of accessible spectral regions has been greatly extended, making possible a new generation of techniques such as time-resolved spectroscopy. These advances enable researchers to explore dynamic processes over multiple timescales, from femtoseconds to seconds, illuminating details of molecular dynamics & reaction mechanisms that were previously out of reach. The appreciate and comprehend ing of the interactions of electromagnetic radiation with matter over almost the entire spectrum has had a revolutionary impact on the fields of analytical chemistry, materials science, astronomy & medical diagnosis. The spectral regions avail different aspects of the characteristics of the materials, & together they provide a unique toolkit covering most if not all of the scientific disciplines.

Electronic Transition Types

Electronic transitions correspond to the promotion of electrons to higher energy levels & are the basis of both absorption & emission spectroscopy. The characteristics of such transitions differ widely with the electronic construction of the atom or molecule in question, thus allowing for the identification of elements through unique spectral fingerprints that yield analysis information. In atoms they are electronic transitions between discrete energy levels defined by principal quantum numbers related to distinct electron configurations. The simplest case is that of the hydrogen atom, for which the transitions between energy levels lead to the well-known Lyman (ultraviolet), Balmer (visible), & Paschen (infrared) series. When dealing with multi-electron atoms, the discrete energy levels of each individual electron are modified by the presence of other electrons & their interactions (for example, through electron-electron repulsions), leading to so-called fine structure in spectral lines. However, in part because of the additional degrees of freedom associated with vibrational & rotational motion, the electronic

Notes

transitions in molecules are much more complicated. Electronic transitions in molecules fall to spare types:

- $\sigma \rightarrow \sigma$: Promoting an electron from a bonding σ orbital to an antibonding σ orbital. They demand substantial energy (usually the vacuum ultraviolet region) & are specific to saturated compounds featuring C-C & C-H bonds. Conventional UV-visible spectroscopy does not observe these transitions as they require too high a photon energy.

- $n \rightarrow \sigma*$ transitions: These transitions consist in the excitation of nonbonding (lone pair) electrons to antibonding $\sigma*$ orbitals. This is common in molecules containing atoms which have lone pairs (O, N, S, halogens); such transitions are generally around 150-250nm & moderately intense. While solvents can have a large effect on such transitions, polar protic solvents are commonly blue-shifted due to hydrogen bonding with lone pairs.

- $n \rightarrow \pi^*$ transitions: these occur in molecules that have both non-bonding electrons & π bonds (carbonyls, nitriles, azo compounds), this is characterised by the promotion of a non-bonding electron to an antibonding π^* orbital. They usually present in the near-UV to visible region (250-350 nm) & are weak ($\varepsilon \approx$ 10-100 $L{\bullet}mol^{-1}{\bullet}cm^{-1}$) but can easily be identified by the influence of solvent polarity, in many instances exhibiting red shifts in more polar solvents.

- $\pi \rightarrow \pi^*$ transitions: Transitions in these occur, where π-bonded electrons are excited to antibonding π^* orbitals, as seen in unsaturated & aromatic compounds. They usually demonstrate high absorption ($\varepsilon \approx$ 1,000-10,000 $L{\bullet}mol^{-1}{\bullet}cm^{-1}$) in the UV-visible range. These processes are markedly influenced by conjugation, the extension of which leads to a bathochromic shift (red shift) & enhancement of the absorbance, that is, with each conjugated double bond present, the shift & the absorbance are increased cumulatively.

- Charge transfer transitions: These are when electrons are transferred between molecular orbitals on different parts of the molecule or on different molecules. Coordination compounds typically involve metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), and ligand-to-ligand charge transfer (LLCT). Doing so often yields intense absorption bands ($\varepsilon >$ 10,000 $L{\bullet}mol^{-1}{\bullet}cm^{-1}$) which contribute to the vibrant colors of many transition metal complexes.

- d-d transitions: These transitions usually happen in transition metal compounds, where an electron from a partially filled d-orbital redistributes to a higher d orbital. In octahedral complexes, the transitions are between t_2g & eg levels, while tetrahedral complexes show transitions between e and t_2 levels. These transitions are weak (on the order of 10^{-1} to 10^{2} L•mol^{-1}•cm^{-1}) due to Laporte selection rule restrictions but provide significant insight into coordination geometry & ligand field strength.

- f-f transitions: Transitions between quite different states are characteristic of lanthanide & actinide compounds(exclusively), as these transitions occur within the 4f or 5f orbitals. Due to the outer electron shielding of f-orbitals, they provide less interaction with the chemical environment that produces sharp & narrow bands. Such transitions are usually disallowed by selection rules & hence are of low intensity.

Factors such as conjugation, electron donating or withdrawing substituents, stereochemistry, & local environment impact the energy & intensity of electronic transitions. The extended conjugation further lowers the energy of the occupied & the unoccupied orbitals leading to bathochromic shifts. Groups with lone pairs that can leak in can increase the binding (auxochromes), whereas electron-withdrawing or electron-donating substituents can shift transition energies significantly via inductive & mesomeric effects. By grasping molecular types & attributes associated with electronic transitions, it allows researchers to interpret complex spectra, analyze unknown compounds, explore reaction mechanisms, & engineer molecules with targeted spectral characteristics for use in sunscreens, dyes, photovoltaic materials to sensors.

Classification of Magnetic Materials

Magnetic materials are categorized according to their response to external magnetic fields, which in turn emanates from their electronic structure & the interactions between magnetic moments. This categorization serves as a guide for discerning magnetic characteristics in various materials & under varying temperature conditions. Diamagnetism arises from the motion of electrons in an atom & is an intrinsic property of matter; every material exhibits some diamagnetic response, though its strength depends on the material. This basic property originates from the orbital motion of pairs of electrons, induced by an external field in compliance with Lenz's law. All materials exhibit some level of diamagnetism, but this is often obscured by stronger effects in materials with unpaired electrons. Examples of pure diamagnetism are seen in superconductors (which demonstrate perfect diamagnetism, known as the Meissner effect), noble gases, many organic compounds, & materials with completely filled electron shells such as bismuth, pyrolytic carbon & mercury. Whatever the case, all paramagnetic materials have a positive magnetic susceptibility (in order of the magnitude of $\chi \approx 10^{-5}$ to 10^{-3}) as a result of some unpaired electrons present in their atoms that provides them with permanent magnetic moments. Without any external field, thermal agitation

Notes

randomizes the direction of these moments, leading to zero net magnetization. Anyway, once a field is applied, the moments partially align with it, generating magnetization following the Curie law: $\chi = C/T$ (where C is the material-specific Curie constant & T the absolute temperature). Most of transition metal compounds, some rare earth elements, molecular oxygen & some organic free radicals are paramagnetic materials.

At temperatures below their Curie temperature (TC), ferromagnetic materials exhibit spontaneous magnetization originating from strong exchange interactions that stabilize parallel alignment of neighboring magnetic moments. Such materials have very large positive susceptibilities & complex magnetization behaviors—featuring magnetic domains & hysteresis. Ferromagnets undergo nonlinear response to applied fields, achieved at saturation magnetization—when all domains are aligned with the field. Iron, cobalt, nickel, & gadolinium are some of the common ferromagnetic elements & many of their alloys. The magnetic moments of antiferromagnetic materials align antiparallel to each other but have ordering within the material, & because they are oppositely aligned there is no net magnetization. This ordering takes place below the Néel temperature (TN) & arises from negative exchange interactions between nearest-neighbor moments. These correlations are destroyed by thermal fluctuations above TN, where the material is paramagnetic, obeying the Curie-Weiss law (with negative Weiss constant): $\chi = C/(T+\theta)$. These include manganese oxide, nickel oxide and many transition metal halides. Ferrimagnetic materials consist of two or more sublattices with anti-parallel magnetic moments of unequal strength leading to a net magnetization. This inequitable cancellation yields ferromagnetic-like behavior such as domain formation & hysteresis, albeit usually with lower saturation magnetization. In this respect, ferrites (MFe_2O_4, where M is a divalent metal ion) are the most technologically relevant class of ferrimagnetic materials since they are used in transformers, inductors, & data storage devices.

This classification system is further expanded with several specialized categories:

Superparamagnetic materials are made from ferromagnetic or ferrimagnetic nanoscale particles small enough to be below the size of single magnetic domains. We can also observe the paramagnetic nature of the particles with an extremely large magnetic moment, because thermal fluctuations can suppress the high-energy barrier to the flipping of moments. Metamagnetic materials undergo a magnetic state transition (for instance the aFM→F) as new external conditions (like an adequate field strength, temperature, or pressure) are applied. In Helimagnetism, the competing exchange interactions between spins reveals a 3D complex ordering by the spiral arrangement of the magnetic moments.

Speromagnetism & spin glass systems hold randomly oriented frozen magnetic moments due to disorder & competing interactions that prohibit normal long-range order. Multiferroics are those materials that display more than one of the ferroic characteristics (ferromagnetism, ferroelectricity, or ferroelasticity) at the same time, which allows cross-coupling effects, allowing to control the magnetism with the electric fields or stress. Magnetic material can be categorized not only with respect to the intrinsic magnetic ordering, but also practical characteristics like coercivity (resistance to demagnetization) & remanence (magnetization retained when the magnetic field is reduced). Using these characteristics, ferromagnetic & ferrimagnetic materials are grouped as:

- Soft magnetic materials (low coercivity, low remanence): easily magnetized & demagnetized, found in transformers & electromagnets.
- Hard (high coercivity, high remanence): Difficult to demagnetize, used for permanent magnets.
- Semi-hard magnetic materials (intermediate characteristics): used in applications that need control of switching behavior.

It also serves as a guide for the discovery of novel magnetic materials with the desired characteristics for various technical applications.

Light-Matter Interactions

Spectroscopic phenomena are generally governed by the interaction of light & matter, which can be resolved into several different mechanisms each of which can extract material property information. All of these interactions are based upon relations between the energy of the photon & energy levels within the material & governed by quantum mechanical rules. When electromagnetic radiation hits a piece of matter, it can be: reflected, refracted, scattered, absorbed, or emitted. The relative contributions of these processes depend on the electronic structure of the material & the wavelength of the radiation. Absorption & emission processes are specifically helpful for spectroscopic studies. When the energy of a photon matches the energy gap between two quantum states of the material, the photon's energy can be absorbed, promoting an electron from a lower energy state to a higher energy state (that is why we need a photon in a matrix to explain the matrix with COM the proof of which is provided in the theory of generation). This occurs according to the Bohr-Einstein frequency condition: $\Delta E = E_2 - E_1 = h\nu$, where ΔE is the energy difference of the states, h is Planck's constant, & ν is the frequency of the absorbed

Notes

photon. Absorption occurs at a probability proportional to the transition dipole moment, which is a measure of the coupling strength of the electromagnetic field with electrons within the material.

The Beer-Lambert law describes the intensity of absorption in solutions: $A=\varepsilon cl$, wherein A signifies absorbance, ε is the molar absorption coefficient (a quantitative indicator of how much a compound interferes with light at a particular wavelength), c marks concentration, & l identifies the length of the path. This relationship allows for the determination of the composition of the sample in a quantitative manner using absorption spectroscopy. Absorption of light by atomic species results in line spectra with sharp, separate features related to transitions between very discrete energy levels. On the other hand, molecular absorption generally gives rise to broader bands resulting from the overlap of additional vibrational & rotational transitions that happen in tandem with the electronic transition. This band broadening is due to the Franck-Condon principle, which dictates that vibronic transitions occur with a probability that depends on how much the vibrational wave functions in the ground & excited electronic states overlap with one another. When electrons fall down from a higher to a lower energy state, electromagnetic radiation is emitted in a process called emission. When a state decays from an excited state to a lower energy state & is not stimulated by an incoming photon the emission is random, as it could be any portion of speed & energy type so long as the energy adds to the total energy to equal the difference. The field of stimulated emission, the underpinning of laser action, is the process of the photon interacting with the atom in the excited state, the impacted atom releasing a second identical photon, this process amplifying the initial input.

Emission is categorized into two main aspects, depending on their timescales:

- Fluorescence: with prompt emission (10^{-9} to 10^{-7} seconds, typically) from an excited electronic state after internal conversion or non-radiative relaxation to the lowest vibrational level of that state. This process is usually present among states with identical spin multiplicity (i.e. singlet to singlet) & leads to emission at longer wavelengths than the excitation light (Stokes shift).

- Phosphorescence has much longer emission lifetimes (10^{-3} seconds to hours) than fluorescence, as phosphorescence involves transitions between states of different spin multiplicities (generally triplet to singlet), which are prohibited. For this to happen, intersystem crossing (more movement between spin states, with spin-orbit coupling allowing intersystem mixing) must occur and, in general, provide larger Stokes shifts than fluorescence.

Notes

Furthermore, scattering phenomena enable new pathways for light-matter interactions. Elastic (or Rayleigh) scattering does not change the photon energy but does redirect it, giving rise to effects such as a blue sky. Raman scattering, where photons can gain or lose energy to match molecular vibrations or rotations, & Brillouin scattering, which involves interaction of light with acoustic phonons in condensed matter, are inelastic scattering processes. While the quantum efficiency or quantum yield of luminescence processes (fluorescence or phosphorescence) gives an idea about the ratio of emitted & absorbed photons & thus information on competing radiative & non-radiative deactivation pathways. Quantum yields vary from close to zero to near unity depending on the molecular structure and environment.

Several environmental factors profoundly impact light-matter interactions:

- Solvent effects include the effects of hydrogen bonding, dipole-dipole interactions, & refractive index on electronic transition energies, which lead to spectral shifts, providing details of solute-solvent interactions.
- Temperature influences spectral line widths & intensities, through population distributions among the energy levels (under Boltzmann statistics) & also by changing the non-radiative decay rates.
- Pressure can influence molecular shapes and intermolecular separations, & thus transition energies & intensities, especially in condensed phases.
- External electric & magnetic fields cause splitting of the energy levels (Stark & Zeeman effects, respectively), providing insights into electronic structure & symmetry.

By mastering the fundamental principles that dictate how light interacts with matter, researchers are able to obtain detailed insights into material characteristics through spectroscopic measurements. To rationalize these interactions, the field of spectroscopy developed rich analytical tools for chemical identification & structural characterization, & they provide the foundation for a broad range of technologies, including lasers, photovoltaics, optical communication, & biomedical imaging & diagnostics.

Electronic Structure and Magnetic Characteristics Relationship

There is a direct connection between quantum mechanical concepts & physical macroscopic phenomena through the complex relationship between electronic structure & magnetic characteristics. This link serves as a capacitance tool in enhancing conceptual appreciate and comprehend ing & engineering of magnetic materials for their use in different applications. Magnetic characteristics arise from two factors

Notes

at the atomic level: orbital angular momentum (L) associated with electrons orbiting the nucleus & spin angular momentum (S) from the electrons themselves. These contributions can then be combined into a total magnetic moment for the atom following quantum mechanical coupling schemes, with the Russell-Saunders (LS) coupling dominating for the lighter elements & the j-j coupling more applicable for the heavier elements.

In the case of transition metal ions the crystal field theory explains how the chemical environment will define the magnetic characteristics. Depending on the ligand fields & the way in which we arrange the the ligands around the d-orbitals, d-orbitals will be split which can change the arrangement of electrons which in turn will affect the magnetic moment. Strong-field the ligands lead to large crystal field splitting (Δ_o) in octahedral complexes, giving rise to low-spin configurations containing paired electrons & diminished magnetic moments. In contrast, weak-field the ligands produce high-spin configurations with maximal unpaired electrons & greater magnetic moments. This trend can be rationalized by the spectrochemical series (for ligand field strength), which orders the ligands on the following basis: $CO > CN^- > NO_2^- >$ phen $> NH_3 >$ en $>$ py $> H_2O > OH^- > F^- > Cl^- > Br^- > I^-$. The effective magnetic moment (μeff) is determined from the spin-only expression, $\mu_{eff} = g\sqrt{S(S+1)}\mu_B$, where g is the Landé g-factor (which is about 2 for electrons), S is the total spin quantum number, & μ_B is the Bohr magneton. This is a reasonable approximation for first-row transition metals, where orbital contributions are increasingly more relevant for heavier elements & must be included in the more complete formula: $\mu_{eff} = g\sqrt{J(J+1)}\ \mu_B$ with J the total angular momentum quantum number.

Unit 5 Electronic Transitions in Metal Complexes

For this reason, electronic transitions in transition metal complexes are among the most exciting subjects of study in inorganic chemistry & present deep information about the electronic structure, bonding and spectroscopic characteristics of these compounds. Transition metal complexes are known to display various colors due to these electronic transitions, especially the ones related to the d orbitals present at the metal center. These transitions are electron transitions between various energy levels in the complex that absorb certain wavelengths of the electromagnetic radiation. Knowledge of crystal field theory, molecular orbital theory, & quantum mechanical selection rules that dictate which transitions are allowed or forbidden helps to explain these transitions.

Characteristics of d-d Transitions

The d-d transitions are electronic transitions between two of the split d orbitals back & forth in a metal complex. In octahedral complexes, the five degenerate d orbitals become split into two sets, giving rise to the higher energy eg set (dx^2-y^2 & dz^2 orbitals) & the lower energy t2g set (dxy, dxz, & dyz orbitals). Here, t2 & e form two sets, with the energy gap between the two sets described as the crystal field splitting parameter, Δo (the 'o' refers to the octahedral arrangement). So the name of the theme is that d-d transitions are low intense. This low intensity results from the Laporte selection rule, which prohibits transitions between orbitals of the same parity (e.g., d→d transitions) in centrosymmetric molecules. However, there can still be (albeit weak) transitions if such vibronic coupling is possible where the center of symmetry is momentarily removed via asymmetric vibrations that render the transitions "vibronically allowed." This is the reason why many transition metal complexes are colored even though they may have theoretical d-d transitions that are "forbidden".

Notes

The colors of the complex (and therefore energies of d-d transitions) depend on several things:

- Electron Configurations: The shape of the d-orbitals & metal:s oxidation state can affect the overall crystal field splitting.
- Nature of the ligands: Strong field the ligands (the ligands towards top of spectrochemical series) cause greater splitting than weak field the ligands.
- The complex geometry: Various geometries (octahedral, tetrahedral, square planar) give rise to different splitting patterns & different transition energies.
- Intrinsic energy of the d orbitals of metal ion: Different metals (e.g. Cu, Ni, Fe, Co, etc.) have different stable forms due to the relative energies of their d orbitals.

The d-d transitions can also be subdivided according to the orbitals involved. For octahedral complexes, there are t2g to eg transitions, and for tetrahedral complexes, there are e to t2 transitions. The strength & nature of these transitions can yield rich information regarding the electronic structure & bond character in the complex. A third key feature is the bandwidth of these transitions. In contrast to atomic transitions sharp spectral lines, d-d transitions in complexes commonly demonstrate broad bands because of the Franck-Condon principle. According to the Born-Oppenheimer approximation, when an electron jumps to a higher level, the nuclear configuration does not collapse immediately. Nonetheless, the new electronic state has a distinct equilibrium nuclear configuration, leading to the development of vibrational fine structure manifesting as a wide absorption band.

Electronic Transition Selection Rules

Notes

There are a number of selection rules that govern whether an electronic transition will happen in metal complexes or not. These rules are based on quantum mechanics & describe the intensity and tendency of spectral bands.

Spin Selection Rule

Transition involving change in spin multiplicity is forbidden by spin selection rule. This can be written mathematically as $\Delta S = 0$, where S is the total spin quantum number. This rule is due to the reason that electromagnetic radiation does not interact efficiently with the spin of an electron. Transitions that break this rule ($\Delta S \neq 0$) are termed spin-forbidden transitions, & would be very weak if observed. The example of a high-spin d^5 octahedral complex such as $[Mn(H_2O)_6]^{2+}$; in such a case the ground state possesses a spin multiplicity of 6 (as it has 5 d electrons, with all of them having parallel spins). Transitions to excited states with different spin multiplicities violate the spin selection rule (forbidden). But when spin-orbit coupling is introduced, the strong selection rules can be weakened, particularly in the case of heavier transition metals. The molar extinction coefficient (ε) is often used to quantify the intensity of electronic transitions. The ε values for spin-allowed transitions are usually 1-1000 $L \cdot mol^{-1} \cdot cm^{-1}$, while spin-forbidden transitions have much smaller ε values (<1 $L \cdot mol^{-1} \cdot cm^{-1}$).

Laporte Selection Rule

The Laporte selection rule is especially relevant for the case of d-d transitions in transition metal complexes. This means that in centrosymmetric molecules (the ones that contain an inversion center) transitions from / to orbitals of the same parity are forbidden. Since d orbitals have g parity, d-d transitions are therefore Laporte-forbidden, because they violate this rule. In order for a transition to be Laporte-allowed, the parity of the initial & final states must change. Consequently, transitions such as g→u or u→g are allowed, whereas g→g or u→u are not. In transition metal complexes:

- d-d transitions (g→g) are Laporte-forbidden
- Charge transfer (MLCT) transitions (d→π*, g→u) are Laporte-allowed
- Laporte-allowed Ligand-to-metal charge transfer (LMCT) transitions (p→d, u→g)

But Laporte-forbidden transitions can still take place via several mechanisms:

- Vibronic coupling — Asymmetric vibrations temporarily break the center of symmetry, allowing the transition to be "vibronically allowed". This is also the reason that most octahedral complexes despite the presence of Laporte-forbidden d-d transitions are colored.

- Orbital mixing: In non-centrosymmetric complexes (e.g., those in tetrahedral coordination), the mixing of the d & p orbitals relaxes the Laporte selection rule. This is the reason tetrahedral complexes are frequently much more colorful than octahedral complexes.

- π-donor or π-acceptor the ligands: These have the ability to mix with metal d orbitals, bringing a p character that partly lifts the Laporte rule.

- Laporte-allowed transitions generally have ε values in the range of 10^3 to 10^5 $L•mol^{-1}•cm^{-1}$, whereas Laporte-forbidden transitions that become partially allowed via the mentioned mechanisms have ε values of 1-10^2 $L•mol^{-1}•cm^{-1}$.

- Lattice Pulse Selection Rule – This rule is almost identical to the selection rule for the atomic orbital angular momentum quantum number & states $\Delta L = \pm 1$, where L is the orbital angular momentum of the laser coupled. This is not a rule that folks use so much when transitioning into transition metal spectra but nonetheless it is important for clarifying certain transitions.

By classification, the selection rules are applicable for predicting & interpreting the intensity of electronic transitions within the framework of metal complexes, which ends the series of the selection rules in the two series of metal complexes. Although these rules classify transitions as either allowed or forbidden, we should keep in mind that forbidden transitions can still take place, just with smaller intensity, due to several mechanisms that loosen the stringent conditions of the selection rules.

Orgel Diagrams

Orgel diagrams are graphically plots that describe the energy of electronic states of transition metal complexes as a function of the crystal field strength. Introduced by Leslie Orgel in the 1950s, these diagrams are a schematic tool for visualizing spectroscopic data, especially for some high-spin complexes with fairly simple electronic configurations.

Orgel Diagrams—Basic Structure

Orgel diagrams plot energy of various electronic states vs crystal field strength (Δ) Orientations of the Orgel diagrams: Attempts to remove electron spin degeneracy (and orbital), so that the ordering is clearer. Note that the horizontal axis is the crystal field splitting parameter & the vertical axis is energy. To the left-hand side at zero field ($\Delta = 0$) the energies are those for the free ion (spherical field) in which case the states are designated using the term symbols from atomic spectroscopy.

Notes

With increasing crystal field strength (greater position along x-axis in this diagram) these free-ion states split (due to crystal field effects) & their energies evolve in characteristic fashions — which depend on electron configuration & complex geometry.

Orgel diagrams are especially useful for:

- The change in energies of the electronic states with crystal field strength.
- Finding possible electronic transitions & their energies to first approximation.
- From spectroscopic data to electronic structure: a correlation.
- In some cases, differentiating between high-spin & low-spin configurations.

The splitting profile of different electronic states in octahedral and tetrahedral crystal fields in the following tables

Table. Splitting of free ion terms in the tetrahedral crystal field.

Electronic state	Symmetry designation in the tetrahedral field (Mulliken symbols)
S	A1
P	T1
D	E + T2
F	A2 + T1 + T2
G	A1 + E + T1 + T2
H	E + T1 + T1 + T2
I	A1 + A2 + E + T1 + T2 + T2

Table 8. Splitting of free ion terms in the octahedral crystal field.

Electronic state Symmetry designation in the octahedral field (Mulliken symbols)

Table 8. Splitting of free ion terms in the octahedral crystal field.

Electronic state	Symmetry designation in the octahedral field (Mulliken symbols)
S	A1*g*
P	T1*g*
D	E*g* + T2*g*

F	A2*g* + T1*g* + T2*g*
G	A1*g* + E*g* + T1*g* + T2*g*
H	E*g* + T1*g* + T1*g* + T2*g*
I	A1*g* + A2*g* + E*g* + T1*g* + T2*g* + T2*g*

Notes

The A, E and T represent singly, doubly and triply degenerate states, respectively. The presence of "g" in symmetry designations of the octahedral field is for the gerade or centrosymmetric environment.

appreciate and comprehend ing Orgel Diagrams for d^1 to d^9 Systems

Orgel diagrams are usually generated for certain electron configurations & geometries. Now, let us take a look at how those can be interpreted for different d-electron configurations:

d^1 systems (e.g.: Ti^{3+} in octahedral field)

In a d^1 system, the lone electron fills the lowest level of the three available. The ground state (which comes from the ^2D free-ion term) is t2g in an octahedral field. eg as the only excited state accessible via a single electronic transition. The Orgel diagram for this system has two lines steming from the ^2D term which diverge as the crystal field strength increases: t2g moves downward and eg moves upward. The energy of these states differ by Δo & only one absorption band can be seen (corresponds to the t2g→eg transition).

For e.g $[Ti(H_2O)_6]^{3+}$ has single broad absorption band at around 20,000 cm^{-1} associated with this transition, resulting that complex being purple.

d^2 Systems(e.g., V^{3+} in octahedral field)

The overall wave function of a ground state for d^2 systems is a $t2g^2$ configuration as a ^3F term. Among excited states are $t2g^1eg^1$ (also from ^3F) and $t2g^1eg^1$ (from ^1D). In fact more than one electronic states diverges from these ^3F & ^1D terms, as is illustrated by the Orgel diagram.

Utilizing a high spin 3d transition metal, for example: $[V(H_2O)_6]^{3+}$, will yield 3 bands of absorption due to the transitions of the ground state $^3T1g(F)$ to the excited states $^3T2g(F)$, $^3T1g(P)$ & the ^1Eg states.

d^3 systems (e.g. V^{2+} or Cr^{3+} in octahedral field)

For d^3 systems the ground state is $t2g^3$ corresponding to the ^4F germ. Excited states are $t2g^2eg^1$ (from ^4F & ^4P). 3d -- splitting as shown here in the Orgel diagram -- & the resulting electronic states. For example,

Notes

$[Cr(H_2O)_6]^{3+}$ has two primary absorption bands that occur from transitions from the ^4A2g ground state to the ^4T2g & ^4T1g excited states.

d^4 to d^7 Systems

For these types of configurations, these Orgel diagrams get complicated because there exist high-spin & low-spin configurations. Tanabe-Sugano diagrams (covered later) are usually more useful for these systems. Orgel diagram still gives valuable insights for high-spin complexes.

d^8Systems (e.q Ni^{2+} in octahedral field)

For example, for high-spin d^8 systems, the ground state comes from the ^3F term & is $t2g^6eg^2$. Among the excited states did we have $t2g^5eg^3$ (from ^3F & ^1D). The Orgel diagram illustrates how these states degenerate at lower crystal field strengths. For example, for $[Ni(H_2O)_6]^{2+}$, three absorption bands are typically seen for transitions from the ^3A2g ground state to ^3T2g excited state (higher energy), $^3T1g(F)$ excited state, & $^3T1g(P)$ excited state (lower energy).

d^9 Systems (e.g., Cu^{2+} in octahedral environment)

For d^9 systems the ground electronic state is $t2g^6eg^3$, arising from the ^2D term. $t2g^5eg^4$ is the only excited state that can be reached via a single electronic transition. The Orgel diagram for this setup is straightforward, conclusively showing the splitting of the ^2D term into ^2T2g & ^2Eg states. $[Cu(H_2O)_6]^{2+}$ displays one broad band of absorption relate to the $^2Eg \rightarrow ^2T2g$ transition that gives this complex its characteristic blue color.

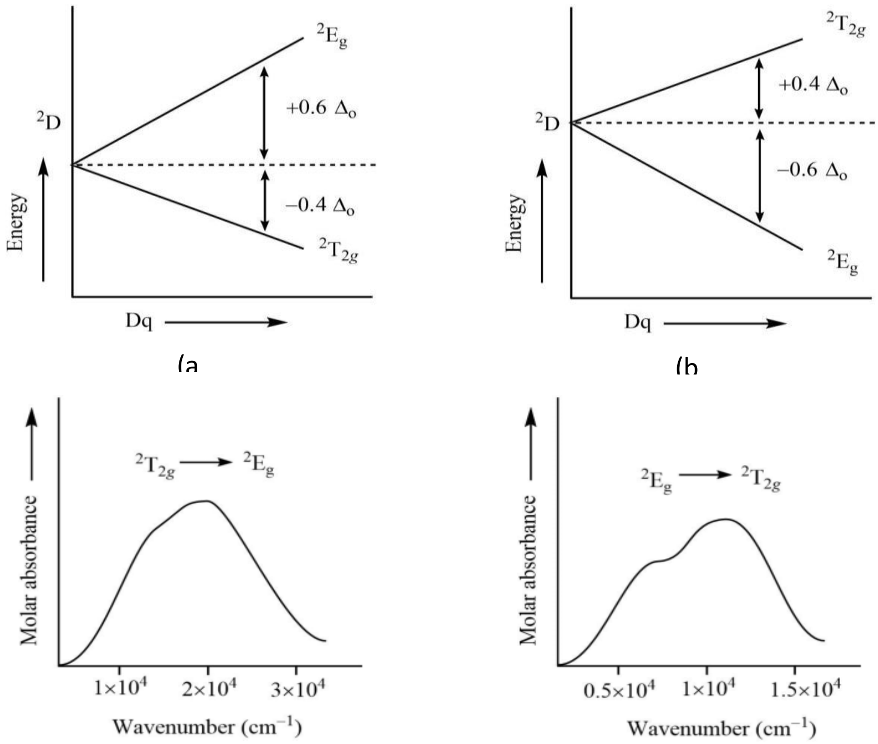


Figure - The splitting pattern of 2D state in octahedral complexes with (a) d1-configuration and (b) d9- configuration; and the corresponding electronic spectra of (c) [Ti(H2O)6]3+ and (d) [Cu(H2O)6]2+.

Limitations of Orgel Diagrams

Orgel diagrams are useful tools but they have numerous limitations:

- In these cases, they are most effective for high-spin complexes that have reasonably simple electronic structures (d^1, d^2, d^3, d^8, d^9).
- They do not explicitly consider the repulsion between electrons.
- They do not resolve the transition between high- & low-spin configurations well.
- They do not give access to the details of the transition intensities.

For more complicated scenarios, particularly those requiring the inclusion of multiple electrons & the possibility of spin-pairing changes, Tanabe-Sugano diagrams provide a more complete method.

Tanabe-Sugano Diagrams

Notes

Tanabe-Sugano diagrams: Tanabe & Sugano proposed in the 1950s a more advanced method to visualize electronic transitions in transition metal complexes. Another feature is that, unlike Orgel diagams, that plot absolute energies, the Tanabe-Sugano diagrams plot the energies of electronic states relative to the ground state. It is because of this that more accurate results are obtained, including for high-spin to low-spin transitions over any range of crystal field splitting.

Tanabe-Sugano Diagrams- Basic Structure

In a Tanabe-Sugano diagram:

- Horizontal axis: Δ/B → Dimensionless parameter describing the ratio of the crystal field splitting parameter to the Racah parameter, a measure of the strength of the crystal field relative to the electron-electron repulsion.
- The vertical axis denotes the energy (E/B), also normalized with respect to the Racah parameter.
- The energy of ground state is always set as reference (zero), appearing as horizontal segment at the diagram bottom.

All other electronic states are plotted with respect to this ground state.

The scheme is for a certain configuration (most-frequently octahedral) looking at a specific d-electron arrangement.

Tanabe−Sugano Diagrams include both inter-electron repulsion & crystal field effects, making them more complete than Orgel diagrams. They are most valuable for:

- Predicting the energies of electronic transitions across a wide range of ligand field strengths.
- Spin-allowed versus spin-forbidden transitions.
- Determination of crystal field parameters (Δ & B) from spectroscopic data
- Interpreting high-spin to low-spin transitions.
- Introduction to Strong & Weak Field Scenarios

Tanabe-Sugano diagrams are useful because they incorporate weak-field & strong-field scenarios & all the combinations in-between.

Weak Field Case

Weak field limit (small Δ/B):

- Electron-electron Coulombic repulsion is greater than crystal field splitting.

The electronic states are similar to the free ion ones.

- High-spin versions are preferred, with electron filling under Hund's rule of illustrated t2g & eg energy levels.
- Electron-electron interactions dominate the determination of the ground state, not crystal field effects.

In a weak field, for example, in a d^5 system:

- The electronic complex in the ground state ^6A1g, from the ^6S term & electron configuration $t2g^3eg^2$.
- ^4T1g, ^4T2g, & ^4A1g excited states are reached through spin-forbidden transitions ($\Delta S \neq 0$) & hence weak.
- These excited states are shown on the Tanabe-Sugano diagram at higher energies than the ground state.

Strong Field Case

Strong field regime (large Δ/B values):

- Coulomb repulsion is not as strong as crystal field splitting.
- Derives main from the arrangement of the crystal field.
- Low-spin states for d^4-d^7: lower energy state t2g orbitals are filled before the higher energy eg orbitals.
- As Δ/B increases, the ground state can also switch between high-spin and low-spin.

Thus, in a strong field d^5 system:

- At a critical value of Δ/B, the low-spin ^2T2g state ($t2g^5$) becomes lower in energy than the ground state ^6A1g (high-spin, $t2g^3eg^2$).
- The low-spin configuration opens up new spin-allowed transitions.
- As demonstrated in the Tanabe-Sugano diagram, there is a sharp change in the arrangement of energy levels at this crossover point.

Weak — Strong Field Regime Transition

Tanabe-Sugano diagrams also give a pictorial representation of the transition between weak & strong field regimes which is one of the most interesting aspects associated with them. For d^4-d^7 configurations, this transition corresponds to a change in the nature of both the ground state from high-spin to low-spin as Δ/B increases.

For example:

Notes

- For d^6 configurations (as in Fe^{2+}), the ground state is ^5T2g (high-spin, $t2g^4$ eg^2), then it becomes ^1A1g (low-spin, $t2g^6$) when Δ / B exceeds a threshold.
- This change can be detected on the Tanabe-Sugano diagram as an intersection of energy levels.
- The spectroscopic characteristics are extremely different at this transition point, where absorption bands change their appearance or disappear.

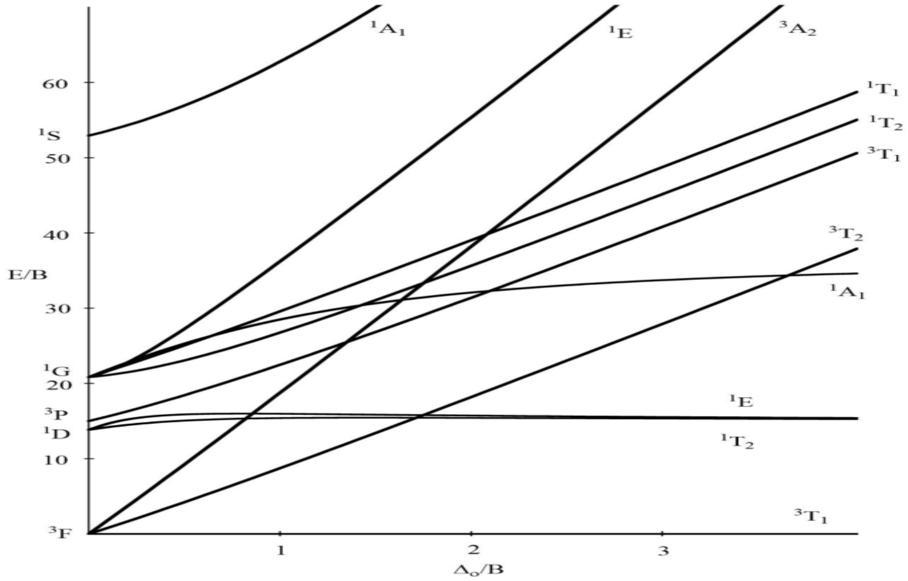


Figure . Splitting of free ion terms for d2 complexes in the octahedral crystal field.

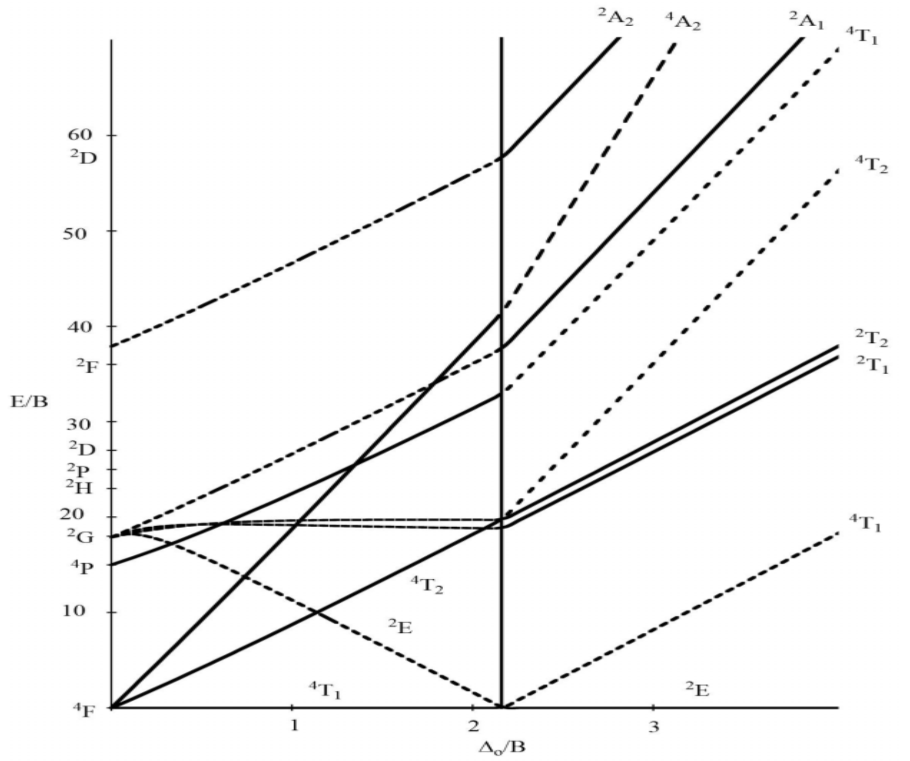


Figure - Splitting of free ion terms for d7 complexes in the octahedral crystal field.

Application to Certain d-electron Configurations

Tanabe-Sugano diagrams have also been constructed for all pertinent d-electron configurations. Here are examples of how they are being used:

d^1 & d^9 Systems

The Tanabe-Sugano diagrams for d^1 (e.g., Ti^{3+}) & d^9 (e.g., Cu^{2+}) systems are relatively straight-forward. Define the crystal-field parameters so the maximum crystal-field strength is represented by Δ, & the energy as E = 0 corresponds to the high-spin state (above is the energy band structure definition, bottom is the spin representation). No high-spin to low-spin transition occurs, & the ground state remains constant across entire regimes of crystal-field strength. The groundstate for d^1 is ^2T2g ($t2g^1$) & the first excited state is ^2Eg (eg^1). That energy difference is equal to Δo.

d^2 & d^8 Systems

From the Tanabe-Sugano diagrams, d^2 (e.g., V^{3+}) and d^8 (e.g., Ni^{2+}) systems give rise to many excited states that stem from the ^3F & ^1D terms. The ground state (^3T1g for d^2 & ^3A2g for d^8) is invariant with respect to the crystal field strength, but the energies of excited states shift in non-linear fashion as Δ/B increases.

d^3 & d^7 Systems

Notes

For d^3 (e.g., Cr^{3+}) & d^7 (e.g., Co^{2+}) scenarios, the Tanabe-Sugano diagrams become fairly intricate. For d^3, the ground state ^4A2g ($t2g^3$) is at all crystal field strengths. For d^7, spin transitions are from high-spin ^4T1g ($t2g^5eg^2$) to low-spin ^2Eg ($t2g^6eg^1$) at high Δ/B-values.

d^4 & d^6 Systems

The Tanabe-Sugano diagrams for d^4 (e.g., Cr^{2+}) & d^6 (e.g., Fe^{2+}) systems exhibit a discontinuous transition from high-spin to low-spin configuration with increasing Δ/B. In the case of d^4, the transition goes from ^5Eg ($t2g^3eg^1$) to ^3T1g ($t2g^4$). For d^6, it is from ^5T2g ($t2g^4eg^2$) to ^1A1g ($t2g^6$).

d^5 Systems

The Tanabe-Sugano diagram is especially interesting for d^5 systems (e.g. Mn^{2+}, Fe^{3+}). The high-spin ground state [of] ^6A1g ($t2g^3eg^2$), is obtained from the ^6S term. Since this is the only sextet state available (all other states have different spin multiplicity), all transitions will be spin-forbidden, hence weak. This is why high-spin d^5 complexes are usually pale or colourless. At very high crystal field strengths, it transitions to a low-spin ^2T2g ($t2g^5$) ground state.

The Tanabe-Sugano diagrams are not a purely theoretical concepts, but also an experimental approach that can be utilized in the data analysis of spectroscopic results. Here's how they can be used:

- This diagram is therefore used though not always so simply to determine the crystal field parameters (Δ, B) by comparing observed transition energies with allowed transitions shown on the diagram.

- Assigning Electronic Transition to Absorption Bands: The diagram makes it possible to assign experimentally observed absorption bands to specific electronic transitions.

- The numerical value of Δ/B can itself predict the energies & intensities of electronic transitions (due to their characteristics of the orbitals involved)

- The diagram helps with appreciate and comprehend ing color: Why do we see colors characteristic of certain d-electron configurations in complexes?

As an illustrative example, say we have an octahedral Ni^{2+} complex (d^8) which displays three bands in its absorption spectrum at 7,000 cm^{-1}, 13,000 cm^{-1}, & 25,000 cm^{-1}. Using d^8 Tanabe-Sugano diagram:

- These bands have been assigned to the transitions of the ^3A2g ground state to ^3T2g, $^3T1g(F)$, & ^3T1g (P) excited states, respectively.

- Δ/B can be obtained from the ratio of the second to first transition energy (≈1.86).

After assigning values, if Δ/B is calculated then B, is computed from that, then Δ is accordingly calculated.-

These data tell us something about the strength of the metal-ligand bond, & thus the position of the ligand on the spectrochemical series.

Notes

Tanabe-Sugano Diagrams — Limitations

Though attractive & useful, Tanabe-Sugano diagrams have their limits:

- In reality complexes may have less than perfect octahedral or tetrahedral symmetry, which the equations assume.
- They ignore spin-orbit interactions, which can be sizeable in heavier transition metals.
- These are not direct insights to transition intensities.
- They do not treat charge transfer transitions, which can be significant in many complexes.
- These provide an approximation based on a single-electron model, & do not encompass multi-electron phenomena.
- Nonetheless, Tanabe-Sugano diagrams are vital tools for appreciate and comprehend ing electronic transitions in transition metal complexes.

Unit 6 Effects on Spectra

Spectroscopic characteristics of transition metal compounds/complexes are strongly dependent on structural & electronic effects. We discuss three central physical mechanisms in influencing the spectral characteristics of these materials: Jahn-Teller distortions, spin-orbit coupling, & charge transfer interactions. Hence & collectively, these effects define the energetics, the intensities & features of electronic transitions & allow shedding valuable light on the intrinsic nature of coordination compounds & their broad use in chemistry, materials science & biology.

Jahn-Teller Distortion in Spectra

Probably, the Jahn-Teller effect is one of the most important factors influencing the electronic structure and spectral characteristics of transition metal complexes. This theorem, postulated by Hermann Arthur Jahn & Edward Teller, in 1937 & states that any non-linear molecular system, once it is in a degenerate electronic state will distort to remove the degeneracy, thus decreasing the total energy of the system. Such spontaneous symmetry breaking is most evident in octahedral complexes of particular electronic configuration, especially

Notes

d^9 Cu^{2+} & high-spin d^4 Cr^{2+} complexes with degeneracy in the eg orbitals (dz^2 & dx^2-y^2) which forces structural distortion. A paradigmatic case of Jahn-Teller distortion happens in octahedral Cu^{2+} complexes with d^9 electronic configuration. In a perfect octahedron, the five d orbitals separate into two groups: the lower-energy t2g (dxy, dxz, dyz) & the higher-energy eg (dz^2 & dx^2-y^2) orbitals. & for Cu^{2+}, the electronic configuration is t2g6eg3 & the ninth electron fills one of the degenerate eg orbitals. This results in an electronically unfavorable condition of the distorted complex, usually stretching along the z-axial (that is, troiger end distillation), which causes the dx^2-y^2 orbital to increase in energy & the dz^2 orbital to decrease. This lifts the degeneracy & increases the stability of the system.

Jahn-Teller distortions have incredible implications on the spectroscopy & characterization of such complexes that are manifold in nature. In absorption spectra, these distortions appear as band splitting, peak broadening, & shifts of the absorption maxima. In Cu^{2+} complexes, where the d orbitals are split into higher & lower energy sets rather than degenerate in a perfect octahedral field, normally octahedral complexes will show one band from the previous allowed transitions where, due to the degeneracy, only a small number of bands exist, but now a set of bands corresponding to the transitions between non-degenerate d orbitals. The splitting of these spectral bands is directly proportional to the extent of geometric distortion. The broad absorption band seen at approximately 800 nm (12,500 cm^{-1}) in hexaaquacopper(II) complexes $[Cu(H_2O)_6]^{2+}$ is a superposition of several transitions & is due to Jahn-Teller distorted geometry. This band is significantly wider than those found in complexes free from Jahn−Teller effects, consistent with the flexibility of the distortion in solution. The wide spectral feature comes from a distribution of differently distorted geometries, which can rapidly interconvert in solution, resulting in time-averaged spectrum with characteristic broadening.

Another unique spectral signature of Jahn-Teller active compounds is temperature dependence. As the energy of thermal fluctuations increases at elevated temperatures, the complex can sample increasingly strained conformations, further broadening the band. Alternatively, at low temperatures the complex may be stuck in particular distorted geometries so that the previously overlapping spectral features can emerge as well-defined separate bands. Jahn-Teller distortions are also seen in vibrational spectra, where they induce characteristic splitting of infrared & Raman modes. The decrease of symmetry induced by the distortion in turn activates vibrational modes that would otherwise be inactive in the undistorted higher-symmetry structure. Eg,S stretching frequencies for metals can exhibit highly patterned behavior each phenomenon of the distortion reflects imbalances in atom ligand bond lengths. The dynamic nature of Jahn-Teller distortions adds to the complexity of spectral interpretations. These systems demonstrate what is known as the "dynamic Jahn-Teller effect," an effect in which the complex rapidly balances between various distorted configurations. This results in temperature-dependent spectra, since the rate of interconversion between distorte geometries changes with T. If interconversion is slow on the timescale of measurement (e.g. at low temperatures), one may observe characteristic spectral features corresponding to discrete geometric configurations. With increasing temperature & concomitant interconversion, these features merge into wider bands corresponding to time-averaged structures.

Notes

Table -Symmetrical and Unsymmetrical *t2g* and *eg* orbitals.

Symmetrical configurations	Unsymmetrical configurations
0 3 6	1 2 4 5
t2g , *t2g* , *t2g*	*t2g* , *t2g* , *t2g* , *t2g*
0 4 2	1 3 2
eg , *eg* , *eg* (high-spin)	*eg* , *eg* , *eg* (low-spin)

Now, the conditions for different kinds of distortion can be summed up as:

Table - . Conditions for Jahn-Teller distortion.

Type of distortion	Configuration required
No distortion	*t2g* (symmetrical) + *eg* (symmetrical)
Slight distortion	*t2g* (unsymmetrical)
Strong distortion	*eg* (unsymmetrical)

Notes

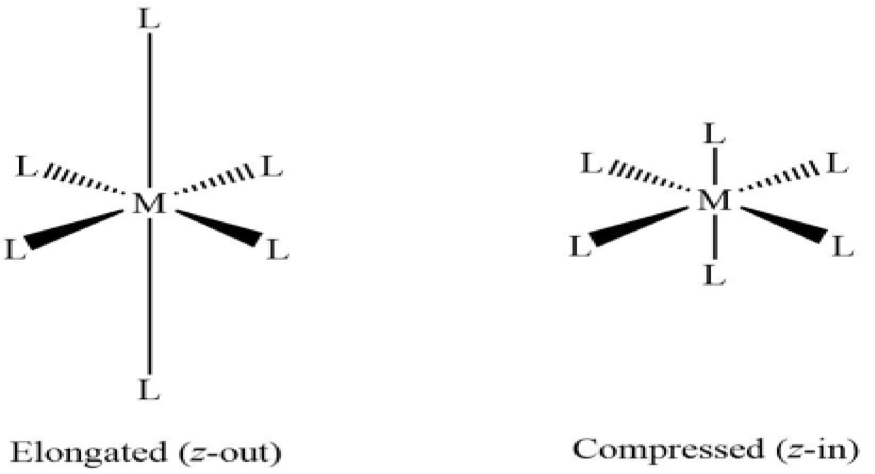


Figure. The Jahn-Teller distortions for an octahedral complex.

Apart from Cu^{2+}, other transition metal ions exhibiting a prominent Jahn-Teller effect are high-spin Mnt(3+) (d^4) & low-spin Nit(3+) (d^7) in octahedral coordinations. For Mn^{3+} complexes the Jahn-Teller effect is due to the undesired occupation of the eg orbitals (realising an e^1g configuration), usually resulting in an elongation along one axis. The d-d transition energies are strongly affected by this distortion, giving rise to characteristic splitting patterns in absorption spectra. These electronic structural attributes contribute heavily to the spectral character of the intensely purple-coloured potassium permanganate ($KMnO_4$). The extent of the Jahn-Teller distortion also relies on ligand nature. Energetic consequences of the distortion are evident in slight blue-shifts of the absorption spectra of strong-field the ligands which tightly interact with the metal d orbitals. In contrast, weak-filed the ligands can lead to smaller distortions & subtle spectral manifestations. Such ligand dependence opens up the means to modulate the spectral characteristics of Jahn-Teller active complexes through careful ligand selection.

In crystal lattices, Jahn-Teller distortions can align & cause cooperative effects that influence further spectral characteristics. These cooperative distortions can induce phase transitions, lower symmetry, & lead to spectral features which are absent from isolated complexes. Jahn-Teller active ionic perovskites, such as $LaMnO_3$, undergo significant temperature-dependent phase transitions with profound implications for their optical & magnetic characteristics. Jahn-Teller distortions are just one part of a highly rich variety of spectral phenomena resulting from the interplay of electronic effects (not just with spin-orbit coupling but also with magnetic exchange interactions) in transition metal compounds.[6] Such interactions often bring forth complex spectral features which depend on the temperature & pressure, accounting not only for the electronic structure but also for the bonding characteristics of these materials. Experimental approaches to the study of Jahn-Teller effects include variable-temperature spectroscopy, MCD, EPR, & resonance Raman techniques. In particular, EPR spectroscopy is highly sensitive to the geometric & electronic effects of Jahn-Teller distortions & provides distinct, well-characterized transitions consisting of anisotropic g-values & hyperfine coupling constants that reflect the diminished symmetry of the distorted complex.

Notes

Static and Dynamic Jahn-Teller Distortion

On the basis of the observed geometry,

the Jahn-Teller distortion can be classified in two types as given below.

1. **Static Jahn-Teller distortion**: Some molecules show tetragonal shape under all conditions i.e., in solid state and in solution state; at lower and relatively higher temperatures. This is referred to as static Jahn-Teller distortion. Hence the distortion is strong and permanent. For example, in CuF2 lattice

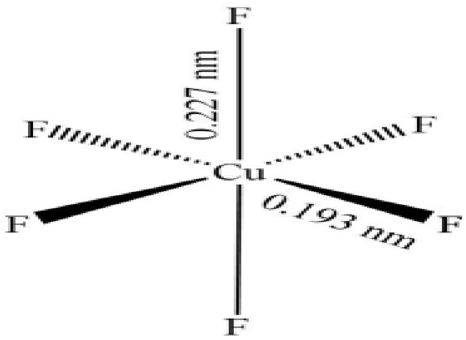


Figure. Static Jahn-Teller distortion in CuF2 lattice.

2. **Dynamic Jahn-Teller distortion**: If the energy gap between z-out and z-in is smaller than the available thermal energy, the complex ions tend to attain both states, i.e., compressed and elongated. This is known as the "Dynamic Jahn Teller Effect". For examples, consider K2Pb[Cu(NO2)6] complex:

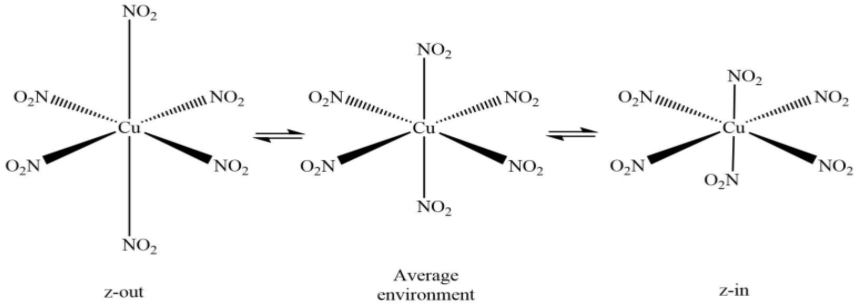


Figure . Dynamic Jahn-Teller distortion in K2Pb[Cu(NO2)6].

Notes

Recent theoretical treatments include vibronic coupling models, where the interaction between electronic & nuclear degrees of freedom is addressed. The models serve as a basis for the interpretation of intricate spectral signatures, such as the pseudo-Jahn-Teller effect semantically caused by the interaction of neighbouring electronic states mediated by vibrational modes. Jahn-Teller effects have been pumped for applications design of optical sensors, switchable materials, & catalysts. Furthermore, the sensitivity of Jahn–Teller distortions to external perturbations such as pressure, temperature & electric fields render them good candidates for construction of responsive materials with tunable optical characteristics. Especially for transition metal based catalysts, small changes to the geometry have a large effect on the catalytic rate, so appreciate and comprehend ing & controlling these distortions can be crucial for improving performance.

Spin-Orbit Coupling and Its Effects

Spin-orbit coupling, a central quantum mechanical coupling, profoundly impacts the electronic structure & spectroscopic characteristics of transition metal complexes. It is a result of the coupling between the spin angular momentum of an electron & its orbital angular momentum, resulting in the lifting of degeneracy of energy levels that are only degenerate by virtue of electrostatic interactions. Spin-orbit coupling typically scales at least as Z^4 (where Z is the atomic number), meaning that the coupling becomes very large for heavier transition metals & lanthanides. Spin-orbit coupling has a geometric physical origin & it arises from relativity. An electron orbits around the nucleus and, in the reference frame of that electron, the nucleus moves around the electron & creates a magnetic field. This magnetic field interacts with the electron's spin magnetic moment, resulting in energy being shifted according to the relative orientation of spin & orbital angular momenta. The Hamiltonian describing this coupling is given by HSO = $\lambda L \cdot S$, where λ is the spin-orbit coupling constant, L is the orbital angular momentum operator, and S is the spin angular momentum operator. For transition metal complexes, the effects of spin-orbit coupling lead to several unique spectroscopic features. Perhaps most fundamentally, spin-orbit coupling allows for off-resonant transitions, thereby relaxing the spin selection rule ($\Delta S = 0$) that would otherwise preclude interconversions between states of differing spin multiplicity. This relaxation processes permit what are called “spin-forbidden” transitions like singlet-triplet transitions in organic materials or high-spin to low-spin transitions in transition metal compounds. Although these transitions are, even in the absence of crystal field effects, weakly allowed with oscillator strengths usually orders of magnitude smaller than those of spin allowed transitions, they nevertheless appear in the absorption & emission spectra with intensities varying with the power of spin-orbit coupling.

One particular application of spin-orbit coupling is evident in the electronic absorption spectra of octahedral d^3 complexes like Cr^{3+}. In these systems, the ground state is ^4A_2g, & transitions to the excited states ^2Eg & ^2T_1g are formally spin forbidden. However, the spin-orbit coupling mixes these excited states with states of the same total angular momentum but different spin multiplicity, adding some allowedness to the transitions. As a result, these transitions show up as faint yet noticeable bands in the absorption spectrum, usually with molar absorptivities (ε) of 1-10 $M^{-1}cm^{-1}$, compared with 10^4-10^5 $M^{-1}cm^{-1}$ for allowed transitions. Dobrý příklad spin-orbitálnė umožňujících přechodních je rubin ($Al_2O_3:Cr^{3+}$), této vlastnosti tak vsak dluží svúj popknown rozceries αn křečovitý harpure of. Absorption spectrum shows two weak bands in the visible region; emission is from the lowest excited state (^2E) to the ground state ($^4A_2$). This emission, called R-line fluorescence, has an exceptionally long lifetime (milliseconds instead of nanoseconds), because the transition involved is spin-forbidden & is only partially allowed due to spin-orbit coupling. For low-spin complexes containing second & third-row transition metals systems where spin-orbit coupling is much stronger, these effects become even more dramatic in the spectra. For octahedral d^6 complexes such as $[Ru(bpy)_3]^{2+}$ & $[Os(bpy)_3]^{2+}$, spin-orbit coupling enables intersystem crossing between singlet & triplet excited states to happen effectively, allowing for high phosphorescence efficiency. The spin-orbit coupling, however, is much greater in the heavier element causing the intersystem crossing to proceed rapidly into the better-emitting triplet state with decay into the ground state proceeding by way of radiative emission.

Spin-orbit coupling not only facilitates transitions otherwise forbidden, but also directly contributes to the energetics of electronic states via the fine structure splitting. This is especially true in the case of lanthanide & actinide complexes, where the energy levels cannot be described using the Russell-Saunders coupling scheme & the J-J coupling scheme has to be applied. In Eu^{3+} complexes, for example, the emission spectrum features bands associated with transitions from the $^5D_0$ excited state to the various levels of the ^7FJ (J = 0-6) ground term, where the energy separations directly reveal the strength of the spin-orbit coupling. Temperature dependent spectral features affected by spin-orbit coupling are useful for identifying the coupling mechanism. Spectral simplification often happens at really low temperatures, when thermal energy cannot be used to populate higher-lying levels in a spin-orbit split manifold, & transitions are mainly originating from the lowest level. As the temperature is raised, each transition appears corresponding to the higher levels within the manifold getting

Notes

thermally populated, which manifests as characteristic changes in the spectral profiles. Magnetic circular dichroism (MCD) spectroscopy is an especially potent method for studying spin-orbit coupling effects in transition metal complexes. A MCD method Jim MCD measures the differential absorbance of left & right circularly polarized light in a magnetic field. The MCD signal is contributed by three mechanisms (A, B, & C terms), with the only contribution that is directly related to the effects of spin-orbit coupling on the ground state arises from the C term. Quantitative information on spin-orbit coupling parameters & state mixing can be obtained from temperature-dependent MCD spectra.

For heavy transition metals such as platinum, iridium, & osmium, the spin-orbit coupling is so strong that it can qualitatively change the description of the electronic structure. For square-planar d^8 Pt(II) complexes, the strong spin–orbit coupling leads to significant mixing of singlet & triplet states, thereby complicating the traditional treatment of purely distinct spin states. Such mixing appears in the photophysical characteristics of Pt(II) complexes, where the emitters display typically features of emission between fluorescence & phosphorescence & are sometimes referred to as "fast phosphorescence." The superb range of spectroscopic characteristics found etween hybridization & ligand field. In octahedral complexes, the symmetry of the ligand field dictates which components of the spin-orbit coupling operator are effective. In strong axial ligand field complexes, for example, orbital angular momentum projection along the z-component may be quenched, resulting in anisotropic spin-orbit coupling effects which show up as directional dependence of spectral transitions. During the past two decades, computational methods for the modeling of SO effects on spectra have been quite advanced reaching from perturbative to fully relativistic approaches. These models all become increasingly accurate in predicting spectral features influenced by spin-orbit coupling when employed with density functional theory (DFT) with relativistic corrections, or complete active space self-consistent field (CASSCF) methods coupled with spin-orbit configuration interaction (SOCI).

Spin-orbit coupling in spectroscopy has many practical applications in a range of fields. Spin-orbit coupling plays a role in magnetic anisotropy in molecular magnetism, which is essential for single molecule magnets. X-ray & electron spin resonance imaging, for instance, benefit from high energy characteristic X-ray emission from heavy metals like gold with intersystem crossing rates heavily dominated by heavy atom induced spin-orbit coupling.258 In photophysical applications, heavy atom induced spin-orbit coupling substantially increase intersystem crossing rates leading to fab-rich phosphorescent materials for organic light-emitting diodes

Notes

(OLEDs).259 The unique spectral signatures derived from spin-orbit coupling also act as sensitive probes of coordination environment & electronic structure in analytical applications. An ongoing study also investigates how the spin-orbit coupling effects can be tuned via chemical approaches, paving new ways to manipulate the spectral characteristics. Such strategies comprise the incorporation of heavy atoms, the tuning of metal-ligand covalency, & the control of molecular symmetry to enhance or suppress certain spin-orbit coupling channels. The combination of these strategies yields flexible methods for unlocking the photophysical characteristics of transition metal complexes for applications from photocatalysis to bioimaging.

Charge Transfer Spectra

Charge transfer has been originated as a certain category of electronic excitations, which are uniquely different from localized d-d transitions concentrated in many transition metal complexes. These transitions represent large redistributions of electron density between parts of the complex, usually between the metal center & the the ligands. The accompanying spectral characteristics frequently overwhelm both the visible & ultraviolet portions of absorption spectra due to their intensities being orders of magnitude greater than associated d-d transitions. Charge transfer spectra are invaluable to metal-ligand bonding, redox characteristics, & photochemical behavior in coordination compounds. Charge transfer transitions are categorized into two classes determined by the direction of the electron transfer: metal-to-ligand charge transfer (MLCT), & ligand-to-metal charge transfer (LMCT). In Metal-to-Ligand Charge Transfer (MLCT) transitions, the electron density is transferred from a primarily metal-based orbital to a primarily ligand-based orbital. On the other hand, LMCT transitions are the transfer of electron density between ligand-based and metal-based orbitals. These types of transitions have large transition dipole moments & therefore possess high molar absorptivities (ε) on the order of 10^3-10^5 $M^{-1}cm^{-1}$, orders of magnitude above the values corresponding to d-d transitions ($\varepsilon \approx 1$-10^2 $M^{-1}cm^{-1}$).

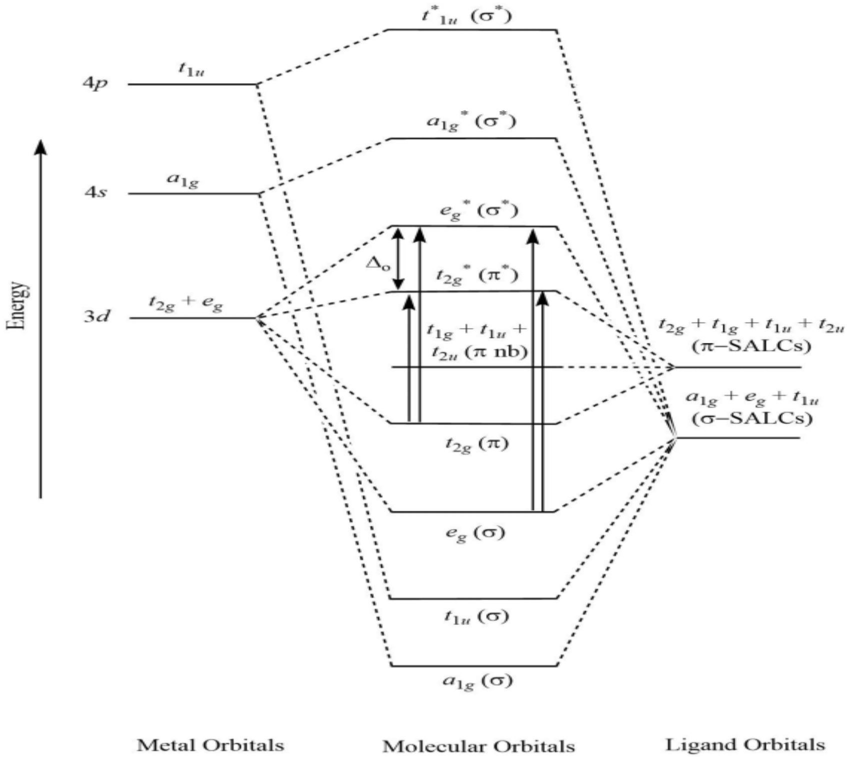


Figure-. Ligand to metal charge transfer in octahedral (ML6) complexes.

The energetics of charge transfer transitions are critically dependent on the redox characteristics of the metal center & the the ligands. MLCT transfers are preferred in the case of complexes including rather rich metals in electrons (low oxidation states) bound to the ligands with low-lying unoccupied orbitals, having π* orbitals generally. Well-studied examples are $[Ru(bpy)_3]^{2+}$ & other polypyridyl complexes of Ru(II), Os(II), & Fe(II) where the metal d orbitals act as electron donors & the π* orbitals of the aromatic the ligands act as electron acceptors. The lowest-energy MLCT transitions in these complexes are readily found in the visible region, imparting intense colors ranging from orange-red for Ru(II) complexes to deep blue-purple for Os(II) analogues. The spectroscopic signature of MLCT transitions is not limited to their high intensity. These transitions frequently display characteristic solvatochromic behavior, where absorption maxima move to lower energies (red shift) in more polar solvents. This dependence on solvent arises from differential stabilization of the excited state, which has more dipole character than the ground state due to charge separation. The extent of this solvatochromic shift can serve as a useful measure of the extent of charge separation in the excited state. In complexes with metals in high oxidation states, coordinated with the ligands with filled orbitals that have relatively high energy, the predominant types of transitions are LMCT transitions. An archetypal case of these are ions of permanganate (MnO_4^-) & chromate (CrO_4^{2-}), in which the oxygen p orbitals increase electron density & the empty metal d orbitals gain it. The purple color of permanganate solutions (with λmax ≈ 525 n a m) is caused by LMCT transitions in the visible region, while the yellow color of chromate solutions is due to LMCT transitions at higher energies (λmax ≈ 370 nm). The energy differences between these transitions correlate with the d orbital energy differences between Mn(VII) & Cr(VI), whereby the metal in the higher oxidation state (Mn) possesses lower-energy acceptor orbitals, resulting in lower-energy LMCT transitions.

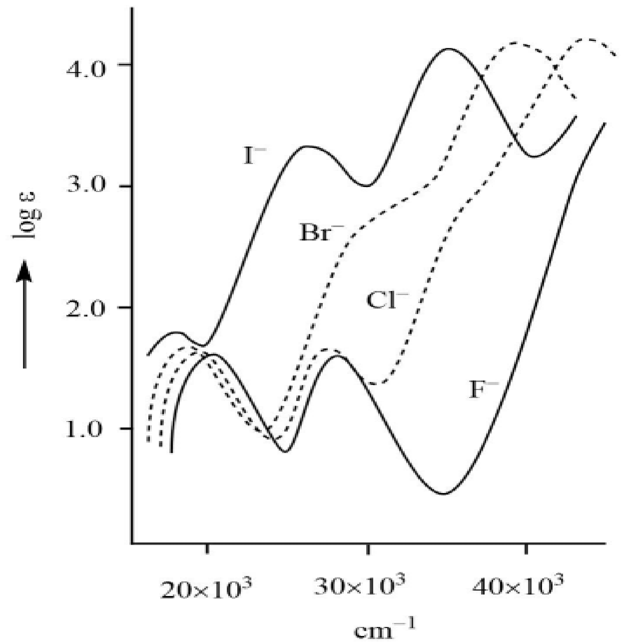


Figure - The UV-visible absorption spectra of [Co(NH3)5(X)]2+ (X = F−, Cl−, Br− or I−).

Charge transfer excitation has particularly important photochemical consequences. In contrast to d-d excited states, which largely lose energy via non-radiative processes or indirectly through weak phosphorescence charge transfer excited states often drive photochemical pathways of diverse nature. MLCT excited states, in this context, can be considered as formally consisting of an oxidized metal center & a reduced ligand, yielding a charge-separated state with unique redox features. This modified redox behavior is foundational for many applications, namely photocatalysis, solar energy conversion & photochemical synthesis. In this regard, the photophysics of MLCT states has been thoroughly investigated in ruthenium(II) polypyridyl complexes, in which the initially populated ^{1}MLCT state decays within a few tens of picoseconds to a ^{3}MLCT state with such near-to-unity

Notes

quantum efficiency, due to the significant spin-orbit coupling brought about by the ruthenium core. The resulting ^{3}MLCT state has a relatively long lifetime (hundreds of nanoseconds to microseconds), allowing it to participate in bimolecular electron transfer reactions with appropriate donor or acceptors. This photophysical behavior forms the basis of applications from dye-sensitized solar cells to photodynamic therapy agents.

These LMCT excited states typically result in the metal center being photo reduced with or without ligand dissociation. A classic example is the photochemistry of hexacyanoferrate (III), $[Fe(CN)_6]^{3-}$, for which LMCT excitation causes reduction of Fe(III) to Fe(II) with simultaneous generation of a cyanide radical. Manifold transition metal oxo complexes undergo similar photoreductive processes & the basis of their photocatalytic activity in water oxidation & other environmentally relevant transformations. In multinuclear complexes and extended structures, complex charge transfer transitions can occur beyond the simple MLCT or LMCT classifications. In MMCT transitions, electrons are transferred between distinct metal centers, as seen in mixed-valence species such as the Creutz-Taube ion, $[(NH_3)_5Ru\text{-py-theta-}Ru(NH_3)_5]^{5+}$. In such compounds, the intervalence charge transfer (IVCT) band affords direct spectroscopic access to the extent of electronic coupling between the metal centers that in turn contains information on electron transfer dynamics in multi-center systems.

On the other hand, complex containing both rich & poor electron the ligands coordinated together to the same metal center can also promote ligand-to-ligand charge transfer (LLCT) transitions. These transitions can happen as independent transitions, or more often overlap with MLCT or LMCT transitions, forming states of complex electronic character. Advanced techniques such as resonance Raman spectroscopy, transient absorption spectroscopy, & magnetic circular dichroism are often required for the spectroscopic identification & assignment of these mixed transitions. With the development of computational methods in chemistry, the theoretical description of charge transfer spectra has made impressive progress. Time-dependent density functional theory (TD-DFT) has become a particularly useful tool for the prediction & interpretation of charge transfer transitions, but standard functionals generally severely underestimate the energies associated with these transitions owing to self-interaction errors. More sophisticated approaches like range-separated functionals have made them more accurate, making it possible to more confidently assign experimental spectra. Charge transfer transitions are of particular chemical interest due to their environmental sensitivity, making them useful as probes in analytical (e.g. chemical sensing) applications. These charge transfer bands can therefore undergo characteristic shifts due to changing solvent polarity, pH, or the presence of an analyte, leading to colorimetric & spectroscopic sensors. The strong absorption and, in some instances, emission related to such transitions provides these detection methods with high sensitivity.

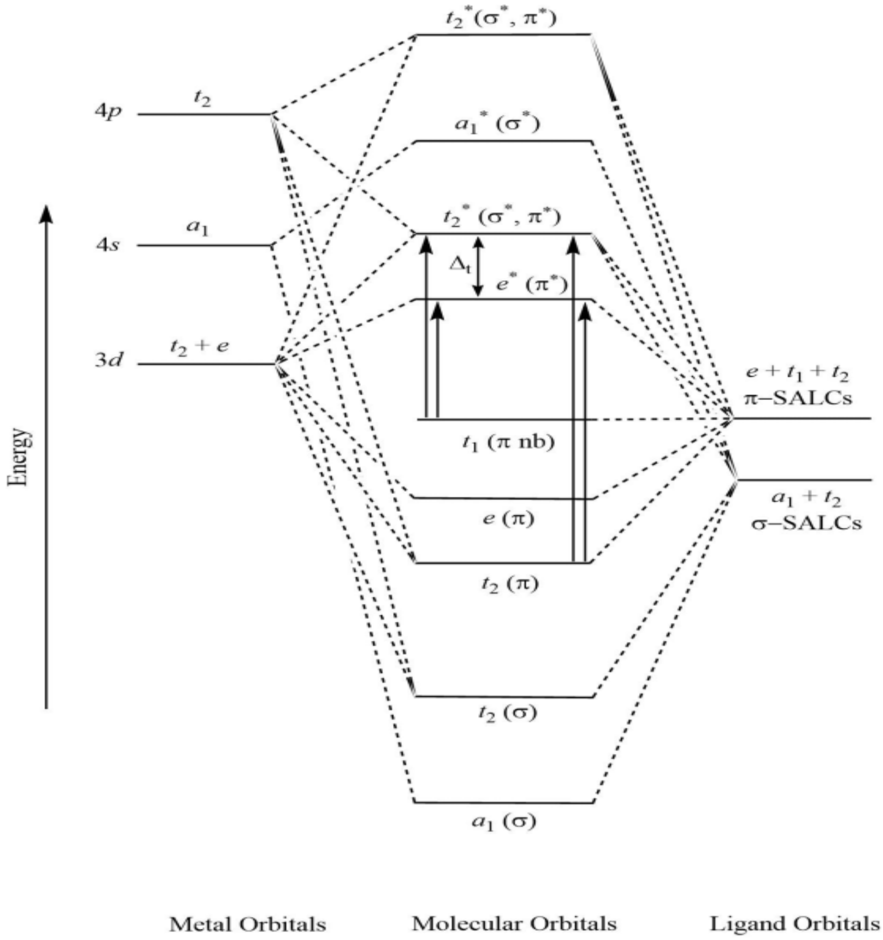


Figure - Ligand to metal charge transfer in tetrahedral (ML4) complexes.

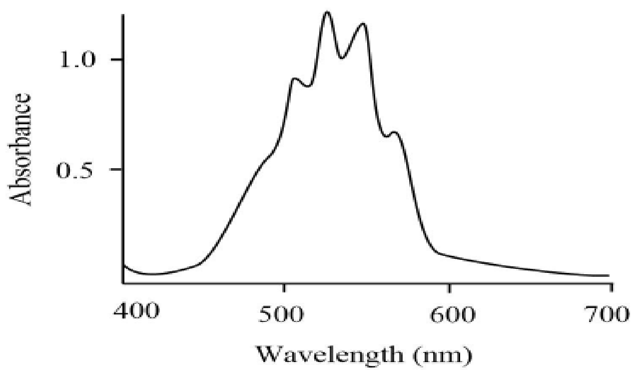


Figure - The UV-visible absorption spectra of MnO4 .

Notes

Charge transfer chromophores are also applied in a wide variety of technical purposes. Transition metal compounds have been widely investigated in solar energy conversion, & ruthenium & osmium polypyridyl complexes with low-energy strong MLCT absorption act as sensitizers in dye-sensitized solar cells by harvesting visible light & inducing the photoinduced electron transfer to semiconductor electrodes. Cyclometalated iridium(III) complexes of mixed MLCT/LLCT character serve as efficient phosphorescent emitters for application in organic light-emitting diodes (OLEDs), widely used display technology & solid-state lighting. The intense absorption of LMCT transitions in metal oxide semiconductors such as TiO_2 and ZnO forms the foundation for their use in photocatalysis & photovoltaics. Recent insights into charge transfer spectroscopy: Emerging trends & future directions for research & development include the need for earth-abundant alternatives to precious metal chromophores, the fabrication of panchromatic absorbers for solar energy applications & the design of stimuli-responsive materials with switchable charge transfer functionalities. SummaryCharge transfer (CT) chromophores have emerged as essential building blocks in many optoelectronic applications, justifying the extensive effort that has been put into the additive synthesis of CT alloys over the past years. However, as revealed by recent studies, the vibrant landscape of charge-transfer phenomena in coordination chemistry has yet to be explored in its full richness for applications & insights to the appreciate and comprehend ing of covalent bond characteristics, due to the boundless availabiliy of synthetic methodologies, spectroscopic tools & theoretical frameworks. This foundational appreciate and comprehend ing of these processes establishes a basis for tackling current problems regarding energy conversion, environmental remediation, & molecular electronics, emphasizing the importance of charge transfer spectroscopy in current-day inorganic chemistry.

Unit 7 Magnetic Characteristics of Metal Complexes

Magnetism is one of the most intrinsic characteristics of matter, & has special prominence in coordination chemistry as it is a compelling probe to the electronic structure & bonding in metal complexes. appreciate and comprehend ing the magnetic characteristics of transition metals complexes is essential to gain valuable information about their coordination environments, oxidation states, & electronic arrangement. Their origins lie in unpaired electrons allowed to occupy d-orbitals of transition metal ions, & thus magnetism data represent an essential diagnostic tool of many coordination chemistry studies & related applications.

Types of Magnetism

The different kinds of magnetic behaviour exhibited by these metal complexes arise from the unique interactions between external fields & the electron configurations of the metal orbitals.

Diamagnetism

Diamagnetism is the simplest shared magnetic behavior, present in all materials, irrespective of their other magnetism. This phenomenon comes from the reaction of paired electrons to the external magnetic field. Under the influence of an external field, the orbital movement of the paired electrons creates an inducted magnetic moment that tends to oppose the external field thus generating a weak repulsion. As a result, diamagnetic materials are repelled by magnetic fields. In coordination compounds, diamagnetism arises if all are paired. This occurs frequently in complexes with d^0, d^{10} or low-spin d^6, d^8 configurations. Notable $ examples includes complexes of Zn^2$ (d^{10} configuration complete) & low-spin octahedral Fe^2$ (d^6) complexes with strong-field the ligands like CN^- or CO. Finally, the diamagnetic contribution is non-zero for all matter & it is only when there are no unpaired electrons that this is the dominant or only contribution to the magnetic characteristics of matter. Diamagnetic materials have a negative, small in magnitude, temperature-independent magnetic susceptibility. Though typically 'overwhelmed' by more robust magnetic influences operating in species where unpaired electrons are present, the diamagnetic term must nonetheless be included to obtain the paramagnetic part of magnetic susceptibility.

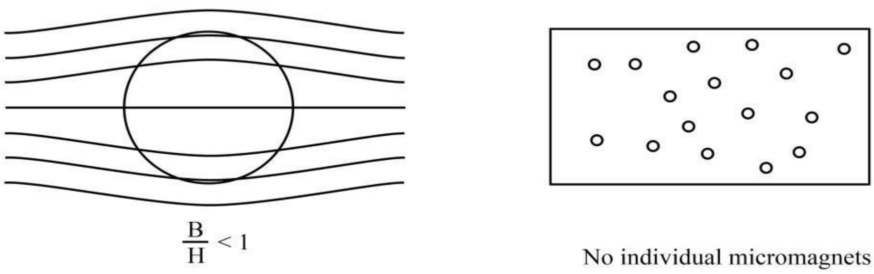


Figure -The behavior of a diamagnetic body in the externally applied magnetic field and corresponding magnetic domain.

Paramagnetism

Paramagnetism is the most common & clinically informative spin, or magnetic property, for transition metal coordination. This happens in materials that have unpaired electrons, which create stable magnetic moments. When there is an external magnetic field, these magnetic moments feel a torque that allign them with the direction of the field, as consequence they are attracted to stronger field intensity regions.

The well known paramagnetic effect is due to two main sources — the inherent spin of unpaired electrons & their orbital angular momentum. The limit of small Δ (i.e., the majority of first-row transition metal complexes) produces an extremely quenched orbital contribution from method 1 which renders the spin contribution as the more substantial. This feature is the basis for the usefulness of the spin-only expression for the calculation of magnetic moments.

Notes

Numerous coordination compounds are paramagnetic:

- High-spin complexes of Fe^{3+} (d^5) having five unpaired electrons
- Co^{2+} (d^7) tetrahedral complexes with three unpaired electrons
- Cu^{2+} (d^9) square planar complexes with one unpaired electron

The paramagnetism can range from very weak to very strong, and thus the extent of paramagnetism is closely related to the number of unpaired electrons present in the system, which is one of the reasons why magnetic measurements are such a powerful tool to determine electronic configurations & to differentiate between low & high spin states of a given metal complex. The paramagnetism' displays a typical temperature dependence which is either the Curie law' (in the case of simple systems) or the `Curie-Weiss law' (which applies to interacting magnetic systems). Upon increasing temperature, quadratics come to play until thermal energy overcomes the aligning potential of individual magnetic moments with the applied field, leading to decreasing paramagnetic susceptibility.

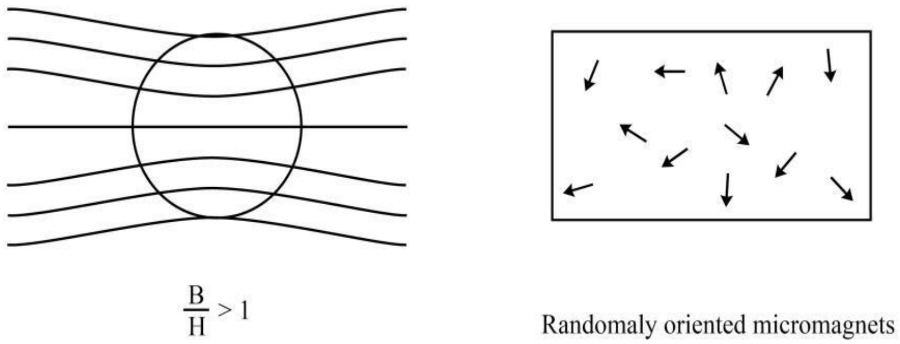


Figure - The behavior of a paramagnetic body in the externally applied magnetic field and corresponding magnetic domain.

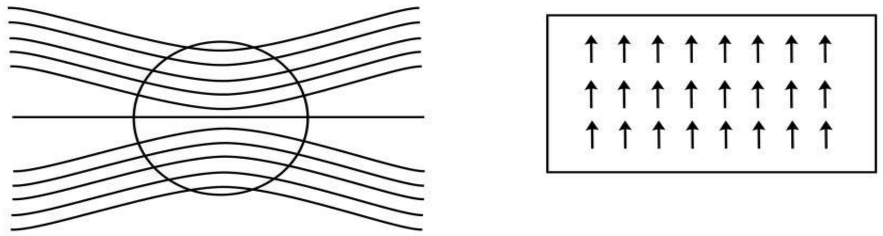
Ferromagnetism

Ferromagnetism is a collective magnetic behavior found in some materials that occurs owing to the interaction of neighboring unpaired electrons via a quantum mechanical exchange mechanism that tends to align their spins parallel in orientation. Such parallel assemblies lead to strongly magnetically ordered domains or regions and, consequently, to spontaneous magnetization even in the zero external field. While ferromagnetism is rare in coordination chemistry with discrete complexes, it plays a significant role in extended structures, such as metal-organic frameworks (MOFs), or polynuclear complexes where two or more metal centers are connected via bridging the ligands capable of facilitating magnetic coupling.

Ferromagnetic materials display a number of unique characteristics:

- Spontaneous magnetisation below certain temperature (Curie temperature)
- Magnetic hysteresis, in which the sample magnetization depends on the magnetic history of the sample
- G-XX Magnonic crystal with up to 65 times increased magnetic susceptibility vs. paramagnetic analogs

Examples, especially in the coordination chemistry field, are certain copper(II) carboxylate dimers & iron(III) oxide clusters with certain bridging geometries that favour ferromagnetic exchange.



$\frac{B}{H} \gg 1$ Parallel alignment micromagnets

Figure - The behavior of a ferromagnetic body in an externally applied magnetic field and corresponding magnetic domain.

Antiferromagnetism

For example, in antiferromagnetism two unpaired electrons on adjacent atoms interact through an exchange interaction that stabilizes antiparallel orientation of their spins. This arrangement creates equal, opposite magnetic moments on each sublattice & hence zero total magnetization when there isn't a field applied externally.

Antiferromagnetic coupling in coordination compounds is often seen in:

- Bridging the ligands at specific geometries in dinuclear complexes
- Metal organic frameworks exhibiting some patterns of connection
- Polymeric clusters with specific metal-metal distances

Notes

Antiferromagnetic materials are characterized by temperature-dependent susceptibility, which has a peak value at the critical temperature known as the Néel temperature. Below this temperature, thermal energy is not enough to break antiparallel ordering of spins. The copper(II) acetate monohydrate dimer is a classic example of an antiferromagnet in coordination chemistry, where two Cu^{2+} ions (each with one unpaired electron) are coupled by four bridging acetate the ligands & through a coupled S = 0 ground state at low temps.

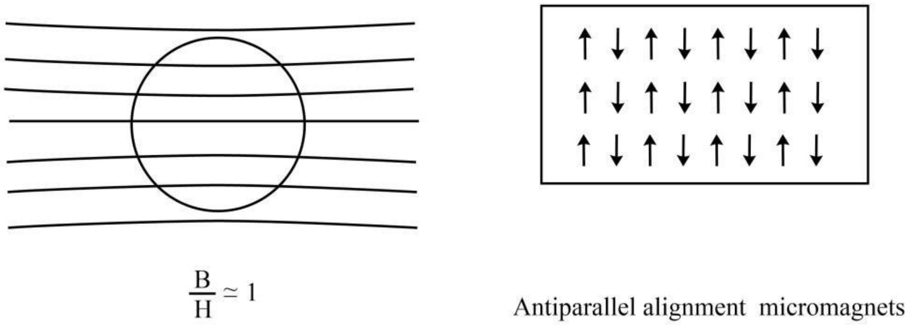


Figure 7. The behavior of an antiferromagnetic body in an externally applied magnetic field and corresponding magnetic domain.

Ferrimagnetism

Ferrimagnetism is similar to both ferromagnetism & antiferromagnetism & occurs in materials that contain two or more distinct magnetic sublattices with unequal but antiparallel magnetic moments. This imbalance gives rise to a net magnetic moment & spontaneous magnetization below a critical temperature. Ferrimagnetism can also arise out of heterometallic (like the same, different metal ions) complexes or extended structures in coordination chemistry, or oxides in solid state chemistry (e.g. different oxidation states of the same metal). A classic example is mixed-valence iron oxide (magnetite, Fe3O4) in which Fe2+ & Fe3+ reside on different crystallographic sites & contribute unequal amounts of antiparallel aligned magnetic moments to a net magnetic moment.

Metamagnetism

The transition from antiferromagnetic/paramagnetic to ferromagnetic state under sufficiently strong external magnetic field is known as metamagnetism. This is the result of the field exceeding the antiferromagnetic exchange interactions, forcing the spins to align with the field. In coordination chemistry, metamagnetic transitions have also been reported for some metal–organic frameworks (MOFs) & coordination polymers with particular structural features that place the antiferromagnetically coupled metal centers at critical distances that allow metamagnetism to ensue at some critical temperature.

Notes

Magnetic Susceptibility

Magnetic susceptibility (χ) quantifies a material's response to an applied magnetic field & serves as the primary experimental parameter measured in magnetic studies of coordination compounds. It is defined as the ratio of the induced magnetization (M) to the applied magnetic field strength (H):

$$\chi = M/H$$

For practical purposes, several different expressions of magnetic susceptibility are employed:

Volume Susceptibility (χ_v)

Volume susceptibility relates the magnetization per unit volume to the applied field strength & is dimensionless in SI units.

Mass Susceptibility (χ_m)

Mass susceptibility (χ_m) normalizes the magnetic response to the sample mass:

$$\chi_m = \chi_v/\rho$$

Where ρ represents the density of the material. Mass susceptibility is commonly expressed in units of cm^3/g or m^3/kg.

Molar Susceptibility (χ_{mol})

Molar susceptibility is particularly useful in coordination chemistry as it normalizes the magnetic response to the amount of substance:

$$\chi_{mol} = \chi_m \times M$$

Where M denotes the molar mass of the compound. Molar susceptibility is typically reported in units of cm^3/mol.

The total molar susceptibility of a coordination compound comprises both diamagnetic & paramagnetic contributions:

$$\chi_{mol} = \chi^{dia} + \chi^{para}$$

For accurate determination of the paramagnetic component (which provides information about unpaired electrons), the diamagnetic contribution must be subtracted:

$$\chi^{para} = \chi_{mol} - \chi^{dia}$$

The diamagnetic correction can be estimated using Pascal's constants, which assign specific diamagnetic contributions to atoms, bonds, & structural features, or through direct comparison with analogous diamagnetic compounds.

Notes

Measurement Techniques

Several experimental methods have been developed to measure the magnetic characteristics of coordination compounds, each with specific advantages & limitations. These techniques vary in sensitivity, sample requirements, & the information they provide.

The Gouy Method

The Gouy method represents one of the oldest & most widely used techniques for measuring magnetic susceptibility of coordination compounds. This classical approach, developed by Louis Georges Gouy in the late 19th century, relies on the force experienced by a sample when placed in a non-uniform magnetic field.

Principle & Apparatus

In the Gouy balance apparatus, a cylindrical sample is suspended from an analytical balance & positioned so that one end lies within a uniform region of a magnetic field while the other end extends into a region of negligible field strength. When the field is applied, the sample experiences a net force along the field gradient. For paramagnetic substances, this force pulls the sample toward the stronger field region, while diamagnetic materials experience a slight repulsion.

The apparatus consists of:

- An analytical balance with high precision (typically 0.1 mg or better)
- A cylindrical sample tube of uniform cross-section
- An electromagnet capable of generating fields up to ~1.5 Tesla
- A sample holder that positions the tube vertically between the magnet poles

Measurement Procedure

The measurement process involves several key steps:

1. The sample is packed uniformly into a cylindrical tube to avoid density gradients
2. The tube is weighed precisely without the magnetic field
3. The magnetic field is applied, & the apparent weight change (Δw) is recorded
4. The volume susceptibility is calculated from the weight change using the equation:

$$\chi_v = (\Delta w \times g)/(H^2 \times A \times m/2)$$

Where:

- g is the gravitational acceleration
- H is the magnetic field strength
- A is the cross-sectional area of the sample
- m is the mass of the sample

For standardization & to eliminate systematic errors, the measurement is typically calibrated using a substance of known susceptibility, such as mercury (II) tetrathiocyanatocobaltate (III), $HgCo(SCN)_4$.

Notes

Advantages & Limitations

The Gouy method offers several advantages:

- Relatively simple instrumentation & methodology
- Ability to measure a wide range of susceptibilities
- Compatibility with solid, liquid, & solution samples
- Minimal sample preparation requirements

However, the technique also presents significant limitations:

- Relatively large sample quantities (typically 0.5-1 g) are required
- Precise packing of the sample is critical to avoid systematic errors
- Temperature control can be challenging, particularly at extreme temperatures
- The method offers moderate precision compared to more modern techniques
- Ferromagnetic impurities can severely distort measurements

Despite these limitations, the Gouy method remains valuable in educational settings & for routine measurements where high precision is not essential.

The Faraday Method

The Faraday method represents a refinement of the Gouy technique that addresses some of its limitations. This approach employs a small sample positioned entirely within a region of uniform field gradient, resulting in a more consistent force experienced by the entire sample.

Key advantages of the Faraday method include:

- Smaller sample requirements (typically 50-100 mg)
- Higher precision, particularly for weakly magnetic materials

- Better temperature control due to the smaller sample size
- Reduced sensitivity to packing irregularities

However, the method requires more sophisticated equipment with precisely engineered magnetic field gradients, making it less accessible for routine laboratory use.

Evans Method (NMR Method)

The Evans method utilizes nuclear magnetic resonance (NMR) spectroscopy to determine magnetic susceptibility through the effect of paramagnetic species on the chemical shift of a reference compound (typically the solvent or an internal standard like tetramethylsilane).

This technique proves particularly valuable for:

- Solution-state measurements of coordination compounds
- Samples available only in small quantities (1-10 mg)
- Temperature-dependent studies in solution
- Investigations of paramagnetic complexes in biological systems

The method measures the difference in chemical shift (Δf) between the reference in the presence & absence of the paramagnetic compound, from which the mass susceptibility can be calculated:

$$\chi_m = (3 \times \Delta f)/(4\pi \times f \times c)$$

Where:

- f is the operating frequency of the NMR spectrometer
- c is the concentration of the paramagnetic species

The Evans method offers exceptional precision for dilute solutions & requires minimal sample preparation, making it the preferred technique for many modern investigations of paramagnetic coordination compounds.

SQUID Magnetometry

Superconducting Quantum Interference Device (SQUID) magnetometry represents the gold standard for high-precision magnetic measurements in contemporary coordination chemistry research. This technique utilizes superconducting loops containing Josephson junctions to detect incredibly small magnetic fields with unparalleled sensitivity.

SQUID magnetometers offer several distinct advantages:

- Exceptional sensitivity (detection limits around 10^{-10} emu)
- Minimal sample requirements (as little as 1 mg)

- Wide temperature range capabilities (typically 1.8-400 K)
- Ability to measure in varying applied fields (up to 7 Tesla in commercial systems)
- High precision for both strong & weak magnetic responses

These capabilities make SQUID magnetometry ideal for:

- Temperature-dependent studies revealing magnetic phase transitions
- Field-dependent measurements identifying metamagnetic behavior
- Investigations of weak magnetic coupling in polynuclear complexes
- Characterization of single-molecule magnets & spin crossover compounds

While the technique requires specialized equipment & cryogenic facilities, its unmatched precision & versatility have established it as the primary method for advanced magnetic studies of coordination compounds.

Vibrating Sample Magnetometry (VSM)

Vibrating Sample Magnetometry provides another sensitive technique for measuring magnetic moments. In this approach, a sample vibrates within a uniform magnetic field, inducing an electrical signal in detection coils proportional to the sample's magnetic moment.

VSM offers a good compromise between precision & accessibility:

- Moderate sensitivity (around 10^{-6} emu)
- Relatively straightforward operation compared to SQUID magnetometry
- Rapid measurement capabilities for routine characterization
- Compatibility with variable temperature & field studies

This technique proves particularly useful for educational settings & industrial applications where high throughput is prioritized over ultimate sensitivity.

Magnetic Moment & Electronic Structure

The magnetic moment of a coordination complex provides direct insight into its electronic configuration, serving as a diagnostic probe for oxidation state, spin state, & bonding characteristics. This

Notes

relationship forms the theoretical foundation for interpreting magnetic measurements in coordination chemistry.

The Spin-Only Formula

For many first-row transition metal complexes, the orbital angular momentum contribution to the magnetic moment is largely quenched by the ligand field, leaving the spin angular momentum as the dominant contributor. This phenomenon gives rise to the spin-only formula, which relates the effective magnetic moment (μ_{eff}) to the number of unpaired electrons (n):

$$\mu_{eff} = g\sqrt{[S(S+1)]}\ \mu_B$$

Where:

- g is the electron g-factor (approximately 2.0023 for a free electron)
- S is the total spin quantum number (S = n/2 for n unpaired electrons)
- μ_B is the Bohr magneton (9.274×10^{-24} J/T)

This expression simplifies to the widely used form:

$$\mu_{eff} = \sqrt{[n(n+2)]}\ \mu_B$$

The spin-only formula provides a remarkably good approximation for many octahedral & tetrahedral complexes of first-row transition metals, particularly those with less than half-filled d-shells.

Expected spin-only magnetic moments for different numbers of unpaired electrons are:

- n = 1: $\mu_{eff} = 1.73\ \mu_B$
- n = 2: $\mu_{eff} = 2.83\ \mu_B$
- n = 3: $\mu_{eff} = 3.87\ \mu_B$
- n = 4: $\mu_{eff} = 4.90\ \mu_B$
- n = 5: $\mu_{eff} = 5.92\ \mu_B$

Experimental magnetic moments typically deviate slightly from these ideal values due to:

- Residual orbital contributions
- Spin-orbit coupling effects
- Temperature-dependent phenomena
- Magnetic exchange interactions in polynuclear complexes

Orbital Contribution & Spin-Orbit Coupling

Notes

While the spin-only formula provides a good approximation for many complexes, significant deviations occur in certain cases due to unquenched orbital angular momentum & spin-orbit coupling. For ions with degenerate ground states (particularly those with t_2g^3, t_2g^5, eg^1, or eg^3 configurations in octahedral fields), the orbital angular momentum is not fully quenched, leading to magnetic moments substantially higher than the spin-only values. Notable examples include:

- Octahedral Co^{2+} complexes (d^7): Theoretical spin-only moment of 3.87 μ_B, but typically exhibit values of 4.3-5.2 μ_B
- Octahedral Ni^{2+} complexes (d^8): Theoretical spin-only moment of 2.83 μ_B, but often show values around 3.2 μ_B

The extent of orbital contribution depends on several factors:

- The specific electronic configuration & ground state
- The symmetry of the coordination environment
- The nature of the metal-ligand bonding
- The strength of the spin-orbit coupling

For second & third-row transition metals, the spin-orbit coupling becomes increasingly significant, often leading to magnetic moments that deviate substantially from spin-only predictions. In these cases, more sophisticated theoretical treatments incorporating the full angular momentum ($J = L + S$) become necessary.

Determination of Electronic Configuration from Magnetic Data

Magnetic measurements serve as a powerful tool for elucidating the electronic configurations of coordination complexes, particularly in distinguishing between high-spin & low-spin states in d^4-d^7 configurations.

High-Spin vs. Low-Spin Complexes

For transition metal ions with d^4-d^7 configurations in octahedral environments, the electronic arrangement depends on the relative magnitudes of the pairing energy (P) & the crystal field splitting parameter (Δ_o):

- When $P > \Delta_o$: High-spin configuration prevails, maximizing the number of unpaired electrons
- When $P < \Delta_o$: Low-spin configuration dominates, with electrons preferentially filling the lower-energy t_2g orbitals

Magnetic measurements provide a definitive method to distinguish between these possibilities:

Notes

- Fe^{2+} (d^6): High-spin state has 4 unpaired electrons ($\mu_{e}ff \approx 4.9$ μ_B), while low-spin state is diamagnetic
- Co^{3+} (d^6): High-spin state has 4 unpaired electrons ($\mu_{e}ff \approx 4.9$ μ_B), while low-spin state is diamagnetic
- Fe^{3+} (d^5): High-spin state has 5 unpaired electrons ($\mu_{e}ff \approx 5.9$ μ_B), while low-spin state has 1 unpaired electron ($\mu_{e}ff \approx 1.7$ μ_B)

This application has proven particularly valuable in characterizing spin crossover compounds that exhibit temperature-dependent transitions between high-spin & low-spin states, manifested as dramatic changes in magnetic susceptibility.

Temperature Dependence & Magnetic Exchange

The temperature dependence of magnetic susceptibility provides additional insights into electronic structure & magnetic interactions:

- Simple paramagnets following the Curie law ($\chi \propto 1/T$) indicate isolated magnetic centers
- Deviations toward higher susceptibilities at low temperatures (positive Weiss constants) suggest ferromagnetic interactions
- Deviations toward lower susceptibilities at low temperatures (negative Weiss constants) indicate antiferromagnetic coupling

In polynuclear complexes, analysis of magnetic exchange interactions through variable-temperature studies can reveal:

- The strength of magnetic coupling (quantified by the exchange coupling constant, J)
- The dimensionality of the magnetic interactions (1D chains, 2D sheets, or 3D networks)
- The pathway & mechanism of magnetic exchange (direct exchange, superexchange, or double exchange)
- The ground state spin value of the coupled system

These parameters provide valuable information about the electronic structure & bonding within & between metal centers.

Calculation Methods & Worked Examples

Practical application of magnetic theory in coordination chemistry involves several calculation methods that extract meaningful electronic structure information from experimental measurements. The following approaches & examples illustrate these principles.

Converting Experimental Data to Magnetic Moments

Notes

The process of converting raw experimental data to magnetic moments typically involves several steps:

1. Determination of mass susceptibility (χ_m) from experimental measurements using appropriate instrumental equations

2. Conversion to molar susceptibility: $\chi_{mol} = \chi_m \times$ molecular weight

3. Application of diamagnetic corrections: $\chi^{para} = \chi_{mol} - \chi^{dia}$

4. Calculation of effective magnetic moment: $\mu_eff = 2.828\sqrt{(\chi^{para} \times T)}$

Where T is the absolute temperature in Kelvin.

Example 1: Magnetic Moment Calculation from Gouy Method Data

Consider a cobalt (II) complex with the formula $[Co(NH_3)_6]Cl_2$ measured using the Gouy method at 298 K. The following experimental data was obtained:

- Sample mass: 0.786 g
- Tube length: 10.0 cm
- Cross-sectional area: 0.25 cm²
- Applied field: 0.8 Tesla
- Observed weight change: 11.2 mg

Calculate the magnetic moment & determine the spin state of the complex.

Step 1: Calculate volume susceptibility

$\chi_v = (\Delta w \times g)/(H^2 \times A \times l)$ $\chi_v = (0.0112 \text{ g} \times 980 \text{ cm/s}^2)/[(0.8 \text{ T})^2 \times 0.25 \text{ cm}^2 \times 10.0 \text{ cm}]$ $\chi_v = 6.86 \times 10^{-5}$ (in cgs units)

Step 2: Convert to mass susceptibility

$\chi_m = \chi_v/\rho$, where ρ is the density (approximately 1.8 g/cm³ for this complex) $\chi_m = (6.86 \times 10^{-5})/1.8 = 3.81 \times 10^{-5}$ cm³/g

Step 3: Calculate molar susceptibility

Molecular weight of $[Co(NH_3)_6]Cl_2 = 58.93 + 6(14.01 + 3) + 2(35.45) = 267.48$ g/mol $\chi_{mol} = \chi_m \times MW = 3.81 \times 10^{-5} \times 267.48 = 1.02 \times 10^{-2}$ cm³/mol

Step 4: Apply diamagnetic correction

Using Pascal's constants, estimate χ^{dia}:

- Co^{2+}: -13×10^{-6} cm³/mol

Notes

- NH_3 (6 groups): 6 × (-18 × 10^{-6}) = -108 × 10^{-6} cm^3/mol
- Cl^- (2 ions): 2 × (-23 × 10^{-6}) = -46 × 10^{-6} cm^3/mol Total χ^{dia} = -167 × 10^{-6} cm^3/mol = -1.67 × 10^{-4} cm^3/mol

$\chi^{para} = \chi_{mol} - \chi^{dia} = 1.02 \times 10^{-2} - (-1.67 \times 10^{-4}) = 1.04 \times 10^{-2}$ cm^3/mol

Step 5: Calculate effective magnetic moment

$\mu_{eff} = 2.828\sqrt{(\chi^{para} \times T)}$ $\mu_{eff} = 2.828\sqrt{(1.04 \times 10^{-2} \times 298)}$ $\mu_{eff} = 4.97\ \mu_B$

Step 6: Interpret the result

The calculated moment (4.97 μ_B) substantially exceeds the spin-only value for three unpaired electrons (3.87 μ_B) but aligns with typical values observed for high-spin octahedral Co^{2+} complexes (4.7-5.2 μ_B). This elevated moment indicates significant orbital contribution from the ^4T_1g ground state.

The result confirms a high-spin d^7 configuration with three unpaired electrons, consistent with the relatively weak-field nature of ammonia the ligands for Co^{2+}.

Example 2: Distinguishing Geometric Isomers

Magnetic measurements can differentiate between geometric isomers with different electronic configurations. Consider two nickel(II) complexes with the formula $[Ni(PPh_3)_2X_2]$, where X represents a halide ligand. The magnetic measurements yield:

- Complex A: μ_{eff} = 3.12 μ_B at 298 K
- Complex B: μ_{eff} = 0 μ_B (diamagnetic)

Determine the likely geometric arrangements for these complexes.

Analysis:

- Complex A exhibits paramagnetism consistent with two unpaired electrons (spin-only value: 2.83 μ_B), with the slightly higher experimental value indicating some orbital contribution
- Complex B is diamagnetic, indicating no unpaired electrons

For a d^8 configuration of Ni^{2+}:

- Tetrahedral geometry typically produces paramagnetic complexes with two unpaired electrons
- Square planar geometry results in diamagnetic complexes with all electrons paired

Therefore:

- Complex A likely adopts a tetrahedral geometry around the nickel center

- Complex B possesses a square planar arrangement

This conclusion is further supported by considering that triphenylphosphine (PPh_3) is a strong-field ligand that favors square planar geometry for d^8 configurations when present in sufficient proportion relative to the weaker-field halide the ligands.

Example 3: Temperature-Dependent Measurements & Exchange Coupling

Consider a dinuclear copper(II) complex $[Cu_2(\mu\text{-}OAc)_4(py)_2]$ for which variable-temperature magnetic susceptibility measurements yield the following data:

Temperature (K)	**χ_{mol} (10^{-3} cm^3/mol)**
300	0.45
250	0.51
200	0.54
150	0.49
100	0.27
50	0.1

Analyze this data to determine the nature of magnetic coupling between the copper centers.

Step 1: Convert to magnetic moment at each temperature

At 300 K: $\mu_eff = 2.828\sqrt{(0.45 \times 10^{-3} \times 300)} = 1.04\ \mu_B$ At 50 K: $\mu_eff = 2.828\sqrt{(0.10 \times 10^{-3} \times 50)} = 0.20\ \mu_B$

Step 2: Analyze the temperature dependence

The effective moment decreases significantly as temperature decreases, with values well below the expected range for independent Cu^{2+} centers (1.7-2.2 μ_B per copper). This behavior indicates strong antiferromagnetic coupling between the two copper(II) ions.

Step 3: Apply the Bleaney-Bowers equation for a coupled dinuclear system

$\chi_{mol} = (2Ng^2\mu_B^2/kT) \times [3/(3+\exp(-2J/kT))]$

Where:

- N is Avogadro's number
- g is the g-factor
- μ_B is the Bohr magneton
- k is the Boltzmann constant
- J is the exchange coupling constant

Notes

Fitting the experimental data to this equation yields $J \approx -300\ cm^{-1}$, indicating strong antiferromagnetic coupling through the acetate bridges. This strong coupling results from the specific geometry of the copper acetate paddle-wheel structure, where bridging acetate the ligands facilitate effective overlap between the magnetic orbitals of the two d^9 Cu^{2+} centers.

Advanced Applications & Modern Developments

Magnetic studies of coordination compounds continue to evolve, with several cutting-edge applications in contemporary research.

Single-Molecule Magnets (SMMs)

Single-molecule magnets represent a revolutionary class of coordination compounds that exhibit magnetic bistability & slow magnetic relaxation at the molecular level. These materials bridge the gap between classical bulk magnets & quantum systems, offering potential applications in high-density information storage & quantum computing.

Key characteristics of SMMs include:

- High-spin ground states with significant magnetic anisotropy
- Energy barriers to magnetization reversal ($\Delta = |D|S^2$) for integer spin or $|D|(S^2-1/4)$ for half-integer spin
- Hysteresis of magnetic origin at low temperatures
- Quantum tunneling of magnetization under specific conditions

Prominent examples include:

- Mn_{12}-acetate cluster, the first discovered SMM with S = 10 ground state
- Dysprosium double-decker phthalocyanine complexes with extremely high anisotropy barriers
- Polynuclear lanthanide clusters with record blocking temperatures

Magnetic characterization of SMMs typically requires sophisticated measurements, including:

- AC susceptibility to determine relaxation dynamics
- Micro-SQUID magnetometry to observe quantum tunneling steps
- Single-crystal magnetic studies to elucidate anisotropy axes

Spin Crossover (SCO) Complexes

Spin crossover phenomena occur in certain transition metal complexes that can switch between high-spin & low-spin electronic configurations in response to external stimuli such as temperature, pressure, or light irradiation. This bistability creates opportunities for molecular switches & sensors.

Magnetic measurements prove essential for characterizing SCO behavior, revealing:

- Transition temperatures & thermal hysteresis
- Completeness of spin conversion
- Cooperativity between metal centers in crystalline materials
- Kinetics of the spin transition process

Iron(II) complexes with nitrogen-donor the ligands represent the most extensively studied SCO systems, with magnetic moments transitioning between ~0 μ_B (low-spin, S=0) & ~4.9 μ_B (high-spin, S=2) upon spin state switching.

Magnetic Resonance Imaging (MRI) Contrast Agents

Paramagnetic coordination compounds, particularly gadolinium(III) complexes, serve as critical components in MRI contrast agents. These materials enhance image contrast by accelerating the relaxation of water protons in biological tissues.

The paramagnetic characteristics directly influence contrast agent efficacy through:

- The number of unpaired electrons (Gd^{3+} with seven unpaired electrons is ideal)
- The electronic relaxation time
- Water exchange rates at the metal center
- Rotational correlation times of the complex

Magnetic studies of potential contrast agents focus on:

- Relaxivity measurements in various media
- Stability constants in physiological conditions
- Coordination geometry & water accessibility
- Temperature dependence of magnetic characteristics

Quantum Information Processing

The discrete, well-defined energy levels of magnetic coordination compounds make them promising candidates for quantum bits (qubits)

Notes

in quantum information processing. Molecular qubits based on coordination compounds offer advantages including:

- Chemical tunability through ligand design
- Coherence times amenable to manipulation
- Potential for creating entangled multi-qubit systems
- Integration into larger molecular architectures

Magnetic characterization of molecular qubits employs specialized techniques including:

- Electron paramagnetic resonance (EPR) spectroscopy with high field/frequency capabilities
- Pulsed EPR methods to determine quantum coherence times
- Ultra-low temperature magnetometry
- Micro-resonator methods for single-molecule studies

Molecular Spintronics

Molecular spintronics represents an emerging field that utilizes the spin characteristics of coordination compounds to create novel electronic devices with enhanced functionality. These systems exploit:

- Spin-dependent electron transport
- Magnetic switching behavior
- Spin filtering capabilities
- Magneto-resistance effects

Magnetic measurements in molecular spintronics research often combine traditional bulk techniques with specialized approaches:

- Spin-polarized scanning tunneling microscopy
- Magneto-transport measurements in molecular junctions
- X-ray magnetic circular dichroism (XMCD) for element-specific magnetism
- Muon spin resonance (μSR) for local probe studies

Unit 8 Advanced Magnetic Concepts

Magnetism, one of nature's four fundamental forces, is an exceedingly more complicated affair than the everyday examples—simple bar magnets & refrigerator magnets—that we know. Magnetism occurs when the movement of charged particles—such as electrons—couples them to an external field. The orbital contribution to the magnetic moment, the cooperative phenomena (ferromagnetism &

antiferromagnetism) & the application of the magnetic measurements for the determination of structure are discussed in this section.

Orbital Contribution to Magnetic Moment

Atoms & molecules exhibit magnetic characteristics due primarily to two sources: the intrinsic spin of electrons and the orbital motion of electrons around the nucleus of an atom. The contribution to the magnetic moment from the orbital degrees of freedom, although often overshadowed by that from spin in introductory treatments, is equally important for appreciate and comprehend ing the bulk magnetic characteristics of materials. For a first approximation & visualization, electrons orbiting around an atomic nucleus can be thought of as little current loops. As per classical electromagnetic theory, a current loop produces a magnetic field that is perpendicular to the plane formed by the loop, creating a magnetic dipole. This magnetic moment has a magnitude which is directly proportional to both the current flowing through the loop, & the area of the enclosed loop. In quantum mechanical language, this means a magnetic moment proportional to the electron's orbital angular momentum. Orbital magnetism, as formulated in quantum mechanics, starts from the orbital angular momentum operator, $\hat{L}$. For an electron in a hydrogen-like atom, the incident operator has an expectation value equaling the orbital angular momentum quantum number l, which can take the values $l = 0, 1, 2,...,$ $n - 1$ for the principal quantum number n. The expression for the magnetic moment originated from this orbital motion is:

$\mu_l = -\mu_o L$

where μ_o is the Bohr magneton (9.274×10^{-24} J/T), a fundamental unit of magnetic moment.

Electrons in atoms do not orbit in well-defined planes in contrast to the classical objects. Rather, their wavefunctions represent probability distributions in 3-dimensional space. "L = 0; S = 1/2" refers to electrons in s orbitals, while "l > 0" is true for electrons in p, d, or f orbitals in which case, these distributions inherit angular momentum that plays a major role in the magnetic characteristics of the atom. Electrons in s orbitals (l = 0), on the other hand, have spherically symmetric wavefunctions with no orbital angular momentum, & therefore do not contribute to the magnetic moment at all via orbital motion. In transition metal and rare-earth compounds, this orbital contribution is particularly pronounced. In transition metals, the partially filled d orbitals (l =2) can produce large orbital magnetic moments. This contribution is however frequently "quenched" in crystalline environments due to crystal field effects. Due to the electrostatic interactions with neighboring atoms in the lattice, crystal field essentially lifts the degeneracy of the free atom by breaking the

Notes

Notes

spherical symmetry, thus allowing coupled states of orbital angular momentum with the crystal lattice, instead of spin. This effect, called orbital quenching, greatly diminishes the orbital contribution of transition metal compounds to the total magnetic moment.

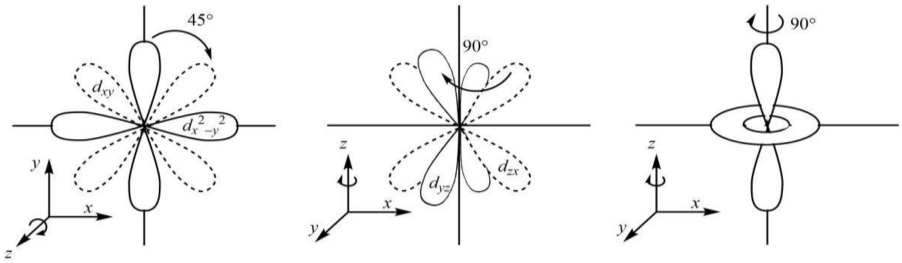


Figure-. The circulation of electron density in a partially filled d-subshell about the z-axis.

On the contrary, for rare-earth elements that have partially filled f orbitals (l = 3), the orbital quenching is very weak because the 4f electrons are strongly shielded from the crystal field by the outer electrons. As a result, these components exhibit massive orbital contributions to their magnetic moments, which might make clear their extraordinary magnetic characteristics. Spin-orbit coupling, the coupling between the orbital & spin magnetic moments, complicates the magnetic behavior even further. This coupling originates from the relativistic motion of the electron around the nucleus, which leads to an effective magnetic field interacting with the spin of the electron. The magnetic strength of spin-orbit coupling scales with atomic number, & thus plays a large role in heavy elements. For light elements ($Z<30$) this interaction is well described in terms of the Russell-Saunders coupling scheme. Using this scheme, one obtains a total orbital angular momentum L from the orbital angular momenta from all electrons, & a total spin angular momentum S from the spin angular mometum of all electrons, which couple to give rise to a total angular momentum J = L + S, with associated quantum numbers L, S, J.

In the Russell-Saunders scheme, total magnetic moment can be expressed as:

$$\mu = -g\, \mu_o \sqrt{(J(J+1))}$$

where g is the Landé g-factor:

$$g=1+[J(J+1)+S(S+1)-L(L+1)]/[2J(J+1)]$$

Equation shows the total magnetic moment is a combination of spin magnetic moment & orbital magnetic moment contributions. For heavier elements the j-j coupling scheme is more valid. This scheme treats the spin-orbit interaction for each electron one at a time, resulting in a total angular momentum per electron given by j = l + s, which combine to give the total angular momentum J. The orbital part of the magnetic moment also gives a contribution for molecular systems, &

Notes

especially, for those containing metal centers. In coordination compounds, orbital contribution can be mixed, but a ligand field (more of a crystal field) can quench this fractional or the full orbital contribution based on the complex's symmetry & the ligand-enzyme interaction. The resultant magnetic anisotropy—the directional dependence of magnetic characteristics—has important implications for molecular magnetism & single-molecule magnets. Orbital contributions to magnetic moment play a critical role in interpreting magnetic data & designing materials with desired magnetic characteristics. Techniques like XMCD [X-ray magnetic circular dichroism] that gain access to orbital & spin contributions separately, can map out the electronic structure of magnetic materials down to the atoms.

(a) Ferromagnetism & (b) Antiferromagnetism

In addition to the magnetic property of single atoms or molecules, collective magnetic behaviors can emerge in condensed matter systems due to the interactions between magnetic moments. These cooperative effects give rise to a diverse variety of magnetic ordering states, of which ferromagnetism & antiferromagnetism are two of the oldest paradigms. Ferromagnetism, the mechanism behind permanent magnets formation, arises from the tendency of neighbouring magnetic moments to align with each other parallel producing a spontaneous magnetization in the absence of an external magnetic field. This alignment continues up to a specific temperature called the Curie temperature (T^c), above which thermal fluctuations exceed the ordering interaction & result in the antiferromagnetic material becoming paramagnetic. The microscopic origin of ferromagnetism is the exchange interaction, a purely quantum mechanical phenomenon without classic counterpart. This arises from the combined effect of the Coulomb repulsion between electrons & the Pauli exclusion principle. The Pauli principle dictates that spatial wavefunctions of the electrons must be antisymmetric if the electrons have parallel spins, meaning that, on average, they will be bumped farther apart than would electrons with antiparallel spins. Indeed, such proximity diminishes the Coulomb repulsion energy between two spins, rendering this parallel configuration thermodynamically favorable in some systems. The simplest model describing ferromagnetic ordering is the Heisenberg model, where the exchange interaction between neighboring spins S_1 & S_2 is described by the Hamiltonian:

$$H = -2J\, S_1 \cdot S_2$$

Here, J is the exchange integral that measures the interaction strength. A positive J promotes parallel relative orientation (ferromagnetism), while a negative J promotes antiparallel relative orientation (antiferromagnetism). The direct exchange mechanism outlined earlier

Notes

works only between nearest-neighbor atoms. In a lot of materials the magnetic atoms are separated by non-magnetic elements, often requiring indirect exchange mechanisms. One example of such a magnetic interaction is superexchange, which takes place in ionic solids in which ions of oppositive charge along with anions (usually oxides) act like they are cations. The magnetic coupling is mediated via the overlapping orbitals of the anion bridging the two transition metal ions. Superexchange can enable either ferromagnetic or antiferromagnetic order, depending on the arrangement of the cation-anion-cation.

Another indirect mechanism is the RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction, most common in metals in which localized (magnetic) moments couple through conduction electrons. The RKKY interaction alternates from ferromagnetic to antiferromagnetic coupling [1], depending on the distance between the material components, causing the appearance of complex magnetic structures in certain materials. For instance, in metallic systems where the d or f electrons are only partially delocalized, the band structure plays an important role in determining magnetic ordering. onsite correlations, Itinerant Ferromagnetism The Stoner scenario of itinerant ferromagnetism that explains the spontaneous spin alignment through a population imbalance between spin-up & spin-down electrons in the conduction band. This happens when the energy cost of flipping electrons from one spin band into the other band is counterbalanced by the decreased exchange energy of spins that are aligned. Examples of classical ferromagnets are iron, cobalt, & nickel, & many of alloys & compounds. They are used extensively in electrical motors, generators, transformers, & data storage devices. Recent advances in nanoscale ferromagnets have opened up new frontiers in spintronics and quantum information processing. Unlike ferromagnetism, where the parallel approach is used to generate magnetic order, antiferromagnets are characterized by the antiparallel alignment of neighboring magnetic moments, which gives rise to strong magnetic ordering but with a zero net magnetization. The antiferromagnetic state exists until the Néel temperature (T_n), above which the material becomes paramagnetic.

The simplest antiferromagnetic structure is two interpenetrating sublattices with equal & opposite magnetizations. However, many antiferromagnets have more complicated arrangements, such as canted antiferromagnetism (weak ferromagnetism) in which the moments are not exactly antiparallel & produce a small net magnetization. Variants within this category are ferrimagnetism, in which points are unevenly aligned in antiparallel fashion, & helical antiferromagnetism, in which the points turn around a crystallographic direction.

Antiferromagnetic ordering is often the result of negative exchange interactions that can be facilitated by superexchange or RKKY mechanisms. In case of transition metal oxides, such as MnO, NiO & Fe_2O_3, the superexchange interaction through intervening oxygen ions leads to antiferromagnetic coupling between the metal ions. Although antiferromagnetic materials do not have the obvious technological applications of ferromagnets, they have received growing attention in recent years. Their insensitivity to stray magnetic fields, absence of stray fields, & potentially faster dynamics make them promising candidates for the next generation of spintronic devices. Antiferromagnetic spintronics utilizes effects like exchange bias, in which the interaction between a ferromagnetic (FM) & NJU1450024 an antiferromagnetic (AFM) layer moves the hysteresis loop of the FM element.

Notes

The interplay between ferromagnetic and antiferromagnetic phases has a rich phase diagram, which becomes particularly interesting among frustrated magnetic systems. When the geometry of the lattice does not allow for the simultaneous satisfaction of all these exchange interactions, the resulting interplay is known as geometric frustration. As an example of these considerations, it is impossible to orient three spins antiparallel to each other, in a triangular lattice with antiferromagnetic interactions. This frustration can give rise to exotic magnetic states like spin glasses, spin liquids, & spin ices with high degeneracy & peculiar dynamic features. A classic way to investigate magnetic ordering is neutron diffraction measuring the interaction of magnetic moments with neutrons directly; another well-established one is Mössbauer spectroscopy, which provides information on the local magnetic environment of specific nuclei. Such experimental approaches are supplemented by computations from density functional theory to Monte Carlo simulations that can predict magnetic phase diagrams & various microscopic mechanisms. It is important to appreciate and comprehend the dance between ferromagnetism & antiferromagnetism to develop new magnetic materials with desirable characteristics. For example, hybrid structures composed of ferromagnetic & antiferromagnetic segments display both exchange bias & spin valve effects & are the basis of practical devices for magnetic sensorics & spintronics including magnetic memory. The realization of new approaches to manipulating the magnetic ordering, such as electric field tunable exchange interactions, suggests future directions for improving magnetic technologies.

In this paper we apply magnetic measurements to determine structural information.

Magnetometric measurements represent valuable tools for exploring structural & electronic characteristics of materials. Investigating the behavior of compounds in magnetic fields yields valuable insights into

Notes

the geometry of precursors, oxidation state, coordination environment, & electronic configuration—often complementary to existing structural techniques & sometimes even more revealing than traditional techniques themselves. The magnetic susceptibility (χ), which is the main parameter studied in magnetic investigations, describes the amount of magnetization (M) of a substance per a unit of an applied magnetic field (H):

$$\chi = M/H$$

For many types of diamagnetic & paramagnetic material in moderate fields, the susceptibility can be considered to be field-independent & is a characteristic property of the material. The molar susceptibility (χ_m) normalizes this quantity for a particular substance to a per mole basis, allowing different substances to be compared. There are several categories of experimental methods to measure magnetic susceptibility. The Gouy balance & Faraday balance methods measure the force exerted on a sample placed in a non–uniform magnetic field. The superconducting quantum interference device (SQUID) magnetometer boasts superior sensitivity due to its ability to sense small differences in magnetic flux linked to a superconducting ring. In vibrating sample magnetometry (VSM), electromotive force due to a vibrating magnetised sample is measured. Each method has particular strengths & weaknesses when it comes to sensitivity, temperature range, and sample needs.

The measured susceptibility is therefore the sum of diamagnetism (due to paired electrons) & paramagnetism (due to unpaired electrons). The diamagnetic correction needs to be applied in order to isolate the paramagnetic component, which carries the structural information:

$$\chi_p = \chi_m - \chi^{dia}$$

where χ_p is the paramagnetic susceptibility & χ^{dia} is the diamagnetic correction, which is usually approximated based on published values (known as Pascal's constants) based on the various atoms & bonds present. For paramagnetic materials with non interacting magnetic sites, the temperature dependence of susceptibility obeys the Curie law:

$$\chi_p = C/T$$

where C is the Curie constant, & T is the absolute temperature. Curie’s Law relates the Curie constant directly to the effective magnetic moment ($\mu_e$ff)through:

$$C = N\mu_o\mu_e ff^2/3k_a$$

where N is Avogadro’s number, μ_o is the permeability of free space, & k_a is Boltzmann’s constant. The effective magnetic moment is in turn tied to the electronic structure of the magnetic centers. For weak interactions among magnetic centers, the Curie-Weiss law is a more satisfactory description:

$$\chi_p = C/(T-\theta)$$

where θ (also called the Weiss constant) accounts for the nature & strength of magnetic interactions: it is positive for ferromagnetic coupling & negative for antiferromagnetic coupling. The effective magnetic moment of transition metal complexes can be considered as a fingerprint for the metal oxidation state & coordination environment. The spin-only formula gives a good approximation in octahedral complexes of first-row transition metals with quenched orbital contributions:

$$\mu_e ff = 2\sqrt{(S(S+1))}\ \mu_a$$

where S is the total spin quantum number & μ_a the Bohr magneton. Analyzing the quantity of experimental $\mu_e$ff with this theoretical value allows determining the number of unpaired electrons which means to determine the electronic configuration. Such deviations from the spin-only value generally imply significant orbital contributions or spin-orbit coupling. For example, $\mu_e$ff for cobalt(II) complexes is generally larger than the spin-only value predicted for three unpaired electrons, an indication of unquenched orbital character. Instead some copper(II) complexes have values slightly less than expected for one unpaired electron due to antiferromagnetic coupling between adjacent centers. The temperature dependence of magnetic susceptibility offers even richer structural detail. For polymanganese complexes comprised of numerous interacting magnetic centers, the shape of the susceptibility curve itself is informative as to the nature of the magnetic coupling pathways. These experimental data can, in principle, be analyzed in terms of a variety of theoretical models, for example the Bleaney-Bowers equation for dimers, or the Fisher model for chains, in order to extract exchange coupling constants.

In coordination polymers & metal-organic frameworks, magnetic measurements can provide insights into the dimensionality of magnetic interactions that characterize these systems, whether they form isolated clusters, chains, layers, or threedimensional networks. Such information is crucial for unraveling structure-property correlations & rationally designing materials with specific magnetic functionalities. In addition to paramagnetic systems, magnetic measurements provide vital structural insight for Ferro-, Ferri- & Antiferromagnetic materials. Temperatures of magnetic ordering transitions (Curie or Néel temperatures) are strongly dependent on the strength of exchange interactions, which then reflects interatomic distances & bonding geometries. This saturation magnetization of ferromagnets is simply obtained from the number of aligned

Notes

moments/unit volume, & thus provides useful information on site occupancies & moment distributions. Magnetic anisotropy — the directionality of the magnetic characteristics — provides another avenue to structural information. In single crystals, the orientation of the magnetic easy axes and easy planes can be determined by measuring the susceptibility in various crystallographic directions. For polycrystalline samples, anisotropy can still be observed by methods such as magnetic torque measurements [17]. Since the strength & nature of magnetic anisotropy is determined by the local coordination geometry & crystal field, it is a sensitive probe of structural distortions.

More sophisticated magnetic techniques also broaden the structural toolkit. Electron paramagnetic resonance (EPR) spectroscopy probes the local environment of paramagnetic centers via the g-tensor & hyperfine couplings. Muon spin rotation(μSR) is a highly sensitive local-magnetic-field probe that offers insights into the magnetic structure and dynamics. The global electron spin density distribution can be mapped by nuclear magnetic resonance (NMR) of paramagnetically shifted nuclei & details of chemical bonding revealed. Magnetic circular dichroism (MCD)—the difference in absorption of left & right circularly polarized light by a sample in a magnetic field—delivers element-selective information about electronic states involved in magnetic behavior. This method can be extended to X-ray energies (XMCD), allowing for separate quantification of orbital & spin magnetic moments & thus direct access to the electronic structure of magnetic materials.

Magnetic measurements utilized for structural determination are applicable to many fields. Magnetic susceptibility is used in bioinorganic chemistry to determine the spin state & nuclearity of metalloproteins active sites. Magnetic studies in geochemistry reveal the mineralogical composition of rocks & the conditions of their formation. In materials science, magnetic measurements inform the design of spintronics, media for data storage & components of quantum computing. Recent developments in instrumentation have expanded the potential of magnetic structural determination. Micro-SQUID methods make it possible to measure the magnetism of single molecules or nanoparticles. Magnetic force microscopy & scanning SQUID microscopy are among the spatially resolved methods that map magnetic structures with nanometre resolution. Single-shot time-resolved measurements now access magnetic dynamics across picosecond timescales, providing the window into transient states & relaxation processes. Complementary techniques, combined with magnetic measurements, yield the most structural insight. Ball-mapping magnetic data against X-ray diffraction patterns can lead to a more refined solution devoid of ambiguity concerning disorder & site occupancies. Characterization of these systems through magnetic methods provides complementary information to spectroscopic techniques (e.g. UV-vis, IR, Raman) & provides a more holistic appreciate and comprehend ing of electronic structure & bonding. Computational methods, particularly density functional theory (DFT) calculations, continue to close the gap between measured magnetic characteristics & the underpinning structural characteristics.

Progressing deeper into the realm of quantum materials, where novel magnetic ground states are realized (skyrmions, spin liquids, & topological magnets) magnetic measurements will remain a cornerstone for structural determination [75, 76]. As such, continued evolution toward more sensitive, more selective, & more informative magnetic probes holds the potential to uncover previously inaccessible structural subtleties & will enable further innovations across chemistry, physics, materials science, & engineering.

Incorporation of Higher Magnetic Concepts

The discussed themes of the orbital contribution to magnetic moment, of ferromagnetism & antiferromagnetism, & of magnetic measurements to deduce determining structures are important & well-connected facets of (the world of) the magnetic phenomenon. This inter-relationship provides a unified platform for magnetic material analysis & design. This orbital contribution to the magnetic moment has a fundamental impact on the tendency for magnetic ordering in materials. However, orbital wavefunctions are inherently anisotropic, particularly in systems with high orbital angular momentum, & they provide preferential directions for magnetic alignment, making magnetization along specific crystallographic axes easier than others. This magnetic anisotropy is an important factor influencing the stability of ferromagnetic & antiferromagnetic states, especially in low-dimensional systems where the effects of symmetry-breaking are pronounced. Furthermore, the coupling between orbital & spin degrees of freedom, which takes place via spin-orbit coupling, can trigger different exchange mechanisms. For example, the Dzyaloshinskii-Moriya interaction—an antisymmetric exchange due to spin-orbit coupling in non-centrosymmetric environments—can cause canting in otherwise collinear antiferromagnetic configurations, leading to weak ferromagnetism. This shows how much orbital effects can radically change magnetic ordering patterns.

Magnetic measurements are therefore an experimental window to these effects (quantifying both the orbital contribution & exchange interactions). The temperature dependence of magnetic susceptibility, in particular deviations from Curie-Weiss behavior, gives insight into exchange pathways, & its dimensionality. Magnetization along multiple crystallographic directions reveals both the extent of magnetic anisotropy & the orbital contribution to the magnetic moment. High-

Notes

precision measurements undertaken with advanced methods such as XMCD spectrometry can directly separate orbital & spin contributions to the magnetic moment, offering a powerful means of studying complex magnetic materials. Torque magnetometry allows establishing the angular dependence that maps the symmetry of magnetic anisotropy & provides information about the local coordination environment & crystal field effects contributing to the orbital contributions.

For materials with long-range magnetic order (either magnetic ferromagnetic or antiferromagnetic), neutron diffraction becomes a unrivaled structural probe, providing a direct image of the spatial arrangement of magnetic moments. The observed features are tied to both the nature of the magnetic order as well as the size & direction of the individual moments, which are critically dependent on orbital contribution. This synergy between these magnetic concepts has practical applications. To achieve high coercivity (resistance to demagnetization) in permanent magnets, both strong ferromagnetic exchange interactions & large magnetic anisotropy through orbital contributions are needed. The synthesis & appreciate and comprehend ing of oxygen coordinatively unsaturated (CUS) oxide embeddings can be critical for the development & optimization of spintronic devices where the control of antiferromagnetic domains is dependent on exchange pathways that are sensitive to crystal structure & orbital effects that can alter magnetic anisotropy. In addition, these magnetic principles can help us appreciate and comprehend various kinds of matter on different scales. At the atomic scale, individual ions' magnetic characteristics are determined by the orbital contribution. Exchange interactions between magnetic centers are the origin of cooperative magnetic behavior on a molecular scale, which dominates coordination complexes. These nanosurface effects alter the direction of both orbital contributions & exchange interactions leading to novel magnetism in nanoparticles & thin films. In ferromagnets & antiferromagnets, domain structures at the macroscopic scale control the bulk magnetic characteristics important for applications.

Combining these ideas has led to major advances in everything from quantum computing to medical imaging. The exchange of magnetic interactions between metal centers & orbital contributions are used to find systems with long coherence times, as seen in quantum bits based on single-molecule magnets. Magnetic resonance imaging (MRI) contrast agents employ paramagnetic complexes that exhibit relaxation characteristics that are highly sensitive to the electronic structure & coordination environment of the metal center. As we look ahead to future progress, the interplay of these magnetic ideas will be a template for finding new materials & new phenomena. Research topics such as topological magnetism, which relies on the interplay between spin-orbit coupling & exchange interactions to realize topologically protected magnetic textures, demonstrates the continued relevance of these fundamental ideas. The interdisciplinary nature of magnetism that traverses the domains of physics, chemistry, materials science, and engineering highlights the importance of a holistic appreciate and comprehend ing that integrates orbital contributions, magnetic ordering, & techniques to determine structures. appreciate and comprehend ing how these interconnected concepts interrelate will allow researchers to tackle problems such as sustainable energy technologies & quantum information processing, meaning that magnetism will continue to be a touchstone area of science for many findable areas of discovery.

Advanced Concepts: Awesome, Alluring, and Awaiting Action So these are some of the most exciting concepts in magnetism, which was already a field rich in evolving just. This magnetic moment can be decomposed into a spin & an orbital contribution, the latter of which is due to the quantum mechanical nature of the electron(s) and provides a basis for appreciate and comprehend ing magnetic anisotropy & spin-orbit effects. The subtleties of many-body physics & the richness of magnetic ordering patterns manifest in the collective phenomena of ferromagnetism & antiferromagnetism, arising from exchange interactions. These phenomena are utilized in both magnetic measurements for structural determination & complementary and, in some cases, more finely detailed information than can be obtained by conventional structural techniques. All these interconnected facets of magnetism lead to discoveries across the map of science, a learning curve helping us to build new bridges — in quantum materials, spintronics & not only.

APPLICATIONS ON DAY-TO-DAY LIFE

Spectral & Magnetic Characteristics of Metal Complexes: Practical Applications

The spectral & magnetic characteristics of metal complexes subtly support many technologies that protect health, bolster security, & elevate quality of life in ways often overlooked by the general populace. Blood glucose monitors utilized by millions of diabetics globally often incorporate enzyme electrodes featuring coordination complexes, whose electron transfer characteristics & spectroscopic responses facilitate precise, real-time monitoring of blood sugar levels; this crucial technology enables diabetics to regulate insulin dosing effectively & avert perilous hyperglycemic episodes through immediate feedback provided by the finely calibrated magnetic & electronic attributes of metalloenzyme mimics. The anti-counterfeiting elements integrated into currency notes, passports, & high-value documents frequently utilize metal complexes with unique spectral signatures that emit specific colors when exposed to particular light

Notes

wavelengths; these security features, imperceptible under standard lighting yet vividly visible under UV lamps, establish authentication systems that are challenging to duplicate without sophisticated expertise in coordination chemistry. Oxygen sensors in automotive engines, essential for ensuring efficient fuel combustion & reducing harmful emissions, operate using zirconia-based materials doped with transition metals, whose magnetic characteristics vary predictably with oxygen levels; these sensors allow engine control systems to dynamically adjust fuel delivery, enhancing fuel efficiency & decreasing pollutant output. Magnetic resonance imaging (MRI) contrast agents, which transformed medical diagnostics, operate solely through the magnetic characteristics of gadolinium & other paramagnetic metal complexes. These agents temporarily modify the relaxation characteristics of water protons in tissues via coordination interactions, uncovering anatomical & physiological details that would otherwise be obscured & facilitating earlier, more precise disease detection. The reflective coatings on energy-efficient windows, which sustain comfortable indoor temperatures throughout the year & diminish heating & cooling expenses, often contain silver & other metallic layers that selectively reflect infrared radiation while allowing visible light to pass through. These "low-e" coatings exemplify the potential of utilizing the interaction between metal complexes & electromagnetic radiation for substantial energy conservation. Anti-microbial wound dressings that accelerate healing while preventing infection often utilize silver complexes whose spectroscopic & electron-transfer characteristics disrupt bacterial metabolism without harming human tissue; these medical devices demonstrate how the redox chemistry of coordination compounds can be selectively deployed for therapeutic benefit. The stunning hues in artisanal glass, exquisite ceramics, & decorative glazes throughout history have depended on transition metal complexes, whose unique spectral characteristics arise from d-d transitions; these aesthetic uses of coordination chemistry have enhanced human cultural expression while illustrating the principles that would ultimately culminate in contemporary spectroscopic analysis. Fundamentally, the hemoglobin molecule, responsible for oxygen transport in the human body, operates through the finely calibrated magnetic characteristics of iron coordination complexes; this vital biological function illustrates how nature has refined coordination chemistry to facilitate respiration & sustain life.

Term Symbols for d-Ions: Practical Applications

The ostensibly abstract mathematical representations of term symbols for d-ions directly inform technologies that bolster security, facilitate scientific progress, & enhance quality of life by accurately describing & predicting the behavior of transition metal complexes. The colorshifting security inks utilized on high-denomination banknotes & official documents contain transition metal complexes, whose unique optical characteristics stem from accurately defined electronic states represented by term symbols. These specialized inks alter color when observed from various angles due to the distinct interactions of their electronic states with polarized light, resulting in security features that are exceptionally challenging to replicate without a sophisticated comprehension of coordination chemistry. Specialized optical filters employed in astronomical observatories & satellite imaging systems frequently incorporate glass doped with transition metal ions, whose selective absorption characteristics, delineated through term symbol analysis, allow scientists to isolate specific wavelengths of cosmic radiation; these precision filters have facilitated discoveries regarding distant planetary atmospheres, stellar formation, & the fundamental structure of the universe by leveraging the quantum mechanical characteristics of d-electron configurations. Gemstone authentication instruments employed by jewelers & gemological laboratories to differentiate natural from synthetic stones often utilize spectroscopic analysis of trace transition metal impurities, whose distinctive absorption patterns—directly correlated to their term symbols—act as definitive identifiers; these analytical methods safeguard consumers against fraud while preserving the value of authentic gemstones. Advanced catalytic systems for environmental remediation, particularly those that decompose persistent organic pollutants in contaminated water, frequently utilize transition metal complexes with meticulously designed electronic configurations; the efficacy of these catalysts in electron transfer reactions is directly linked to the energy levels & transition probabilities forecasted through term symbol analysis. The specialized phosphors utilized in medical X-ray imaging systems, which convert harmful radiation into visible light, often contain rare earth & transition metal ions. Their luminescence characteristics, defined by term symbol notation, enhance detection sensitivity & reduce patient radiation exposure, thereby facilitating essential diagnostic functions & improving patient safety. Next-generation quantum computing architectures utilizing transition metal-based qubits depend heavily on a comprehensive appreciate and comprehend ing of electronic structure & magnetic characteristics characterized by term symbols; these innovative computing platforms offer unparalleled computational capabilities for drug discovery, materials design, & complex systems modeling. Colorimetric sensors employed for environmental monitoring of heavy metal contamination in water supplies operate through ligand-metal interactions that yield specific spectral shifts indicative of electronic state transitions characterized by term symbols; these accessible testing technologies allow communities to ascertain water safety without the need for advanced laboratory infrastructure. Our scientific appreciate and

Notes

comprehend ing of photosynthesis, the process that sustains nearly all life on Earth, has significantly improved through the analysis of electronic states & transitions in chlorophyll & related metalloenzymes. This illustrates how the mathematical framework of term symbols directly enhances our comprehension of the fundamental energy conversion processes that underpin the biosphere.

Electronic Transitions in Metal Complexes: Practical Applications

The electronic transitions in metal complexes, especially the d-d transitions dictated by selection rules & illustrated by Orgel & Tanabe-Sugano diagrams, directly facilitate technologies & applications that improve daily living in several fields. High-quality camera lenses & professional photography equipment often utilize advanced optical filters that contain transition metal complexes embedded in glass. These complexes, with precisely characterized d-d transitions, selectively absorb specific wavelengths. Such specialized filters enhance image contrast, diminish atmospheric haze, or produce artistic effects by leveraging the quantum mechanical characteristics that dictate the transmission & absorption of wavelengths. Smart windows, prevalent in energy-efficient structures & luxury vehicles, automatically modify their tint according to sunlight intensity. They employ electrochromic materials with transition metal complexes, whose d-d transitions significantly alter under minimal voltage application. These dynamic glazing systems improve visual comfort, lower cooling expenses, & safeguard interiors from UV damage by utilizing regulated electronic transitions in reaction to environmental factors. The gemstone industry heavily depends on the comprehension of electronic transitions; the vivid red of natural rubies is attributed to d-d transitions in chromium ions, whereas the distinctive green of emeralds arises from analogous transitions in vanadium & chromium—insight that enables gemologists to verify natural stones & create synthetic counterparts with identical spectroscopic characteristics for cost-effective jewelry alternatives. Colorimetric sensors utilized in home pregnancy tests & rapid medical diagnostics often incorporate coordination complexes that exhibit significant color changes due to modifications in d-d transitions upon the presence of specific biomarkers; these user-friendly testing platforms facilitate swift health monitoring without the need for specialized equipment by converting biochemical data into visible color alterations through coordination chemistry

Table -. Expected stereochemistry of transition metal complexes using the number of unpaired *d*-electrons from crystal field theory.

Weak-field Unpaired electrons	Stereochemistry	Strong-field Unpaired electrons	Stereochemistry
0 (d^0)	Symmetrical	0 (d^0)	Symmetrical
1 1 (d^1, $t2g$)	Slightly distorted octahedron	1 1 (d^1, $t2g$)	Slightly distorted octahedron
2 2 (d^2, e^2 or $t2g$)	Tetrahedron or slightly distorted octahedron	2 2 (d^2 e^2 or $t2g$)	Tetrahedron or slightly distorted octahedron
3 3 (d^3, $t2g$)	Perfect octahedron	3 3 (d^3, $t2g$)	Perfect octahedron
3 1 4 (d^4, $t2g$ eg)	Square-planar or tetragonal	4 4 2 or 0 (d^4, $t2g$ or e)	Slightly distorted octahedron or tetrahedral
3 3 2 5 (d^5, e^2 $t2$ or $t2g$ eg)	Tetrahedron or perfect octahedron	5 1 (d^5, $t2g$)	Slightly distorted octahedron
4 2 4 (d^6, $t2g$ eg)	Slightly distorted octahedron	6 0 (d^6 $t2g$)	Perfect octahedron
3 5 2 3 (d^7, e^4 $t2$ or $t2g$ eg)	Tetrahedron or slightly distorted octahedron	6 1 1 (d^7, $t2g$ eg)	Square planar or tetragonal
6 2 2 (d^8, $t2g$ eg)	Perfect octahedron	6 2 0 (d^8, $t2g$ eg)	Square planar or tetragonal
6 3 1 (d^9, $t2g$ eg)	Square planar or tetragonal	6 3 1 (d^9, $t2g$ eg)	Square planar or tetragonal
0 (d^{10})	Symmetrical	0 (d^{10})	Symmetrical

Notes

Specialized catalysts that facilitate environmentally sustainable manufacturing processes for pharmaceuticals & fine chemicals typically attain their selectivity through meticulous engineering of metal complex electronic states & transitions; these green chemistry methodologies minimize waste production & energy usage while generating vital medicines & materials by leveraging the correlation between electronic structure & catalytic activity. The vivid, resilient pigments found in premium artistic paints, automotive finishes, & architectural coatings often obtain their remarkable color stability & weather resistance from transition metal complexes, which exhibit d-d transitions at energies that mitigate photochemical degradation; these substances improve aesthetic durability while minimizing maintenance needs due to their intrinsic electronic characteristics. Military camouflage technologies increasingly utilize coordination compounds with near-infrared electronic transitions that align with the spectroscopic signatures of natural vegetation; these sophisticated materials improve soldier safety by obscuring personnel from both visual & electronic detection through meticulously designed electronic characteristics. Fundamentally, semiconductor manufacturing processes that produce computer chips utilize photoresists containing coordination complexes, whose electronic transitions facilitate nanoscale pattern transfer. These materials convert electronic designs into physical structures via light-induced electronic transitions, resulting in the integrated circuits that drive the digital age.

Jahn-Teller Distortion, Spin-Orbit Coupling, & Charge Transfer: Practical Applications

The intricate quantum mechanical phenomena of Jahn-Teller distortion, spin-orbit coupling, & charge transfer transitions in metal complexes are fundamental to several technologies that improve healthcare, security, energy efficiency, & information processing capacities. High-density data storage devices that retain our digital photographs, documents, & communications increasingly employ magnetic materials whose efficacy relies on meticulously regulated spin-orbit coupling in transition metal compounds; these storage technologies facilitate the conservation of extensive information resources while reducing physical space demands through quantum mechanical effects that stabilize magnetic domains at nanoscale dimensions. The near-infrared night vision technologies that augment military & emergency response capabilities operate via specialized detectors utilizing charge transfer processes in coordination compounds; these essential safety & security systems enable visualization in otherwise impenetrable darkness by transforming invisible infrared radiation into electronic signals through electronic transitions between metal centers & the ligands. Specialized medical

Notes

imaging contrast agents for liver & spleen visualization often incorporate superparamagnetic iron oxide nanoparticles, whose magnetic characteristics are affected by spin-orbit coupling effects. These diagnostic tools improve tumor & pathology detection by offering tissue-specific contrast through quantum mechanical interactions between electronic & nuclear spin states. Premium automobile paints exhibit vibrant colors that retain their aesthetic appeal over years of sun exposure, often utilizing metal complex pigments. These pigments possess exceptional photostability due to charge transfer bands that absorb harmful ultraviolet radiation without degradation. Such specialized coatings enhance vehicle appearance & value retention through coordination chemistry principles that harmlessly dissipate solar energy. Oxygen sensors in medical devices that assess patient oxygenation during surgery & recovery often utilize ruthenium complexes, whose luminescence characteristics significantly vary due to oxygen-induced electronic transitions; these essential monitoring systems deliver real-time feedback on patient status via optical signals influenced by charge transfer processes modified by molecular oxygen. High-efficiency photocatalysts employed in self-cleaning surfaces & air purification systems attain their exceptional activity via charge transfer transitions that produce reactive species upon light absorption; these environmental technologies improve indoor air quality & minimize maintenance needs by utilizing sunlight to initiate electron transfer between metal centers & coordinated the ligands. Electrochromic displays, characterized by vibrant colors, utilized in e-readers & specialized information displays, often incorporate coordination compounds that exhibit significant color changes upon the addition or removal of electrons, with Jahn-Teller effects frequently influencing the pronounced spectral shifts; these low-power display technologies improve readability while reducing energy consumption through principles of coordination chemistry. Notably, the advancement of future technology hinges on emerging quantum computing architectures utilizing transition metal-based qubits, which frequently incorporate Jahn-Teller active systems. These systems exhibit electronic degeneracy that facilitates the manipulation of quantum states for information processing. Such sophisticated computing platforms possess the potential to revolutionize drug discovery, materials design, & artificial intelligence by processing specific problems exponentially faster than traditional computers, illustrating how intricate quantum mechanical phenomena in coordination compounds may ultimately reshape information technology through their distinctive electronic characteristics.

Multiple-Choice Questions (MCQs)

1. Electronic spectra of metal complexes arise due to:

a) Vibrational transitions

Notes

b) d-d electronic transitions

c) Nuclear magnetic resonance

d) Covalent bond formation

2. Term symbols in d-orbital configurations represent:

a) Electronic configurations of the ligands

b) Total angular momentum states of metal ions

c) Hybridization states

d) The oxidation state of a metal ion

3. Laporte's selection rule states that:

a) d-d transitions are allowed in octahedral complexes

b) Transitions within the same parity (g → g or u → u) are forbidden

c) Spin-forbidden transitions are most intense

d) All electronic transitions are allowed

4. Orgel diagrams are useful for interpreting electronic spectra of:

a) Octahedral & tetrahedral complexes

b) Square planar complexes only

c) Lanthanide & actinide compounds

d) Organic molecules

5. Tanabe-Sugano diagrams are used to:

a) Predict the color of transition metal complexes

b) Determine the effect of ligand field strength on electronic transitions

c) Explain molecular orbital interactions

d) Study diamagnetism in complexes

6. Jahn-Teller distortion primarily affects:

a) Tetrahedral complexes

b) Octahedral complexes with partially filled degenerate orbitals

c) Square planar complexes

d) High-spin d^5 complexes

7. Charge transfer spectra are observed when:

a) Electrons transition between metal & ligand orbitals

b) d-d transitions occur

c) Vibrational coupling takes place

d) The ligands undergo bond breaking

8. The Gouy method is used to measure:

a) Electronic spectra of metal complexes

b) Magnetic susceptibility

c) Ligand field splitting energy

d) Conductivity of coordination compounds

9. The spin-only magnetic moment is calculated using:

a) μ=n(n+1)\mu = \sqrt{n(n+1)}μ=n(n+1) BM

b) μ=2.83S(S+1)\mu = 2.83 \sqrt{S(S+1)}μ=2.83S(S+1) BM

c) μ=2.83n(n+1)\mu = 2.83 \sqrt{n(n+1)}μ=2.83n(n+1) BM

d) μ=1.73n\mu = 1.73 nμ=1.73n BM

10. Ferromagnetism in metal complexes is characterized by:

a) Opposing spins canceling each other

b) Parallel alignment of magnetic moments

c) Random spin orientations

d) Complete absence of unpaired electrons

Short Answer Questions

1. Define term symbols & explain their significance in d-orbital configurations.

2. What ared-d electronic transitions, & why are they important in spectroscopy?

3. Explain Laporte's selection rule & its implications for transition metal complexes.

4. What is the difference between Orgel diagrams & Tanabe-Sugano diagrams?

5. Describe the effect of Jahn-Teller distortion on the spectral characteristics of metal complexes.

6. What is the significance of charge transfer spectra, & how do they differ from d-d transitions?

7. Explain the Gouy method & how it is used to measure magnetic susceptibility.

8. How does spin-orbit coupling influence electronic spectra?

Notes

9. Write the formula for the spin-only magnetic moment & explain each term.

10. Differentiate between ferromagnetism & antiferromagnetism in metal complexes.

Long Answer Questions

1. Explain the construction of term symbols for d-orbital configurations & their physical meaning.

2. Discuss the selection rules for electronic transitions in metal complexes, including Laporte & spin selection rules.

3. Explain Orgel diagrams for weak field complexes & describe their applications for d^1 to d^9 systems.

4. Discuss the Tanabe-Sugano diagrams, explaining how they help in appreciate and comprehend ing electronic transitions in strong & weak field cases.

5. Describe the Jahn-Teller effect, including its origin, types of distortion, & impact on spectral characteristics.

6. Explain charge transfer spectra, their origin, & how they differ from ligand field transitions.

7. Discuss the various types of magnetism (paramagnetism, diamagnetism, ferromagnetism, antiferromagnetism) observed in metal complexes.

8. Explain the Gouy method & how it is used to determine the magnetic moment of metal complexes.

9. Derive the spin-only magnetic moment formula & calculate the moment for a high-spin d^5 complex.

MODULE -3

REACTION MECHANISMS OF TRANSITION METAL COMPLEXES – PART I

Notes

Objectives

- To comprehend the essential principles of metal complex reactivity, it is crucial to differentiate between inert & labile complexes.
- To examine the energy profile of metal complex processes by distinguishing between intermediates & transition states.
- To investigate the kinetics & mechanisms of octahedral substitution processes, emphasizing associative (A) & dissociative (D) pathways.
- To investigate the acid & base hydrolysis of metal complexes, finding critical parameters that affect reaction rates & the mechanism of the conjugate base.
- To examine anion processes, their kinetics, & practical applications in catalysis & synthesis.

Unit 11 Introduction to Reaction Mechanisms

Metal complexes provide a broad & compelling class of compounds at the heart of coordination chemistry. These complexes involve a central metal atom or ion coordinated to one or more surrounding molecules or anions (called the ligands) that deliver electron pairs to the metal centre, forming coordinate covalent bonds. The relationships between the reactivity of metal complexes are critical to widespread areas of science, from industrial catalysis to biological systems, in which metalloenzymes are involved in most essential processes of life. The reactivity of metal complexes is determined by a complex interaction of factors such as the metal center, the characteristics of the the ligands (electronic and steric) & external factors like solvent, temperature & pressure. Particularly intriguing about coordination chemistry is the incredible range of reaction pathways accessible to such complexes. Ligand substitution (substitution of one ligand for another), redox processes (in which the oxidation state of the metal is altered), & reactions that change the structural framework of the complex fall into these pathways. It is critical to appreciate and comprehend how these reactions follow to inform the control & predict the behavior of metal complexes across applications. In the context of homogeneous catalysis, metal complexes are referred as catalyst that can improve reaction conditions allowing selective transformation of homologs and/or modifications to take place with higher efficiency. The successful design of efficient catalysts is based on the knowledge of

Notes

the interaction between metal centers & substrates, & how the ligands can modulate this interaction.

In biological systems, metalloenzymes like hemoglobin, cytochromes, & nitrogenase carry out essential functions via precisely controlled reactions at their metallocenters. Investigating these natural metallic aggregates has influenced the design of bio-inspired catalysts that strive to mimic the efficacy and specificity of biochemical pathways. A metal complex's reactivity is fundamentally tied to its electronic structure, coordination geometry, & metal-ligand bonding character. Because of their partially filled d-orbitals, transition metals possess unique chemical characteristics that give rise to stable coordination complexes of a variety of coordination numbers, as well as structures. The bonding occurs between the d-orbitals of the transition metal & the the ligands giving rise to molecular orbitals which influences stability & reactivity of the complex. Today we know that ligand effects can modify the energies of d-orbitals through mechanisms described through crystal field theory (and its more sophisticated extension, ligand field theory), which can produce behavior such as high-spin versus low-spin states that alter reactivity patterns. Related to this are the 18-electron rule (or effective atomic number rule) that allow us to appreciate and comprehend the relative stability of some complexes, notably organometallics.

The analysis of reactivity mechanisms is fundamental for expanding our appreciate and comprehend ing of metal complex reactions, and their associated kinetics also matter. Reaction rates can differ wildly—some metal complexes exchange the ligands at the millisecond mark or faster, while others can survive for days or years in similar environments. This profound difference in kinetically behave leads to the most basic classification in coordination chemistry: the distinction between inert versus labile complexes.

Inert & labile complex definition

The distinction between "inert" & "labile" metal complexes is one of the most significant conceptual categories in coordination chemistry; it was first proposed by Henry Taube in the 1950s. It should be emphasized that this distinction is kinetic not thermodynamic in nature, referring to the speed with which complexes undergo ligand substitution reactions rather than the absolute stability of the complexes. The slow rate of ligand exchange is a characteristic of inert complexes. In the presence of a solution of possible replacement the ligands, inert complexes retain their coordination sphere over extended periods of time—with half-lives well above minutes or hours under standard conditions (room temperature & in aqueous solutions). Classic examples of inert complexes: octahedral complexes of trivalent chromium [Cr(III)], cobalt [Co(III)], & rhodium [Rh(III)], & square planar complexes of platinum(II) [Pt(II)]. For example, the hexaamminecobalt(III) complex $[Co(NH_3)_6]^{3+}$ can retain its coordination sphere (CM) in aqueous solution for days even in the presence of competing the ligands.

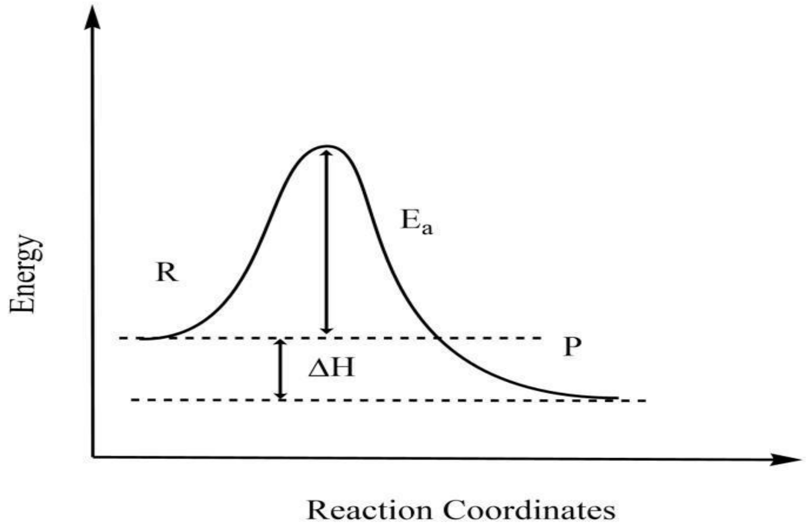


Figure - The general reaction coordinates diagram.

The lack of reactivity of these complexes can be attributed to a number of factors but electronic configuration is by far the most important. As such, transition metal ions that adopt d^3 (such as Cr^{3+}), low-spin d^6 (such as Co^{3+}) & d^8 (such as Pt^{2+}) electronic configurations readily form inert complexes as their respective ligand substitution reactions exhibit large activation energies. High activation barriers often arise from reorganization of the coordination sphere on the way to substitution, including spin state changes or large rearrangements of the bonding electrons. Conversely, labile complexes partake in rapid ligand exchange reactions, with half-lives on the order of seconds or less under standard conditions. Most divalent first-row transition metal complexes, such as nickel(II) [Ni(II)], copper(II) [Cu(II)], & zinc(II) [Zn(II)], & many alkali & alkaline earth metal complexes also fall into the category (for example, see ref 36, & references therein). The hexaaquamanganese(II)–complex $[Mn(H_2O)_6]^{2+}$, for example, exchanges its water–the ligands for those from the solvent adjacent to it on time scales that approach instantaneous, for which reason it is difficult to investigate the kinetics of such reactions without specialized techniques.

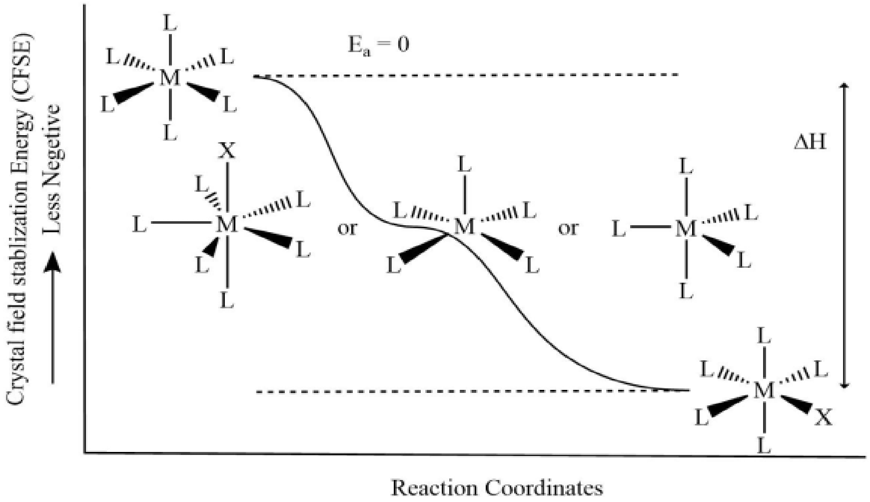


Figure - The reaction coordinates diagram for ligand displacement reactions in labile metal complexes.

Lability is particularly ascribed to electronic configurations that readily allow adaptations within the coordination sphere. Labile complexes are usually formed when metal ions have d^5 (eg Mn^{2+}), d^9 (eg Cu^{2+}), or d^{10} (eg Zn^{2+}) configuration of high-spin. Electrons in antibonding orbitals or a lack of significant crystal field stabilization energy cannot stabilize complexes with lower coordination numbers against competing processes that reduce coordination number through ligand substitution. This difference can lead to significant practical consequences between the inert & labile complexes for their applications. Inert complexes are beneficial in cases where stability & permanence are essential, including in some aspects of imaging agents, lengthy persisting catalysts, or therapeutic compounds expected to remain bio-active in biological climates. For example, the slow substitution kinetics of cisplatin [cis-$Pt(NH_3)_2Cl_2$] allows this anticancer drug to arrive onto its target DNA before significant degradation occurs. In contrast, labile complexes are preferred for fast exchange or catalytic turnover. Common catalytic processes rely on the capacity of the metal center to bind the substrates, mediate the reaction, & release the products in a catalytic cycle. The lability of iron in hemoglobin & myoglobin is vital to the efficient binding & release of oxygen in biological systems.

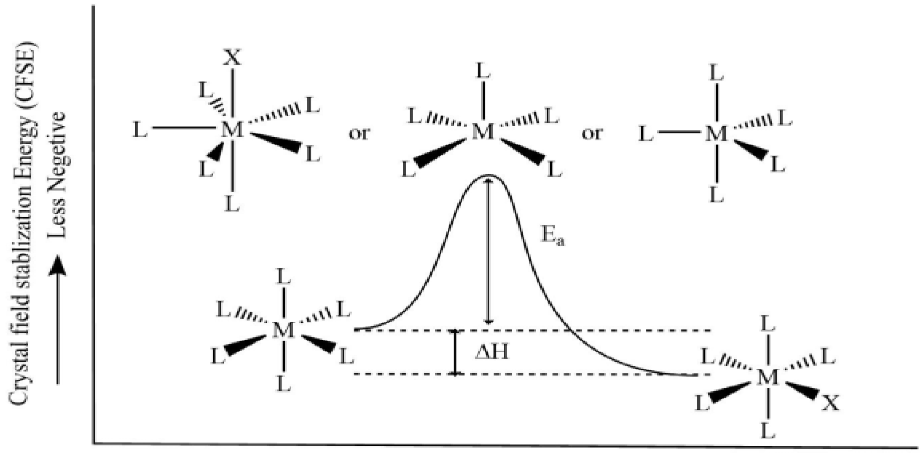


Figure - . The general reaction coordinates diagram for ligand displacement reactions in inert metal complexes.

Again, to emphasize, the inert-labile distinction is relative, as well as context-dependent. What is considered to be an inert complex with respect to one conditions set may be considered as labile in other conditions set (high temperature, different pH, or in the presence of certain catalytic systems). Furthermore, the descriptive distinction between inert & labile behavior is not discrete: rather, a continuum of kinetic behaviors exists among metal complexes. In addition, the inert-labile classification should not be confused with thermodynamic stability (attack). A thermodynamically stable complex (one with an energetically favorable free energy of formation) may be kinetically labil, & one which is less thermodynamically stable may be kinetically inert. This explains why some complexes, although their final decomposition is thermodynamically favored, can be very stable for a long time due to high activation barriers.

The x-ray structure of the bis-anionic, terminal metalloligand reveals that my appreciate and comprehend ing of the factors that goven the inert or labile behaviour of a complex is a fundamental aspect of coordination chemistry. By controlling these parameters—like the type of metal, oxidation state, ligand field strength, & coordination geometry—chemists design complexes with kinetic characteristics suitable for specific applications, ranging from catalysis to materials science to medicine. That inert-labile classification serves as a basis in reaction mechanism studies of metal complexes, which illuminate further details of the ligand-exchange processes, redox reactivity, & bond cleavage & formation during the conversion of coordinated substrates. Coordination chemistry strives to adjust/ appreciate and comprehend the susceptibility of metal complexes to change through its pursuit of reactivity.

Notes

Thermodynamic versus Kinetic Stability

Thermodynamic vs Kinetic Stability of Metal Complexes When talking about the stability of metal complexes, a differentiation needs to be made between thermodynamic stability & kinetic stability, as the two concepts refer to different phenomena in the chemical world. Thermodynamic stability involves the energy change that occurs when a complex forms or dissociates, while kinetic stability has to do with the rate of these processes. Thermodynamic stability is characterized by the equilibrium constant for complex formation, or by the standard Gibbs free energy change ($\Delta G°$) of the reaction. The formation of a thermodynamically stable complex has a negative $\Delta G°$ meaning that the process is spontaneous. The stability is determined by metal-ligand bond strength, chelate & macrocyclic effects, resonance stabilization, & entropic factors. The hexacyanoferrate(III) complex $[Fe(CN)_6]^{3-}$ is an example of this quality, as the cyanide the ligands have both very strong σ-donor & π-acceptor attributes & accumulate relatively strong metal-ligand bond energies. Likewise, during complexation with chelators such as ethylenediamine (en) or ethylenediaminetetraacetate (EDTA), thermodynamically stable complexes are produced thanks to the chelate effect in which the thermodynamic stability of the complex improves thanks to the entropic advantage that arises from having multiple donor atoms belonging to the same ligand.

Kinetic stability, in contrast, refers to the energy barrier that needs to be overcome for a reaction to take place. A kinetically stable (inert) complex has a large activation energy for ligand substitution, even when the substitution is thermodynamically favorable. This inactiveness is frequently due to electronic configuration, steric hindrance or the necessity for substantial reorganization in the course of the reaction. Thermodynamic versus kinetic stability are not always straightforward. For example, $[Co(NH_3)_6]^{3+}$is both thermodynamically & kinetically stable, as it is relatively low in formation energy & has slow ligand exchange rates. Others may be thermodynamically stable yet kinetically labile, as in many Ni(II) complexes, where the bonds are strong but ligand exchange occurs rapidly. However, some complexes may be thermodynamically unstable yet kinetically stable, lasting for extended periods despite spontaneous decomposition being energetically favorable.

Factors Influencing Inertness & Lability

The inert or labile nature of a metal complex will depend on several factors, & the electronic configuration of the metal ion has a major influence in this behavior.

Crystal Field Effects and Electronic Configuration

Notes

Particularly, the electron configuration of the metal ion (especially the electron distribution in the d-orbitals) significantly contributes to the kinetic characteristics of the complexes. For example, the crystal field stabilization energy (CFSE)—the energetic benefit associated with the splitting of d-orbitals by the ligands—correlates with kinetic inertness. For this reason, such metals create complexes that are more difficult to reduce.

For octahedral complexes, particular electronic arrangements are known to be correlated with inertness:

• d^3 configuration (e.g. Cr^{3+}): all 3 electrons can fit in the t_2g orbitals so large CFSE is there & higher energy e*g orbitals are unset.

• Low-spin d^6 configuration (as in Co^{3+}): All six electrons are in the lower-energy t_2g orbitals, resulting in maximum CFSE ($\Delta = 2/5$).

• d^8 configuration with square planar complexes (example: Pt^{2+}): Square planar complexes having singular/non-degenerate set of orbitals will have high CFSE.

In contrast, complexes with low CFSE are more likely to be labile:

• For high-spin d^5 configuration (e.g., Mn^{2+}), we have five e^- in t_2g & e*g are all filled: because all of them occupied one by one per level, the net CFSE is zero.

• d^9 (e.g. Cu^{2+}): The Jahn-Teller distortion generally associated with this configuration actually assists in replacement of a liganding atom.

• d^{10} configuration (e.g. Zn^{2+}): all d-orbitals filled & no CFSE gain possible.

Charge & Size of the Metal Ion

The charge density of the metal ion, which is defined by its charge and ionic radius, affects the extent of its interaction with the the ligands. Overall, complexes with more inert characteristics are formed by ions of metals with higher charge densities. Thus, trivalence ions like Al^{3+}, Cr^{3+} & Fe^{3+} form much more inert complexes than divalent ones. This trend within the periodic table that second & third-row transition metals form increasingly more inert complexes compared to their first-row analogues, is due in part to the heavier elements having larger size & more diffuse d-orbitals. This gives rise to both stronger covalent bonds and larger activation energies for the ligands to substitute.

Notes

$[AlF6]^{3-}$ >	$[SiF6]^{2-}$ >	$[PF6]^{-}$ >	$[SF6]^{0}$
+3	+4	+5	+6

Similarly, the rate of water exchange increases with the decrease of cationic charge as:

$[Al(H2On)]^{3+}$ <	$[Mg(H2On)]^{2+}$ <	$[Na(H2O)n]^{+1}$
+3	+2	+1

Nature of the The ligands

The characteristics of the the ligands coordinated to the metal significantly influence the kinetic behavior of the complex:

- Field strength: Strong-field the ligands that cause large crystal field splitting (such as CN^-, CO, & phosphines) tend to promote inertness, particularly for d^6 metals where they can enforce low-spin configurations.
- Chelating the ligands: Multidentate the ligands that form chelate rings with the metal often enhance kinetic inertness due to the increased stability of the coordination sphere & the requirement for multiple bonds to break simultaneously.
- Steric factors: Bulky the ligands can impede the approach of incoming nucleophiles, affecting the mechanism & rate of substitution reactions.

Coordination Number & Geometry

The spatial arrangement of the ligands around the metal center influences reaction pathways & activation energies:

- Octahedral complexes often have higher activation barriers for ligand substitution compared to tetrahedral ones, partly due to the more crowded coordination sphere & the greater reorganization needed during substitution.
- Square planar complexes (common for d^8 configurations) exhibit unique mechanistic behavior, with substitution typically occurring via associative pathways.

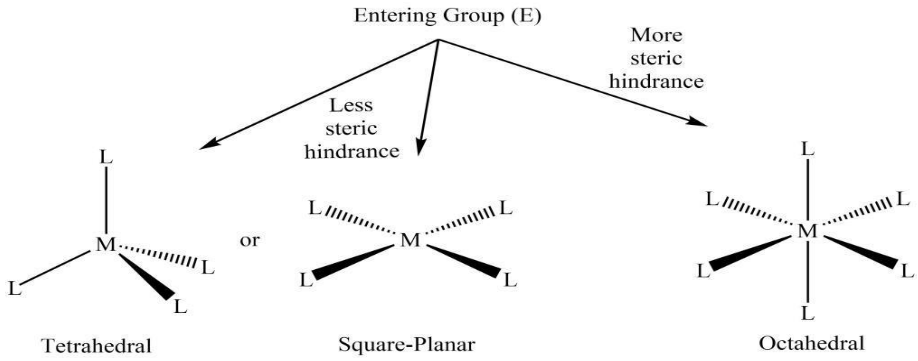


Figure -. The general diagram comparing the steric and site availability for ligand attack in four- coordinated and six coordinated complexes of non-transition metals.

Notes

Solvent Effects

The solvent plays a crucial role in ligand substitution reactions:

- Polar, coordinating solvents can stabilize charged intermediates & transition states.
- Solvent molecules can compete with other the ligands for coordination sites, acting as incoming or leaving groups.
- Hydrogen bonding interactions between solvent & the ligands can affect activation energies & reaction rates.

Experimental Determination of Inertness & Lability

The classification of a complex as inert or labile requires experimental determination of its ligand substitution kinetics. Several techniques are employed for this purpose:

Conventional Kinetic Methods

For relatively slow reactions (typical of inert complexes), conventional methods such as UV-visible spectroscopy, NMR spectroscopy, or conductivity measurements can track the progress of substitution reactions over time. These methods allow the determination of rate constants & activation parameters ($\Delta H^‡$, $\Delta S^‡$, & $\Delta G^‡$) that characterize the kinetic behavior. For example, the substitution of chloride in $[Co(NH_3)_5Cl]^{2+}$ by water can be monitored by the change in absorption spectrum as the reaction proceeds, yielding rate constants that confirm its inert nature.

Fast Reaction Techniques

For labile complexes with very rapid ligand exchange, specialized techniques are required:

Notes

- Stopped-flow methods: Rapidly mix reactants & monitor the initial stages of fast reactions with time resolution down to milliseconds.
- Temperature-jump relaxation: Perturb an equilibrium system with a sudden temperature change & observe the rate of return to equilibrium.
- NMR line broadening & exchange spectroscopy (EXSY): Analyze the effects of chemical exchange on NMR spectra to extract rate information.
- Pressure-jump methods: Similar to temperature-jump but using pressure perturbations.

These techniques have revealed that water exchange on many first-row transition metal aqua complexes occurs with half-lives on the order of microseconds to milliseconds, confirming their labile character.

Isotopic Exchange Studies

Isotopically labeled the ligands (such as ^{18}O-labeled water or ^{36}Cl-labeled chloride) can be used to track exchange processes without changing the chemical identity of the complex. Mass spectrometry or spectroscopic techniques can then detect the incorporation of the labeled atoms, providing information about exchange rates even in systems where no net chemical reaction occurs.

Implications of Inertness & Lability in Applications

The kinetic behavior of metal complexes has profound implications for their practical applications across various fields:

Catalysis

Catalytic processes often require a delicate balance of lability & inertness:

- The metal center must be labile enough to allow substrate binding & product release.
- It must also maintain sufficient integrity during the catalytic cycle to prevent decomposition.

Industrial catalysts like Wilkinson's catalyst $[RhCl(PPh_3)_3]$ & hydroformylation catalysts exemplify this balance, with rhodium complexes exhibiting moderate ligand exchange rates that facilitate catalytic turnover while maintaining structural integrity.

Medicinal Chemistry

The kinetic characteristics of metal-based drugs significantly influence their biological activity:

- Cisplatin's anticancer activity depends on its kinetic inertness, allowing it to reach DNA before undergoing hydrolysis to form the active aqua species.
- Gadolinium contrast agents for MRI must be sufficiently inert to prevent the release of toxic Gd^{3+} ions in the body.

Environmental Chemistry

The mobility & bioavailability of metal ions in the environment are influenced by the kinetics of their complexation with natural the ligands:

- Rapidly exchanging metal ions tend to be more bioavailable.
- Kinetically inert species may persist in environmental compartments, affecting long-term exposure & remediation strategies.

Analytical Chemistry

Many analytical applications of metal complexes, particularly in chromatography & extraction, rely on controlled kinetic behavior:

- Extraction processes often require rapid complex formation for efficiency.
- Certain separations exploit differences in the kinetic lability of different metal ions.

Mechanistic Classification Based on Kinetic Behavior

The inert-labile distinction provides a foundation for more detailed mechanistic classifications of ligand substitution reactions. Based on kinetic studies, several distinct mechanisms have been identified:

Dissociative (D) Mechanism

In a purely dissociative process, the rate-determining step involves the departure of the leaving ligand, creating an intermediate with reduced coordination number. This mechanism is common for inert octahedral complexes & shows characteristic kinetic behavior:

- First-order kinetics (rate depends only on the concentration of the complex)
- Negative activation entropy ($\Delta S^‡ < 0$) due to the more ordered transition state
- Independence of rate on the nature or concentration of the entering ligand

Notes

Associative (A) Mechanism

In a purely associative process, the rate-determining step involves the formation of a bond with the entering ligand, creating an intermediate with increased coordination number. This mechanism is common for square planar complexes (particularly d^8 configurations like Pt(II)) & exhibits:

- Second-order kinetics (rate depends on concentrations of both complex & entering ligand)
- Negative activation entropy due to the more ordered transition state
- Strong dependence of rate on the nucleophilicity of the entering ligand

Interchange Mechanisms (Id & Ia)

Most reactions occur via interchange mechanisms, where bond-making & bond-breaking occur in a concerted manner without discrete intermediates. These are further classified as:

- Interchange dissociative (Id): Bond-breaking character dominates the transition state.
- Interchange associative (Ia): Bond-making character dominates the transition state.

The distinction between these mechanisms provides deeper insight into the intimate details of ligand substitution reactions & helps explain the factors that determine whether a complex behaves as inert or labile.

Advanced Concepts in Inertness & Lability

As research in coordination chemistry has advanced, several sophisticated concepts have emerged that refine our appreciate and comprehend ing of inertness & lability:

Trans Effect & Trans Influence

In square planar complexes, the rate of substitution of a ligand is strongly influenced by the ligand trans to it—a phenomenon known as the trans effect. The ligands with strong trans effects (such as CO, CN^-, & H^-) accelerate the substitution of the trans ligand, effectively creating regions of localized lability within an otherwise inert complex. This concept has been extended to the trans influence, which describes the ground-state weakening of the bond trans to certain the ligands, affecting both thermodynamic & kinetic characteristics.

Stereochemical Considerations

The stereochemistry of the complex can significantly influence its kinetic behavior:

- Facial (fac) versus meridional (mer) isomers may exhibit different substitution rates due to differences in electronic & steric environments.
- Chirality can affect reaction pathways, particularly in biological systems where enzymes may recognize one enantiomer preferentially.

Non-classical Substitution Mechanisms

Beyond the classical D, A, & I mechanisms, research has revealed more complex pathways:

- Reductive elimination/oxidative addition sequences in organometallic chemistry.
- Electron transfer-induced substitution, where redox processes facilitate ligand exchange.
- Photochemically activated substitution, where electronic excitation lowers activation barriers.

Computational Approaches

Modern computational methods have provided unprecedented insight into the factors governing inertness & lability:

- Density functional theory (DFT) calculations can predict activation barriers & transition state geometries.
- Molecular dynamics simulations reveal the role of solvent reorganization & thermal fluctuations.
- Ab initio methods help elucidate the electronic factors that determine kinetic behavior.

These advanced concepts continue to refine our appreciate and comprehend ing of inertness & lability, enabling more precise control over the design of metal complexes for specific applications.

Unit 12 Energy Profile of Reactions

Chemical reactions are all about energy changes and the transformation of reactants into products. These changes in energy are critical for predicting whether the reaction you want will happen, & even if you perform a reaction, at what rate & what mechanism.

Free energy diagram: Reaction Pathway & Activation Energy

Notes

The reaction pathway describes the detailed path that reactants follow as they are converted to products. This can be represented by a smooth path on an energy landscape, showing how the potential energy of the system evolves as bonds are broken & formed. Use a theoretical construct known as the reaction coordinate, which just means the degree (x-ordinate when plotting a reaction energy profile) along the reaction, typically from reactants (some point in the left on the x-axis of the energy profile) to products (some point on the right). All we have to know is that to get a reaction to proceed the reactants need to have enough energy to go over an energy barrier called the activation energy (E_a). Activation energy blue is the minimum energy needed to convert a reaction into an activated complex which then goes on to form products. The energy barrier we observe exists because when bonds are broken, the system gets stuck in a higher-energy state before new bonds are formed. The concept of an activation energy was first introduced by Svante Arrhenius in 1889 who suggested that not all the colliding molecules have enough energy to surpass this barrier. This made him come up with the Arrhenius equation:

$$k = A \bullet e\text{^}(-E_a/RT)$$

Where:

- k is the rate constant
- A is the pre-exponential factor (collision frequency related)
- E_a is the activation energy
- R is the gas constant
- T — the absolute temperature

The general concept of an activation energy barrier accounts for why many reactions (thermodynamically favorable reactions with negative ΔG) may occur slowly or not at all at room temperature. Glucose, for instance, has a thermodynamically favorable combustion (ΔG 0) — the activation energy of the forward reaction is higher than that of the reverse reaction. The Hammond postulate gives more information about the structure of transition state & states that the transition state of an exothermic reaction resembles the reactants while the transition state of an endothermic reaction resembles the products. This principle is useful for predicting how the rates of reaction will change due to structural modification.

Intermediate vs Transition State

This is especially important for the default reaction mechanism & energy profile interpretation, which looks at reaction intermediates & transition states. Though both are intermediates & formed during a reaction, they have different fundamental nature & energy characteristics. A transition state is the highest-energy configuration along a reaction coordinate, meaning that it is reached as old bonds are being partially broken & new bonds are being partly constructed. Three main features characterize the transition states:

Notes

- Glimpse of Transition: Transition states are very short-lived, on the order of 10^-13 to 10^-14 seconds, which is about the time taken by a single molecular vibration.
- Partial bonds: They have partially formed and partially broken bonds, usually shown as dashed lines in structural depictions.
- Energy maxima: Transition states are energy maxima in reaction energy profiles — energy decreases whether the system proceeds toward reactants or products.
- In no way isolateable: Because of their high energy & instability, transition states are not isolable or visible to standard spectroscopic techniques; however, indirect information on the structure of transition states can be collected from kinetic isotope effects & computational modeling.
- First-order saddle points: Transition states can be described in terms of potential energy surfaces as first-order saddle points—maxima in one dimension (the reaction coordinate) but minima in all other dimensions.

By contrast, reaction intermediates are well-defined chemical species (as opposed to vague game-players) that exist during multi-step reactions & have definite, if sometimes short, lifetimes. Intermediates have the following key characteristics:

- Relative Stability: The intermediates have due to the presence of energy minima between reactants & products are more stable than the transition states.
- Intermediates: many are isolated (likely); some are reactive species so have relatively longer lifetimes than transition states
- Intermediates differ notably from transition states in that they have complete electronic structures even with normal bond orders.
- Spectroscopic accessibility: Many intermediates can be either detected or even characterized by rapid spectroscopic techniques (e.g. stopped-flow spectroscopy, flash photolysis, or low-temperature NMR).
- Kinetic importance: This leads to the formation or decomposition of intermediates, which can affect reaction kinetics & thus may show as steps in rate equations.

Notes

The multi-step reaction energy profile illustrates the differences between intermediates & transition states: On such a profile, intermediates are manifested as local energy minima (valleys) as a function of their position along the reaction coordinate while transition states appear as energy maxima (peaks). Each step in the reaction must surmount an activation energy barrier through a transition state to produce either intermediates or the final products.

Take the SN1 reaction of tert-butyl bromide with water: $(CH_3)_3C\text{-}Br + H_2O \rightarrow (CH_3)_3C\text{-}OH + HBr$

The energy profile for this process is as follows:

- Reactors at the initial energy level
- A transition state for heterolytic cleavage of the C-Br bond
- Intermediate carbocation [$(CH_3)_3C^+$] & bromide ion [Br^-] at a local energy minimum

A second transition state representing the nucleophilic attack of water on the carbocation (Products in the ultimate energy level)

Here, the carbocation intermediate lies at a local energy minimum between two energy peaks, each end of which is topped with a transition state. Not all carbocations have a potential energy well, so this would mean that not all of them would be considered intermediates in a reaction, but since the tertiary carbocation is relatively stable, it stays in solution long enough to be considered a true intermediate & not just a transition state. The difference between concerted & stepwise mechanisms also lays bare the difference between transition states & intermediates. In concerted reactions such as the Diels-Alder cycloaddition, reactants convert to products in a single transformation between them in the absence of isolable intermediates through a single transition state. The energy profile displays one activation barrier. Stepwise reactions (e.g., SN1 mechanism) each involve one or more intermediates & thus have multiple transition states as well as a more complex energy profile with multiple peaks & valleys. The rate-determining step in a multi-step reaction is simply the step that contains the highest energy transition state in the energy profile. This rate-limiting step has a high activation energy & thus limits the overall reaction rate. In the SN1 example above, the first step (the formation of the carbocation) generally has the higher activation energy, therefore it is the rate-determining step. This methodology was subsequently supplemented, enabling computational chemistry to change the face of discovery by bringing us the structures & energies of intermediates & transition states of reaction energy profiles that we could heretofore only hypothesize based on classical considerations. Computational methods, including density functional theory (DFT), can predict activation energies to within a good degree of accuracy & can provide

Notes

mechanistic insight that may be very difficult or even impossible to obtain experimentally.

We also gain insights for these reaction energy profiles through experimental techniques. Kinetic isotope effects, e.g., can reveal bond-rearrangement events occurring in the transition-state region. Hammett correlations provide indirect information on charge development in the transition state as substituents are observed to modulate reaction rates. Multi-surface reactivity, such as photochemical reactions or spin-state changes, makes energy profiles more complicated. For example, a feature like a conical intersection, a point of avoided crossing, allows for a non-adiabatic transition between potential energy surfaces. Another sophisticated approach to appreciate and comprehend ing energy profiles, particularly for redox reactions, is the Marcus theory of electron transfer reactions. In this case, the activation energy for electron transfer is a function of the reaction free energy ($\Delta G°$) & the reorganization energy (λ)—the energy necessitating the reorganization of the nuclear conformation of the reactants, products, & surrounding solvent.

In practical applications across chemistry & biochemistry, appreciate and comprehend ing reaction energy profiles is crucial. Computational prediction of reaction barriers is used to make synthetic approaches more efficient in drug design. To explain how proteins lower activation barriers during enzyme catalysis, we analyze energy profiles that include electrostatic stabilization, strain, & proximity effects. In the field of materials science, energy profiles assist in creating catalysts for various industrial processes by revealing rate-limiting steps & possible catalytic methods. Innovative spectroscopic methods keep challenging the limits of our capability to investigate reaction dynamics. Femtosecond spectroscopy exposes the timescale around transition states & reveals ultra-fast processes. Time-resolved X-ray crystallography & electron diffraction can freeze the structural changes occurring during the reactions, & they provide snapshots of systems in the process of evolving along their reaction coordinate. This idea can also be applied to biological & physical processes; even in protein folding, phase transitions or conformation transitions of the molecules. These processes can also be viewed as being represented as traverses on complex, multidimensional energy landscapes with multiple minima, maxima, & saddle-points.

Finally, the energy profile of a reaction is a powerful conceptual tool & can help to appreciate and comprehend a transition state. Chemists can predict, explain, & control reaction outcomes by distinguishing transition states from intermediates & analyzing the energetics of reaction pathways. 11 (2014): 376302 from an analysis of reaction energy profiles of Nakamura et al.

Notes

Unit 13 Kinetics of Octahedral Substitutions

Octahedral substitution reactions are a hallmark of coordination chemistry, governing the ligand-pairing events in octahedral metal complexes. The kinematic profiles of these reactions are controlled by multiple factors, with different mechanistic pathways governing them. The kinetics of octahedral substitution has far-reaching significance in elucidating catalytic processes, biological systems, & materials science applications involving metal centers. The ligands also have an important role to play in the arrangement around the light absorbing center, & octahedral complexes — where the coordination sites are symmetrically arranged into an octahedron around a centrally located metal atom — provide a special case for a ligand substitution. The spatial distribution of these sites imposes its own electronic and steric constraints unique to the protein environment that impact both the approach of incoming the ligands & the departure of leaving groups. While tetrahedral or square planar geometries do not markedly affect substitution processes, octahedral coordination can pose unique hurdles for ligand substitution, leading to distinct mechanistic pathways that enable these reactions to occur in a sufficiently rapid manner.

An octahedral substitution can be illustrated in general for the symbology as $[ML_5X] + Y \rightarrow [ML_5Y] + X \rightarrow [ML_5Y_2] + [3- 3]^-$. Although this depiction seems simple, the mechanism is often much more complex, with extensive electronic reorganizations, bond breaking & forming events, & even substantial rearrangements in the coordination sphere. The kinetics of these reactions have uncovered that octahedral substitution moieties tend to be classified into distinct mechanistic categories that primarily differ based on whether the rate-determining step is associated with association of the entering group or dissociation of the leaving group, or whether it is a more complex interchange between these processes. This classification allows one to appreciate and comprehend the wide range of metal complex & reaction condition dependent behavior.

A mechanisms of octaheдral substitutions

Octahedral substitution has been thoroughly studied & categorized according to its kinetic profile, activation parameters, & the effect of entering & leaving groups on reactivity. Octahedral complexes diverge in their pathways, as they often undergo associative processes, unlike their square planar counterparts, due to the geometry's increased sterics & electronic species. A large body of work has defined the principal mechanistic pathways for octahedral substitution in terms of broad types of processes: dissociative, associative, & interchange. These classes are based on how the rate-determining step is characterized by nature & the structure of either the transition state or intermediate created during the intermediate. In dissociative mechanism (D), the leaving group leaves prior to much interaction with the entering group. This gives an intermediate with lower coordination number (usually five-coordinate) which then reacts with the incoming ligand to restore the octahedral geometry. This type of mechanism is characterized by a rate law that does not depend on the concentration of the entering ligand, since the rate-determining step occurs before the entering ligand gets involved in the reaction.

Notes

Instead, in the associative pathway (A), engagement of the incoming group occurs prior to substantial dissociation of the departing group. This gives rise to an intermediate by expulsion of the leaving group, resulting in coordination number expansion (usually achieved for coordination by seven-coordinate N-intermediates), until the octahedral configuration can be recovered. The rate law derived from this mechanism reflects a dependence on the entering ligand concentration, meaning that this step is indeed rate-determining. In between these extremes is the interchange mechanism, where (the entering group forms a bond simultaneously with the leaving group) are not made & broken in a strictly sequential manner but instead involve a concerted transfer of groups where some bond is formed with the entering group while simultaneously some other bond is broken with the group leaving the reactive center (not necessarily to the same extent). This mechanism can be further subdivided into a dissociative interchange (Id) & associative interchange (Ia) depending on whether breaking or formation is more advanced in the transition state. The energetics of these mechanisms are markedly different. Since leaving groups do not provide assistance in breaking the metal–ligand bond in dissociative pathways, these pathways are generally characterized by higher activation enthalpies. However, they tend to exhibit positive entropies of activation due to the greater disorder of a five-coordinate intermediate. In contrast, associative mechanisms typically exhibit lower activation enthalpies but negative activation entropies, which is consistent with the ordering effect of coordi- nating the complex with the incoming ligand in the transition state.

Associative (A) & Dissociative (D) Pathways

Octahedral substitution occurs by two principal pathways, gate (G) & associative (A) or dissociative (D) pathways. This leads to a larger coordination sphere, and, typically, a seven-coordinate intermediate. In this mechanism, the kinetics are second-order, & the rate law is of the type: rate = kcomplex. Associative mechanisms forming a seven-coordinate intermediate are sterically demanding. This steric eversion or constraint partly explains the relative scarcity of associative mechanisms in octahedral versus square planar substitution. For

Notes

smaller metal ions that have largely open coordination sites & strongly nucleophilic entering groups, however, the associative pathway is favored. Important attributes of this associative pathway are that they possess a negative volume of activation ($\Delta V^\ddagger$) associated with compression of the system in the transition state & a pronounced dependence on the nucleophilicity of the entering group with a relative insensitivity to the nature of the leaving group. Associative character in substitution reactions can be found in complexes of d^3 configuration (such as Cr(III)) & complexes with labile metal centers.

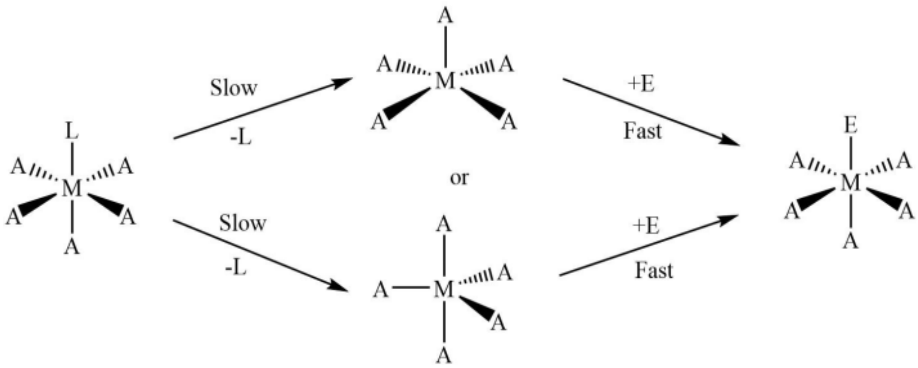


Figure - Pathway for ligand displacement reactions in octahedral metal complexes through SN1.

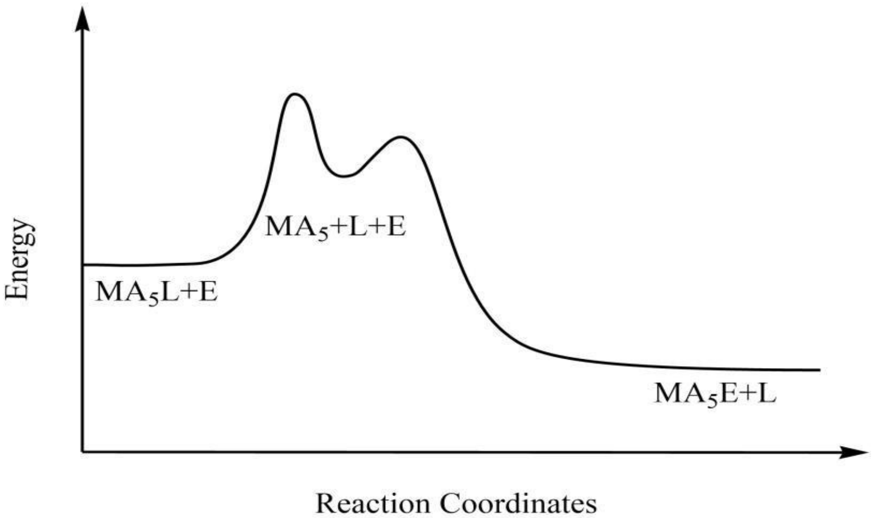


Figure - The typical reaction coordinate diagram for ligand displacement reactions in octahedral metal complexes through SN1 mechanism.

The dissociative (D) pathway, on the other hand, sees the leaving group depart before any sensible interaction with the entering ligand, leading to a five-coordination intermediate. This process proceeds via a first order mechanism, & is written in the form of the following rate law: rate = k[complex], which is independent of entering ligand concentration. The dissociative mechanism predominates octahedral substitution reactions especially on the inert metal centers defined by d^6 low spin complexes such as Co(III) & Rh(III). For larger metal ions & sterically hindering coordination environments, the formation of five-coordinate intermediates is often favored energetically, rather than expanding to seven-coordinate species as in associative mechanisms. This observations is consistent with the characteristics of dissociative mechanisms with positive volumes of activation ($\Delta V^‡$), facilitated by expansion of the system in the transition state, a strong dependence of $\Delta V^‡$ on the nature of the leaving group, & relative insensitivity to the identity of the entering group [increase in the leaving group size]. If the departing group is a ligand attached to a metal, the dissociative pathways involve breaking a metal-ligand bond, while the activation energy for dissociative processes is often related to the metal-ligand bond strength associated with the leaving group.

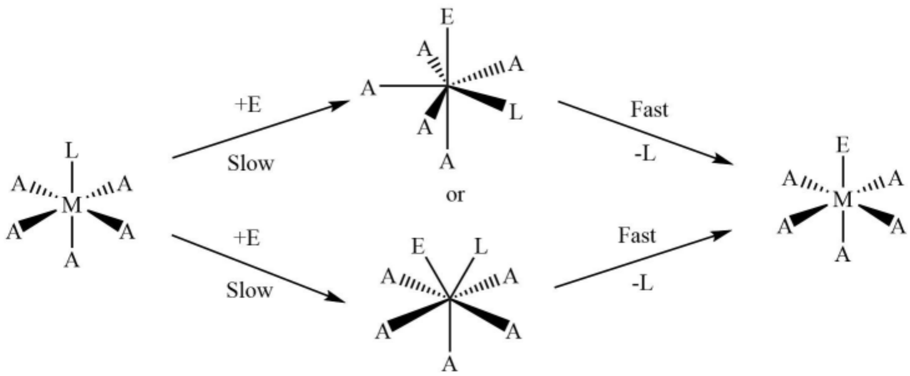


Figure - The general reaction mechanism for ligand displacement reactions in octahedral metal complexes through SN_2 pathway.

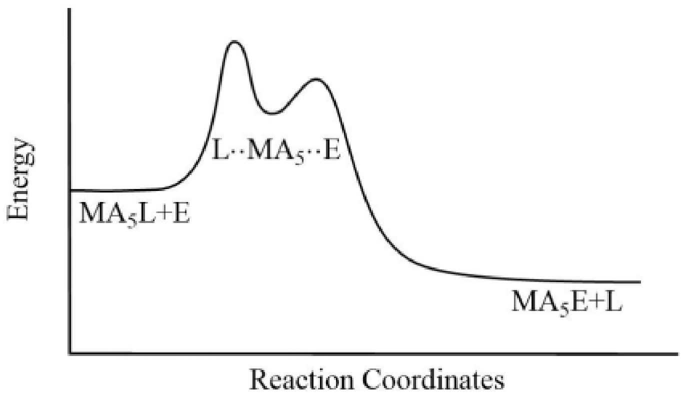


Figure - The typical reaction coordinate diagram for ligand displacement reactions in octahedral metal complexes through SN2 mechanism.

The interchange mechanisms (Id & Ia), in which concerted bond breaking and bond formation takes place & no isolated intermediates form, are found between these two extremes. In the dissociative interchange (Id) mechanism, bond-breaking proceeds further than bond-forming in the transition state, while the associative interchange (Ia) mechanism has more advanced bond forming than the bond breaking in the transition state. Careful kinetic studies involving determination of activation parameters (ΔH‡, ΔS‡, ΔV‡) & variations of entering & leaving group characteristics generally provide the best means of distinguishing between these mechanisms. The stereochemical implications are also important as different mechanisms can afford different stereochemical selections of products. Retention of configuration is often found with dissociative mechanisms in octahedral complexes containing chelating the ligands, because the five-coordinate intermediate retains its geometric orientation as the entering group approaches. In contrast, if the incoming group approaches from a different side to that of the departing group, then isomerization will occur as it is an associative mechanism.

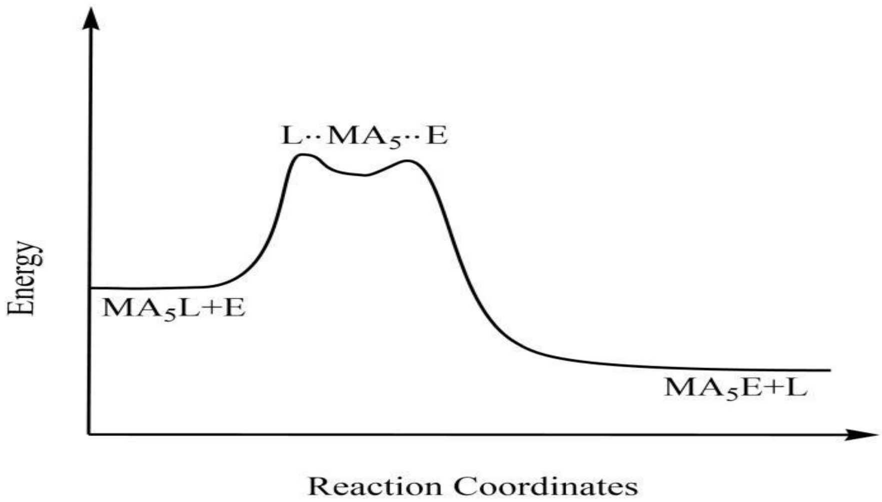


Figure - The typical reaction coordinate diagram for ligand displacement reactions in octahedral metal complexes through the interchange mechanism.

Factors That Affect the Rate of Reaction

The fundamental principles dictating coordination chemistry & allows for the rational design of complexes with modulated reactivity profiles. Substitution rates are critically dictated by the electronic configuration of the metal center. The CFSE has a large impact on the activation energy for ligation substitution. Complexes with great CFSE, however, like for instance low-spin d^6 (e.g. Co(III), Rh(III), Ir(III)) have low substitution rates, for the reason that a large amount of energy is required to distort the octahedral geometry during the reaction. In contrast, zero CFSE complexes (e.g., high-spin d^5 (Mn(II)) or d^{10} (Zn(II)) configurations, tend to be more reactive. This step: metal substitution rates, which depend on the d-electron count influencing metal-ligand bond strengths & the stability of the intermediates. For example, d^3 complexes such as Cr(III) have intermediate reactivity, whereas d^8 complexes like Ni(II) can be quite labile. Principles of the spectrochemical series & the nephelauxetic effect also modify these electronic effects by affecting the extent of orbital overlap & the covalent character of metal-ligand bonds.

Ligand effects are another important aspect of octahedral substitution kinetics. The trans influence, where some the ligands can promote the substitution of groups trans to them, has both σ-bonding & π-bonding contributions. Strong σ-donors & π-acceptors generally present well-defined trans effects for example, by destabilizing the trans bond due to direct competition for metal orbitals, or via electronic polarization. Substitution rates in multidentate ligand systems are significantly affected by the chelate effect. Chelating the ligands tend to reduce substitution rates because of the entropic cost of their dissociation. This effect is an extension of the chelate effect, & combined with what is known as the macrocyclic effect it accounts for the extreme inertness of complexes of cyclic polydentate the ligands such as porphyrins & crown ethers. Steric effects are far-reaching in their influence on substitution mechanisms and rates. Bulky the ligands may promote dissociative processes by relieving ground-state strain in the complex, thereby lowering the activation energy for ligand dissociation. On the flip side, they could obstruct associative pathways by preventing the proximity of incoming groups. The cone angle, a concept originally applied to phosphine the ligands, gives a quantitative atomistic descriptor of steric demand that has been shown to correlate with rates of substitution in many systems.

Solvent effects appear via a number of mechanisms involved in octahedral substitution reactions. Only incoming the ligands are the competition for solvent coordination, especially in the case of dissociative mechanisms, where solvent molecules can occupy the empty coordination site of the five coordinate intermediate. The stability of charged intermediates & transition states depends on the polarity of the solvent, while its ability to form hydrogen bonds will impact which leaving groups or entering the ligands are specifically stabilized. The solvent dielectric constant determines the activation energies for charge-separating or charge redistributing reactions in the transition state. In particular, higher dielectric constants tend to speed reactions in which charge separation increases in the transition state. Moreover, specific solvent-solute interactions (e.g. hydrogen bonding, dipole-dipole interactions) can have a significant impact on reaction mechanisms & rate constants. Pressure effects can give mechanistic insights, because associative & dissociative mechanisms have different sensitivity to changes in pressure. In associative mechanisms, involving volume decrease in the transition complex, higher pressure increases their rate (negative volume of activation). In contrast, the sheer of

Notes

dissociative mechanisms, which are associated with the transition state by volume expansion, are hindered by pressure (positive volume of activation). These principles have been used to clarify mechanisms under circumstances where traditional kinetic behaviors would be ambiguous.

Seen in Eyring or Arrhenius plots, the temperature dependence of substitution rates gives activation parameters that illuminate the transition state. Compurature or low energy free activation energies, along with positive activation entropies correspond to a dissociative character while smaller enthalpies & negative entropies indicate an associative character (19). The isokinetic relationship, where compensation between entropic & enthalpic components occurs across a series of thermnetically linked reactions, further highlights the mechanistic unity(56, 57). An interesting class of octahedral substitution is the substitution in coordinated the ligands. In such cases, the metal center modifies the reactivity of coordinating the ligands but does not directly engage in bond making or breaking. For example, metal coordination can promote carbonyls for nucleophilic attack or aryls for electrophilic substitution. These effects result from both electronic perturbation of the ligand & steric constrictions afforded by the coordination environment. Acids–bases may catalyze wts reaction of substitution in aqueous systems. The lability of leaving groups can be increased through their protonation79, as this alters the local electron density at the metal-ligand bond. Clearance of incoming the ligands may similarly enhance their nucleophilic character through deprotonation, promoting associative mechanisms. This pH dependence of substitution rates is often a manifestation of these acid-base equilibria being superimposed onto the inherent substitution mechanism.

Dissociative substitution rates are strongly influenced by leaving group ability. Leaving group lability in turn depends on the bond strength with the metal, the stability of the free ligand & solvation effects. A rough guide to leaving group abilities is given be the order of the ligands in the spectrochemical series, as weak-field the ligands (for example, I^-, Br^-, Cl^-, F^-) usually leave more readily than strong-field the ligands (for example, CN^-, CO, phosphines). Associative mechanisms are mainly dependent on the nucleophilicity of the entering group. This is due to the complementary reactivity of softer nucleophiles (I^-, PR_3, thioethers) to soft metal centers as predicted by Pearson's hard-soft acid-base (HSAB) principle which extends well to coordination chemistry, where nucleophilicity trends often track those of organic chemistry. But some orbital interactions & steric factors can cause exceptions to simple electronegativity-based predictions.

Kinetic Models with Special Cases

In addition to the classical A & D mechanisms, an extended version of the kinetic model of the octahedral substitution reaction has been proposed which takes this complexity into account. For example, the Eigen-Wilkins mechanism when logic for pre-equilibrium there is a formation of an outer-sphere complex prior to the actual substitution metallochromism. It has proved especially successful at explaining substitution kinetics in aqueous systems where solvation is key. The intimate mechanism, realized by Langford & Gray, offers a more detailed perspective of interchange processes by contemplating the synchronicity of bond breaking & forming. It brings together the two ends of the spectrum–pure associative & pure dissociative processes–since almost all real systems lie somewhere in between, exhibits some concerted behavior. Substitution in trans-effect complexes illustrates how judicious placement of the the ligands can profoundly accelerate certain substitution reactions. Distinct from the thermodynamic trans effect, the kinetic trans effect proceeds through a σ-bonding and π-bonding derived mechanism gave. Trans-directing the ligands that stabilizer the transition state or weaken the trans bond can enhance substition rates by order of magnitudes (e.g., H^-, CH_3^-, & PR_3).

Mechanistic insights can be gleaned from stereochemical aspects of octahedral substitution. Rearrangement or inversion of arrangement upon substitution is frequently used as a diagnostic test for pathway differentiation. Thus, for example, configuration retention is often accompanied by dissociative pathways, whereas associative channels can give rise to isomerization, depending on the approach trajectory of the entering moiety. An interesting special case is the situation where this kind of substitution occurs, but without cleaving the metal-ligand bond, which is called linkage isomerization. Isomerization can occur after coordination to the metal for ambidentate the ligands such as thiocyanate (SCN^-/NCS^-), nitrite (NO_2^-/ONO^-) & sulfoxide (R_2SO). This can result in more complex kinetic behavior than standard substitution reactions can accommodate, because the need to remain attached to the metal center places constraints on how processes can occur. In many systems, especially those involving redox active metal centers, electron transfer catalyzed substitution mechanisms have been characterized. For example, substitution in Co(III) can be dramatically accelerated by reduction to Co(II) allowing for fast ligand exchange followed by reoxidation to Co(III). This “reduction mechanism” sidesteps the high activation barrier for direct substitution at the inert Co(III) center.

A general route for activation of substitution in otherwise inert complexes is photoinduction. Light absorption can excite electrons into antibonding orbitals, reducing the strength of certain metal-ligand bonds & enabling their scission. This strategy has been particularly fruitful for d^6 systems such as Cr(III) & Co(III) in scenarios where

Notes

Notes

thermal substitution is tantamount to an endless wait. Due to the electronic interaction amongst metal centres, such substitution in polynuclear complexes leads to further complexity. Bridging the ligands can also affect electronic communication throughout the complex, leading to cooperative effects whereby substitution at one metal center affects reactivity at another. This has been very well characterized in biological systems such as hemoglobin where ligand binding is cooperative. Solvation effects on substitution mechanisms are significant in general & are not limited to pure dielectric type effects. The stabilization of intermediates & transition states through solvent coordination can also alter reaction pathways, uniquely switching mechanisms dependent on solvent characteristics. For example, substitution reactions that proceed through dissociative pathways in non-coordinating solvents can take on associative character in strongly coordinating media.

Pressure studies have emerged as a resource for mechanistic elucidation. Activation volume ($\Delta V^‡$) gives straightforward insights into the nature of the transition state: negative $\Delta V^‡$ corresponds to compressed (associative nature) & positive $\Delta V^‡$ corresponds to expanded (dissociative character). This strategy has proven especially useful for clarifying mechanistic uncertainties in systems where traditional kinetic methods provide nondiscriminatory answers.

Further Applications and Modern Developments

In particular, the rules of octahedral substitution kinetics have wide application to the problems of chemistries of many kinds & on many scales. Ligand exchange processes are critical for catalyst design & optimization in homogeneous catalysis. Precatalyst activation typically proceeds through substitution steps that can result in catalyst deactivation by undesired ligand exchange reactions. Thus, rational designer of catalytic structures requires detailed overview of substitute mechanisms and factors governing them. Metal ion substitution kinetics are crucial to many biological processes, in the field of bioinorganic chemistry. While selective coordination & release mechanisms control the transport of metals between different environments, it remains difficult to survey the binding profiles of individual metalloproteins in complex mixtures. For example, metalloproteins such as hemoglobin & myoglobin operate via a controlled binding & release mechanism for oxygen, metalloenzymes are frequently more complex requiring coordination steps for substrate & subsequently product release that obey similar design tenets of simple coordination complex. Because the specific applications of novel contrast agents in medicine, especially MRI, focus, knowledge of substitution kinetics is crucial for their development. To develop optimal gadolinium-based contrast agents, one must find the right balance between the exchange rate of the water molecules & stability within biological conditions. These agents are engineered with precisely coordinated environments that maximize exchange dynamics.

Platinum anticancer drugs (Pt(II) complexes), for example, are members of metal-based therapeutic agents that act via the mechanisms of substitution, ligand-induced exchange. Their therapeutic value stems from their kinetic inertness in the bloodstream & controlled substitution reactions in the target tissue. This kinetic property is now being optimized in efforts to design drugs that have enhanced selectivity & reduced side effects. In material science, they are used in the syntheses of coordination polymers, metal-organic frameworks (MOFs), & other advanced materials through exchange reactions. This enables the post-synthetic modification of such materials through substitution reactions at metal centers, facilitating the introduction of functionality after the structural backbone has been established. Recent methodological developments have greatly improved our structural insight into substitution mechanisms. High-pressure NMR techniques which allow for direct observation of volume changes during reaction therefore provide decisive evidence for mechanistic assignments. Time-resolved spectroscopic techniques such as stopped-flow methodologies, as well as ultrafast laser spectroscopy, enable the observation of short-lived intermediates that have remained largely out of reach.

Computational methods are now potent tools for probing substitution mechanisms. Now, density functional theory (DFT) calculations have reached a point where they are able to accurately predict activation parameters & reaction pathways, including structures of transition states that cannot be directly observed in the laboratory. Ab initio molecular dynamics simulations show that solvation effects are dynamic in nature & provide insights into the myriad roles that solvent molecules play in promoting substitution. Experimental & computational techniques have been utilized to develop a more detailed picture of substitution mechanisms than is offered by A & D classification alone, as well as taking into account orbital interactions, solvent dynamics, & environmental factors (including both diaxial interactions & steric or electronic effects). This integrated approach has been especially useful in elucidating substitution in complex biological systems and heterogeneous environments.

Unit 14 Anation Reactions

Anation reactions are a prototypical class of ligand substitution reaction in the coordination chemistry of coordination complexes in which a neutral ligand is substituted for an anionic ligand within a metal complex. The term "anation" is used in a more restricted sense to describe replacement of a coordinated water molecule in a complex with an anion. The reactions are essential in learning the fundamentals

Notes

of inorganic reaction mechanisms & have important applications in varied industries, catalytic systems & analytical methods. Anation reaction studies reveal clues to the reactivity patterns of transition metal complexes & help us appreciate and comprehend the determinants of anation mechanisms. Inscribing the mechanistic routes & kinetic parameters of these reactions enables us to predict the outcome of reactions, design novel coordination compounds with desired attributes, & improve industrial processes that utilize metal-ligand interactions.

Mechanism & Kinetics

Other reactions, which proceed through interchange mechanisms, have characteristics of both types of mechanisms. The exact mechanism is dictated by several factors such as the electronic configuration of the metal center, steric constraints of the the ligands, & the reactivity of the incoming & outgoing species. In the (A) associative mechanism, the incoming anion first forms a bond with the metal center resulting in higher coordination number in the transition state. This mechanism is defined by a negative entropy of activation ($\Delta S‡$), & is a common feature for square planar d8 complexes such as Pt(II) & Pd(II) [6]. In this system, the rate-determining step is the formation of the metal-ligand bond with the incoming substituent, & the rate is sensitive to the concentration as well as nucleophilicity of the incoming anion. The dissociative mechanism (D), in contrast, starts with the leaving group exiting, producing a coordination vacancy at the metal center prior to binding of the entering anion. A positive entropy of activation characterizes this mechanism and is characteristic of octahedral d3 & high-spin d5 complexes, i.e., Cr(III) & Mn(II) compounds. The step facilitating the cleavage of both the metal-ligand bond & leaving group determines the rate of reaction, with the rate now less dependent on the entering anion's identity & concentration. A good number of anation pathways are through interchange mechanisms (Ia or Id) that encompass co-operative bond-making & bond-breaking events. In the associative interchange (Ia) mechanism, bond formation with the incoming species is dominant, whereas in the dissociative interchange (Id) mechanism, bond breaking with the outgoing species is dominant. These are proposed as endpoints on a continuous spectrum between purely associative & purely dissociative signaling mechanisms.

The kinetics for anation reactions can be described by the following rate equation:

$$\text{Rate} = kMLn(H2O)$$

Where MLn(H2O) is the metal complex with a coordinated water molecule, X- is the incoming anion, & k is the rate constant for second order. On the other hand, the rate law can also be more complex depending on reaction conditions, catalyst presence, & the existence of parallel reaction pathways.

Various factors are at play in determining the kinetics of anation reactions:

The electron nature of the metal center: The classical picture states that electron-rich metal centers with filled d-orbitals tend to support associative mechanisms, whereas electron-deficient metals tend to favor a dissociative pathway. Lability of the leaving group: Weakly coordinating the ligands such as water are replaced more readily than strongly coordinating the ligands like amines or cyanides. The nucleophilicity of the incoming anion: Generally more nucleophilic anion will react faster in associative processes. For halides, the general trend is I- > Br- > Cl- > F- in terms of nucleophilicity.

- **Steric factors**: The presence of bulky the ligands in the coordination sphere may prevent the approach of entering groups to the coordination site causing reductions in the rate of reaction, particularly in associative mechanisms.

- **Trans effect**: In square planar complexes, the nature of the ligand that is trans to the leaving group has a strong effect on the reaction rate. Functions of some group 18, 17, and 16 metal complexes, in addition to, various other the ligands are also studied in chemical sciences.

- **Solvent effects**: The dielectric constant, donor characteristics, & hydrogen-bonding capabilities of the solvent can have a drastic impact on the stability of charged intermediates & transition states.

- **Prevention of mechanistic ambiguity:** Currently used pressure effects for mechanistic discrimination suffer from mechanistic ambiguity: Associative mechanisms typically have negative volumes of activation ($\Delta V^‡$) & are accelerated with higher pressure, whilst dissociative mechanisms have positive $\Delta V^‡$ values & are decelerated under pressure.

We study anation processes as a function of temperature (reaction temperatures typically spanned50 °C) yielding Arrhenius plots typical of anation reactions, with activation energies generallyreporting in the range 40–100 kJ/mol. Kinetic studies yield activation parameters which shed mechanistic light. The use of a large negative activation entropy ($\Delta S^‡$) indicates an associative mechanism with increased ordering of the transition state, while a positive $\Delta S^‡$ indicates a dissociative mechanism with increasing disorder. Hence, a negative value of volume of activation ($\Delta V^‡$) implies compression in the transition state, consistent with an associative pathway, whereas a

Notes

positive $\Delta V^{\ddagger}$ indicates expansion, indicative of a dissociative mechanism.

Partial & complete destruction of symmetry during concerted octahedral mechanism which results in the substitution of water in $[Co(NH_3)_5H_2O]^{3+}$ by various anions, is therefore an Id mechanism. The rate-determining step is the breaking of the Co-OH2 bond, after which the entering anion rapidly coordinates. The reaction occurs via the formation of a five-coordinate intermediate or transition state, & the rate is relatively unaffected by the identity of the entering group but highly responsive to the electronic characteristics of the metal center & the other the ligands in the coordination sphere. In contrast, the anation of square planar complexes, e.g. $[Pt(NH_3)_3H_2O]^{2+}$, will generally occur via an Ia mechanism. The formation of a trigonal bipyramidal transition state or intermediate is the rate-determining step for this reaction, making its reaction rate greatly dependent on the entering anion's nucleophilicity. The trans effect is an important factor governing the site & rate of reactions, with the ligands that are both strong σ-donors & π-acceptors exhibiting the strongest trans effects.

In solutions of low dielectric constant, ion-pairing effects can further complicate the kinetics of anation reactions. The electrostatic interaction between the charged complex & the incoming anion can result in the formation of an outer-sphere complex that may assist in the later ligand substitution. The ion-pairing effect causes simple second-order kinetics decay constantly to deviation, & thus requires more complex rate laws. Different factors can also catalyze or inhibit the reactions of a nation. – For example, acids can facilitate anation reactions by protonating the leaving group so as to generate a better leaving group. Likewise, bases may facilitate some anation reactions by deprotonation of coordinated water to generate hydroxo complexes with differing substitution kinetics. Well, it turns out that metal ions, especially ones that can undergo redox transitions, are able to catalyze anation reactions via electron transfer processes or via formation of bridged intermediates.

Applications and Industrial Examples

Anation reactions are present in coordination chemistry, & there are a myriad of applications in different fields. A few well-known examples and their industrial use cases are:

Chloro substitution of pentaamminecobalt(III) complex

The anation reaction of $[Co(NH_3)_5H_2O]^{3+}$ with chloride ions leading to the formation of $[Co(NH_3)_5Cl]^{2+}$ is a classically studied anation reaction that occurs via a dissociative interchange (Id) mechanism. It has been used extensively as a model system for the the ligands, metal,

& leaving group influence on octahedral substitution kinetics. The rate law of this reaction is:

$$Rate = k[Co(NH3)5H2O]3+[Cl-]$$

The kinetics show a rather flat dependence on the entering anion nature but very strong trends with the electronic characteristics of the metal center & other the ligands in the coordination sphere; the reaction proceeds through a five-coordinate intermediate or transition state. Such a reaction is pertinent to cobalt-based catalysts in a wide range of oxidations.

Accumulative Reactions in Platinum Anticancer Drugs

Cisplatin (cis-[PtCl2(NH3)2]), an anticancer drug that is widely used in the treatment of various cancers, is activated by the key anation reactions in biological entities important for its therapeutic action. Within a few minutes the chloride the ligands are replaced either one or both by water molecules in what is known as an aquation process (the reverse of anation) leading to the generation of the reactive species cis-[PtCl(H2O)(NH3)2]+ & cis-[Pt(H2O)2(NH3)2]2+ respectively. After being metabolically activated, these aqua complexes will undergo anation reactions with DNA—specifically to the N7 positions of guanine bases—to produce intra- & inter-strand crosslinks that block DNA replication & result in cell death. Kinetics & mechanism of these anation reactions have been studied in-depth to design more effecient platinum-based anticancer drugs having lesser side effects. Second & third-generation platinum drugs [carboplatin & oxaliplatin (78)] have been developed based on more recent appreciate and comprehend ing of how the rate of aquation & subsequent anation reactions affect biological activity (79), leading to alternative leaving groups & different kinetic profiles.

Hydrometallurgical processes for extracting and recovering metals from ores & secondary sources depend on anation reactions. For example, gold recovery through cyanide leaching proceeds through formation of the stable complex [Au(CN)2]- via an anation reaction:

$$Au + 2CN^- + 1/2O2 + H2O \rightarrow [Au(CN)2]^- + OH^-$$

The recovery of copper by solvent extraction, on the other hand, involves anation reactions that facilitate the formation of complexes between the target copper ions & extractants that contain oxygen or nitrogen donor atoms. The formed complexes can be selectively extracted into an organic phase & separated from impurities, followed by stripping through reverse anation reactions to recover the copper. The kinetics & selectivity of these anation reactions are important criteria for the efficiency of the associated hydrometallurgical processes and appreciate and comprehend ing the factors that

Notes

influence them has resulted in more selective extractants compounds & more efficient recovery methods.

Anation in Catalytic Systems

Many catalytic cycles consist of substrate molecule anation-like steps in which coordinated solvent or other the ligands are replaced by substrate molecules. For instance, in the Monsanto acetic acid process, carbon monoxide is aminated with rhodium catalyst, replacing a coordinated iodide ligand:

$$[Rh(CO)_2I_2]^- + CO \rightarrow [Rh(CO)_3I_2]^- + I^-$$

From this, oxidative addition, then migratory insertion & reductive elimination, yield the entire catalytic cycle for methanol carbonylation to acetic acid. This process is kinetically highly dependent on the kinetics of the initial anation reaction that can be demonstrated via first-order kinetic studies. Likewise, for olefin hydrogenation catalysts like Wilkinson's catalyst $[RhCl(PPh_3)_3]$, anation reactions in which triphenylphosphine is displaced by hydrogen or olefin substrate are pivotal steps in the catalytic cycle. A more thorough appreciate and comprehend ing of these anation processes has driven the advancement of more effective & selective catalysts for a wide range of industrial transformations.

Anation in Water Treatment

In this, the electrochemical processes based on anation reactions have been used as water treatments methods for the removal of toxic heavy metals & anions. Against this background, anation reactions, where arsenate or arsenite anions displace coordinated water or hydroxide the ligands from the surfaces of iron (III)-rich oxide materials or from iron containing coordination compounds, play an important role in the effective removal of arsenic from drinking water. In the same manner, fluoride ions from drinking water may be eliminated by adsorbing them onto aluminum-containing adsorbents, where fluoride anions take part in anation reactions with regard to aluminum hydroxide or alumina to substitute surface hydroxyls. The efficiency of these methods themselves relies on the kinetics & thermodynamics of the correlated anation reactions, & optimization efforts are focused on improving the rate & extent of the anation processes.

Anation in Analytical Chemistry

Diverse analytical methods for anion detection & analysis are based on thenation reactivity. As an illustration, colorimetric & spectrophotometric methods for halides, cyanide, thiocyanate, & other anions usually depend on their anation reactions of these anions with transition metal complexes, which produce color or spectral variations. The classical Volhard method for the determination of chloride consists of anation of chloride with silver ions to give insoluble silver chloride, then back-titration of excess Ag+ with thiocyanate to yield a colored complex with iron(III). These analytical methods can be more sensitive & selective with good appreciate and comprehend ing of the kinetics & equilibria in the anation reactions.

Notes

Anation in Corrosion Processes

Anation reactions are very important to the corrosion processes, especially in passive oxide layer breakdown on metal surfaces. As an example, in the case of stainless steel exposed to chloride-containing environments, the pits of localized attack involve anation reactions, whereby chloride ions displace oxygen or hydroxide the ligands in the passive oxide layer, creating defects & initiating localized corrosion. Different metals & alloys have a tendency to pitting corrosion, given the kinetics of these anation reactions, and corrosion inhibitors usually act as preventing or retarding these reactions. Research on the factors influencing these anation processes has resulted in more corrosion-resistant alloys, more efficient corrosion inhibitors, etc.

Anation in Electrodeposition

Reactiom of the Anation reactions are directly make the electrodeposition it self would be during metal plating & electroplating as functional coatings. As the composition & structure of metal-ligand complexes in plating bath ultimately determine the quality & characteristics of electrodeposited coatings, it can be inferred that the equilibria & kinetics of anation reactions between metal ions and diverse the ligands impact the composition & structure of electrodeposited coatings. Nickel plating is an example wherein the formation of numerous nickel-ligand complexes through anation reactions affects the deposition rate, current efficiency, & characteristics of the deposited nickel. Additives such as brighteners used in plating baths typically work by altering these anation equilibria and kinetics. This knowledge has allowed the development of more efficient & environmentally friendly plating processes.

What is a Supramolecule?

Anation reactions have gained considerable attention in supramolecular chemistry to construct functional molecular assemblies & materials. This strategy has been widely employed for the assembly of metal-organic frameworks (MOFs) & coordination polymers via anation reactions between metal centers & coordinated solvent molecules or the ligands in a metal-ligand complex to afford coordination networks with extended structures.

Many molecular capsules, cages & containers also depend on anation reactions for their assembly & guest recognition characteristics. The results of these anation reactions govern the selectivity & the dynamics of these assemblies & uncovering these factors has led to more selective & responsive supramolecular systems.

Anation in environmental chemistry

Anation reactions are important for the speciation, mobility, & bioavailability of metal ions in natural waters & soils. As an example of specific issue: the fate & transport of toxic heavy metals, like cadmium, lead & mercury, in the environment is highly regulated by their anation reactions with different ligand ex. Likewise, the speciation of metal ions, which is controlled by anation equilibria & kinetics, determines neither their bioavailability nor their toxicity to aquatic organisms. Such processes are crucial for establishing the environmental fate & ecological impacts of metal pollutants & for developing effective remediation strategies.

Anation in Biological Systems

Nitrogenase reactions are abundant in living organ-isms, especially in metalloenzymes and other metalloproteins. The metal center of metalloenzymes can bind a diverse range of biological the ligands in anation reactions, resulting in changes in activity, selectivity, & regulation of these enzymes due to their dependence on metal coordination environments. An example is the importance of the coordination of oxygen to iron in the center of hemoglobin, which requires the loss of a water molecule. Like all other such zinc-dependent enzymes, anation reactions (i.e., the replacement of a coordinated water molecule in the first reaction step with substrate) will occur, setting up the catalytic steps that follow. Studying such biological anation processes has great potential to inspire design of novel & more selective metalloenzyme >> inhibitors in therapeutic applications but also reveal molecular insights into physiological & pathological processes.

Anation in Materials Science

Anation reactions have become widely applied in materials science for the synthesis & modification of functional materials. To illustrate, anion exchange reactions are employed to intercalate anions into layered double hydroxides (LDHs) to tailor the characteristics for the materials to be used in catalysis, drug delivery & remediation. Likewise, surface modification of metal oxides by anation reactions with different organic & inorganic the ligands are commonly applied to tune their characteristics for use in sensors, catalysts, & electronic devices. More efficient & selective processes rely on the kinetics & thermodynamics of the pertinent anation reactions, & an appreciate and comprehend ing of these factors has yielded more effective synthetic methods & more functional materials.

Notes

Towards the Future: Outlooks & Inequities

As much progress has been made in ourlation appreciate and comprehend ing of nation reactions, a few challenges & opportunities remain:

- Developing more streamlined computational approaches to predict the mechanisms and rates of anation reactions, especially in more complex systems featuring multiple metal centers & multidentate the ligands.
- appreciate and comprehend ing the role of solvent dynamics & hydrogen bonding in anation reactions including aqueous & mixed solvent systems.
- Spanning the effect of external stimuli (light, pressure, electric fields) on anation reactions & their use in variousexploitation systems.
- Metal-ligand interactions are fundamental in emerging fields including artificial photosynthesis, water splitting, & CO2 reduction, thus opening inventiveness for possible anation reactions with remarkable implications.

More selective & efficient anation based processes for recovery & recycling of critical metals from electronics & other secondary sources

Exploring the ternary reactions involved in production & transformation of metal containing nanoparticles & clusters & then use them to synthesize air-sensitive functional nanomaterials. Investigate the emergence of a nation of reactions as new all-map agents, especially for metal-reliant biology. With the continued development of experimental techniques, computational methods, & theoretical frameworks, it will be no surprising that this appreciate and comprehend ing of anation reactions & their applications will grow deeper than we can currently anticipate. This appreciate and comprehend ing will facilitate the development of more efficient & selective chemical reactions, effective therapeutic agents, delivering practical materials, which together will enhance the sustainable growth of the chemical, pharmaceutical & materials industries. To summarize, anation reactions are a fundamental type of ligand substitution process in coordination chemistry with applications in various areas of research

Notes

& industry. The mechanistic & kinetic appreciate and comprehend ing derived from these reactions have played a crucial role in our insights into chemical reactivity & have led to many industrials processes & technological applications. With time, our knowledge of reactions also advances, & we can look forward to more such creative applications & findings in the times to come.

PRACTICAL APPLICATIONS

Practical Applications of Metal Complex Reactivity in Everyday Life

Metal complex chemistry may appear esoteric & restricted to laboratory settings, however its principles substantially influence several facets of our everyday existence. The differentiation between inert & labile complexes directly affects the efficacy of numerous household items & medical therapies we routinely depend on. Reflect on the water you use daily; its purification frequently entails metal complexes that specifically adhere to pollutants. Water treatment facilities employ iron & aluminum complexes that establish labile bonds with contaminants, facilitating their effective removal by precipitation & filtering. The precise reactivity rates of these complexes dictate the speed & efficacy of drinking water purification. Activating your tap without apprehension regarding waterborne diseases is a result of meticulously engineered metal coordination chemistry functioning at an industrial level. The pharmaceuticals that numerous individuals consume daily exemplify a significant application of metal complex reactivity concepts. Platinum-based anticancer agents, such as cisplatin, operate effectively due to their optimal formation of inert & labile coordination bonds. In the circulation, these complexes exhibit reasonable stability; however, upon encountering cancer cells, ligand substitution processes transpire, facilitating the binding of platinum to DNA & inducing cell death. The efficacy of these life-saving therapies is directly contingent upon the regulation of substitution reaction kinetics. Likewise, gadolinium-based contrast agents utilized in MRI imaging depend on meticulously regulated ligand exchange rates to deliver diagnostic insights while reducing toxicity.

Even a seemingly trivial task such as laundering garments entails highly complicated chemistry. Numerous laundry detergents use sequestering agents that create compounds with calcium & magnesium ions present in hard water. These complexation reactions adhere to associative pathways, wherein water molecules in the coordination sphere of metal ions are substituted by chelating agents such as EDTA or citrates. In the absence of this mechanism, metal ions would precipitate with soap, resulting in the well-known "soap scum" that diminishes cleaning efficacy. The velocity of these substitution processes dictates the efficacy of your detergent in addressing hard water issues & effectively laundering your garments. The food you

Notes

ingest frequently derives advantages from regulated metal complex reactions. Food preservation sometimes depends on chelating chemicals that sequester metal ions, which would otherwise facilitate oxidation reactions resulting in spoiling. Upon opening a package of processed food that retains its color & flavor, you observe the outcomes of meticulously engineered ligand substitution processes that sequester pro-oxidant metals. The stability constants & reaction processes of these food-grade metal complexes significantly influence shelf life & food safety. In agriculture, the efficacy of fertilizers that cultivate our food relies on metal complex chemistry. Micronutrients such as iron, manganese, & zinc must be supplied to plants in absorbable forms. Contemporary fertilizers frequently incorporate these metals as complexes with diverse organic the ligands that experience regulated dissociative substitution in soil, releasing the vital metals at rates commensurate with plant absorption. The kinetics of these release systems dictate whether crops obtain consistent nutrition or undergo cycles of deficiency & toxicity.Our electronic devices also exemplify the uses of metal complex reactivity. The fabrication of integrated circuits entails multiple etching & deposition processes in which metal complexes are essential. Copper interconnects in computer chips are often deposited by procedures in which copper complexes are reduced while preserving particular coordination environments that affect the quality of the resultant metal layers. The mechanics of acid & base hydrolysis examined in inorganic chemistry directly influence the optimization of industrial processes for the electronics we utilize continuously.

Catalytic converters in our vehicles exemplify a significant application of metal complex chemistry in daily life. These devices depend on meticulously engineered complexes of platinum, palladium, & rhodium that enable the transformation of poisonous emissions into less deleterious compounds. The reaction mechanisms entail meticulously regulated ligand substitution procedures in which exhaust components substitute coordinated molecules on the catalyst surface. The distinction between successful & inefficient catalytic converters mostly hinges on the optimization of substitution reaction kinetics, which directly influences air quality in our communities.

Multiple-Choice Questions (MCQs)

1. Labile metal complexes are characterized by:

a) High activation energy & slow ligand exchange

b) Low activation energy & fast ligand exchange

Notes

c) High oxidation state & inert nature

d) Formation of highly stable chelates

2. The reaction coordinate diagram of a metal complex reaction shows:

a) The energy of reactants, intermediates, & products

b) The oxidation state changes of the metal

c) Only the activation energy of the reaction

d) The rate law of the reaction

3. In an associative (A) substitution mechanism, the reaction proceeds by:

a) Formation of a five-coordinate intermediate

b) Formation of a seven-coordinate intermediate

c) Direct dissociation of the leaving ligand

d) Electron transfer between metal ions

4. The dissociative (D) pathway in ligand substitution is characterized by:

a) Expansion of the coordination sphere

b) Loss of a ligand before the new ligand binds

c) Concerted ligand exchange

d) Outer-sphere electron transfer

5. Which of the following factors increases the rate of ligand substitution in an octahedral complex?

a) High oxidation state of the metal

b) Strong ligand field stabilization energy (LFSE)

c) Presence of a bulky incoming ligand

d) Low charge density on the metal ion

6. Acid hydrolysis of metal complexes involves:

a) Ligand replacement by OH^- ions

b) Protonation of coordinated the ligands leading to ligand loss

c) Formation of a metal-carbon bond

d) Electron transfer reactions

7. The conjugate base mechanism in base hydrolysis suggests that:

a) The metal-ligand bond is protonated before dissociation

b) The metal complex reacts with OH^- before ligand dissociation

c) The leaving ligand is stabilized by solvation

d) Hydroxide ions act as leaving groups

8. Anation reactions involve:

a) Substitution of a neutral ligand by an anionic ligand

b) Oxidation of metal complexes

c) Ligand protonation

d) Reduction of the metal ion

9. The rate of base hydrolysis of a metal complex is typically affected by:

a) The identity of the leaving ligand

b) The oxidation state of the metal

c) Solvent polarity

d) All of the above

10. Which of the following is an example of an anation reaction?

a) $[Co(H_2O)_6]^{3+} + Cl^- \rightarrow [CoCl(H_2O)_5]^{2+} + H_2O$

b) $[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-}$

c) $Cu^{2+} + NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$

d) $Pt^{2+} + CO \rightarrow [Pt(CO)_2]^{2+}$

Short Answer Questions

1. Define inert & labile metal complexes & provide examples.

2. What is the difference between intermediates & transition states in reaction mechanisms?

3. Describe the associative (A) & dissociative (D) mechanisms in octahedral substitution.

4. How does oxidation state affect the ligand substitution rate in metal complexes?

5. What is the mechanism of acid hydrolysis in transition metal complexes?

6. Explain the evidence supporting the conjugate base mechanism in base hydrolysis.

Notes

7. What factors influence the rate of base hydrolysis in metal complexes?

8. Define anation reactions & give an example of an industrial application.

9. Compare the kinetics of ligand substitution in square planar vs. octahedral complexes.

10. How does solvent polarity influence ligand substitution reactions?

Long Answer Questions

1. Explain the energy profile of ligand substitution reactions in metal complexes, including activation energy & reaction pathway.

2. Discuss the associative (A) & dissociative (D) mechanisms in detail, with examples of metal complexes following each mechanism.

3. Explain the factors affecting reaction rates in octahedral substitution, including steric, electronic, & solvent effects.

4. Describe the mechanism of acid hydrolysis, including key steps & influencing factors.

5. Discuss the conjugate base mechanism of base hydrolysis & provide supporting experimental evidence.

6. Compare the kinetics of ligand substitution in inert & labile complexes, with examples.

7. Explain anation reactions, their mechanism, & provide examples of industrial applications.

8. Describe the thermodynamic & kinetic factors that determine whether a complex will undergo an associative or dissociative pathway.

9. Compare ligand substitution rates in high-spin & low-spin complexes, explaining the role of LFSE.

10. How do experimental techniques such as UV-Vis spectroscopy & NMR help in studying metal complex reaction mechanisms?

MODULE -4

REACTION MECHANISMS OF TRANSITION METAL COMPLEXES – PART II

Objectives

- To comprehend the mechanics & dynamics of substitution processes in square planar metal complexes, focusing on the trans effect & its applications.
- To categorize & examine redox processes in metal complexes, emphasizing one-electron transfer mechanisms.
- Distinguish between outer-sphere & inner-sphere electron transfer reactions by elucidating their mechanisms & affecting factors.
- To present the Marcus-Hush theory of electron transport, addressing its principles, cross-reactions, & kinetic ramifications.

Unit 15 Substitution Reactions in Square Planar Complexes

Square planar complexes are an interesting class of coordination complexes known for their unique substitution pathway. These complexes, which are formed by d8 metal ions like Pt(II), Pd(II), Au(III), Rh(I), & Ir(I), have substitution reactions that are mechanistically & kinetically distinct from their octahedral analogs. The square planar environment with vacant sites available at the axial coordination generates a milieu prone to nucleophilic attack, thus initiating displacement processes that have been the subject of numerous studies with applications in diverse fields from catalysis to medicinal chemistry [abstract omitted]; however, so far this chemistry had never been investigated for THPTA & its close derivatives.

Mechanisms & Kinetics

In a striking departure from the dissociative pathways present in octahedral complexes, substitution reactions in square planar complexes predominantly follow an associative mechanism. This essential difference stems from the electronic distribution & geometrical approachability of the metal dosage form. For example, when treating the reaction of square planar complex $[MA_3X]$ with entering group Y the reaction generally proceeds through a trigonal bipyramidal transition state or intermediate, & the rate-determining step in the reaction is the production of this five-coordinate species not the breaking of metal-leaving group however. These substitutions display second-order rate laws in their kinetic profile, with the rate being directly proportional to both the concentration of the complex & the buried nucleophile. The general equation of rate can be written as:

Notes

$$Rate = k_2MA_3X$$

That is consistent with the associative nature of the mechanism because bond formation with the entering group occurs before bond breaking with the leaving group. But a broader kinetic analysis highlights a more intricate picture. In a number of systems, especially for coordinatively competent solvents, the law observed has the form:

$$Rate = (k_1 + k_2[Y])[MA_3X]$$

This second term rate law describes a concerted two pathway model where k_1 is a solvent coordinated mechanism (solvolysis) & $k_2[Y]$ the direct attack by Y. The solvent pathway involves the initial coordination of a solvent molecule which is then followed by its displacement in a subsequent step by the entering group Y. In strongly coordinating solvents—water or methanol, for example—this solvent participation is particularly impactful. For square planar substitution reactions, the energy profile presents a significantly different pathway than for octahedral complexes. Their lower activation energy makes the associative pathway more favorable, thus the tendency for square planar complexes to undergo substitution more easily than octahedral ones with the same metal center. In the associative mechanism, the entering group forms a bond to the transition state, resulting in a build-up of partial negative charge that can be stabilized by placement of electron-withdrawing groups on the metal complex (or other means for stabilization).

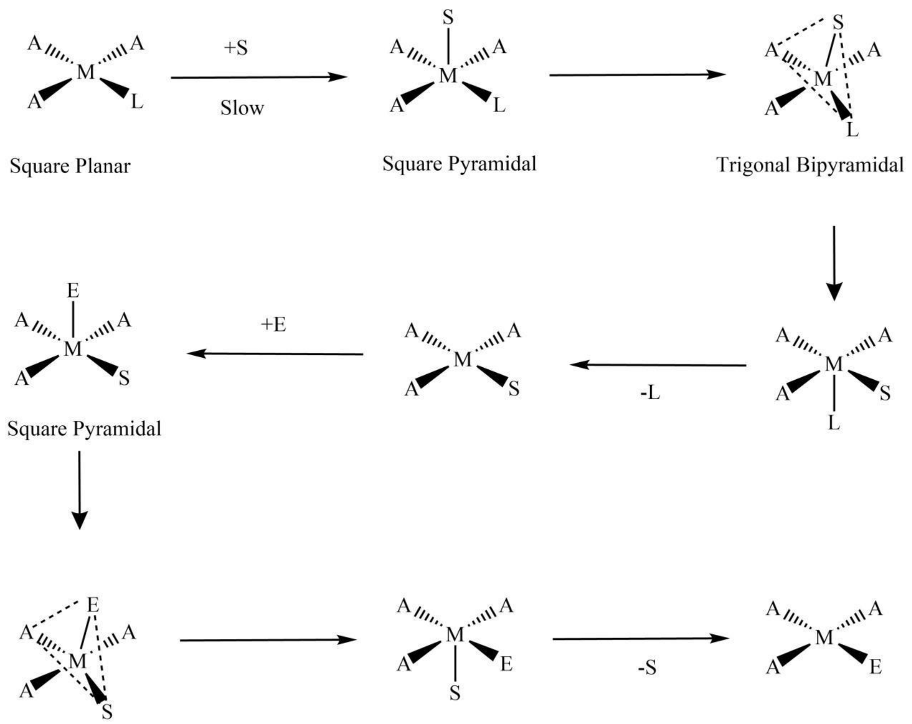


Figure - The systematic mechanism of solvent-assisted ligand displacement reactions in square planar complexes.

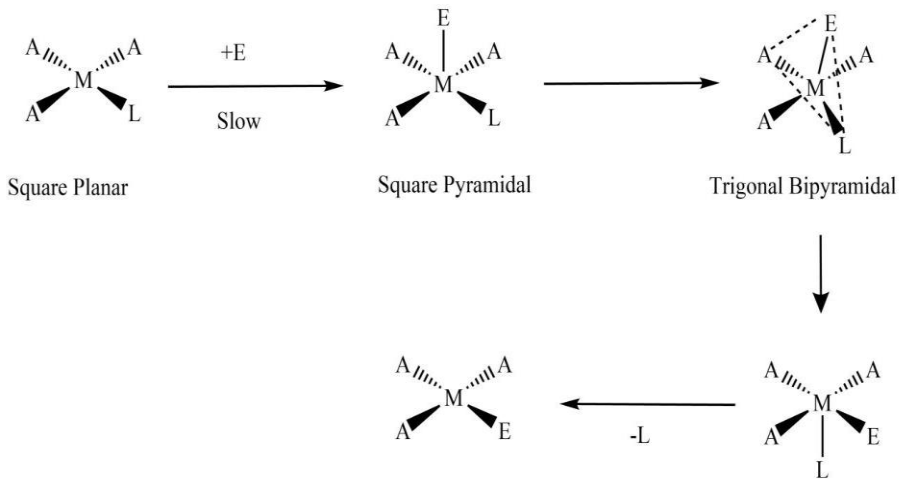


Figure- Mechanism of ligand displacement in square planar complexes via normal associative pathway.

Dissemination of these substitutions is affected by a number of factors. The identity of the metal center is the most important determinant, with general reactivity trends for similar complexes observed to be of the form Ni(II) > Pd(II) > Pt(II) following the trends of the decreasing size & increasing effective nuclear charge. This ordering corresponds to a Δk of $\sim 10^5$ between Ni(II) & Pt(II) complexes. The electronic characteristics of the non-involved the ligands play a profound role in influencing the rates of the reaction as well. Typically, this leads to greater electrophilicity of the metal center, which promotes the reactivity towards nucleophiles to undergo substitution reactions & faster trans-substitution reaction rates. The entering groups determine microkinetic details that can strongly influence the reaction kinetics. Soft donor atoms, such as phosphines & thioethers, are particularly good nucleophiles. In fact, the reactivity of nucleophiles with square planar complexes is greatly enhanced for nucleophiles bearing soft donor atoms & for square planar complexes that contain soft metal centers (Pt(II)). This preference is consistent with the hard & soft acids & bases (HSAB) theory, which postulates that soft-soft interactions are energetically favorable. The generalized order of nucleophilicity for different entering groups toward Pt(II) complexes is:

$$Br > I > SCN > Cl > R_3P > NH_3 > H_2O$$

This is directly opposite the trend seen for nucleophilicity in organic chemistry, & reflects the unusual electronic effects present in transition metal complexes. The lability of the leaving group also affects reaction rates, as weaker bonds between the metal and its the ligands lead to facile substitution. Lability of the leaving group for Pt(II) complexes is thus typically:

$$NO_2^- > SCN^- > I^- > Br^- > Cl^- > H_2O > NH_3$$

Notes

This order is dictated by thermodynamic & kinetic elements such as bond strength, sterics, and transition state stabilization. Another source of complexity is the steric environment around the metal center. Large the ligands can slow down the rates of substitution by preventing access of the entering group to the metal center, increasing the activation energy for the appearance of the trigonal bipyramidal transition state. This steric effect is also very pronounced in complexes with chelating the ligands or sterically demanding substituents. So, solvent effects are seen in more than one way in square planar substitutions. In addition to participating in the reaction mechanism, solvents affect reaction rates from their ability to stabilize or destabilize reactants, transition states & products. These reactions are often facilitated by polar solvents that stabilize the charged transition state, & the presence of coordinating solvents may not only buffer the charges but also compete with the entering group, complicating the kinetics.

Temperature dependence studies of these reactions have provided valuable thermodynamic parameters. $\Delta H^‡$ For square planar substitutions varies from about 60 to 120 kJ/mol, with $\Delta S^‡$ values correspondingly negative, very much as expected for the associative mechanism, which reduces the translational degrees of freedom in the transition-state. These parameters were critical for revealing the reaction energetics as well as the subtle mechanistic insights. Further mechanistic studies, especially those that utilize isotope effects & pressure studies, have helped to cement our appreciate and comprehend ing of square planar substitutions. Pressure effects wherein acceleration of these reactions are observed is typically because of the associative mechanism where the transition state has a smaller volume compared to the substrates, & this has been experimentally confirmed after theoretical predictions. Studying the isotope effect, & especially with ^{15}N-labeled ammonia the ligands, has been useful in assessing the extent of bond formation & breaking present in the transition state, supporting the argument for an associative mechanism. Contemporary computational methods have greatly improved our mechanistic insights. Using DFT calculations, detailed information about the reaction coordinate has been mapped including transition state geometries, energy barriers & electronic redistribution patterns that would not be easily obtainable by experimental techniques alone. These computational studies have typically supported the associative approach but have exposed subtle features concerning the contribution of ligand-metal orbital interactions in controlling reactivity landscapes.

What is the Trans Effect?

One of the more interesting aspects of square planar substitution chemistry is the trans effect, a kinetic phenomenon with major implications for both synthetic strategy as well as mechanistic insight. The trans effect describes the ability of coordinated ligand to preferentially labilize the group trans positioned relative to it in a square planar complex directing site of subsequent substitution. This effect is observed as a faster substitution for the ligand located trans to certain directing groups, & can be harnessed as a powerful means for regioselective synthesis of square planar complexes.

Notes

Trans effects follow a well-established hierarchy of increasing strength:

F^-, H_2O, OH^- < NH_3 < py < Cl^- < Br^- < I^-, SCN^-, NO_2^- < CH_3^- < CO, CN^-, C_2H_4 < H^-, PR_3

This ordering shows that π-acidic the ligands (e.g. CO & CN^-) & strong σ-donors (e.g. H^- & phosphines) generally generate the largest trans effects. The difference between trans effect (a kinetic effect) & trans influence (a ground state thermodynamic effect that weakens the bond trans to a given ligand) is instrumental in appreciate and comprehend ing square planar reactivity fully. Although these phenomena are often correlated, their mechanistic origins & manifestations can be quite different. Three different theoretical arguments describe the trans effect, but the most accepted ones are the σ-trans effect & the π-trans effect. Pi-acentric σ-trans effect refers to the polarization of charge density in the metal-ligand σ-bonding framework. Such a strong σ-donor ligand donates electron density to the metal, which subsequently redistributes the accumulated electron density preferentially along the trans direction, weakening the trans metal-ligand bond, making it more vulnerable to substitution. The polarization effect argues that strong σ-donors such as H^- & phosphines have strong trans-issues, which could explain why they tend to give them.

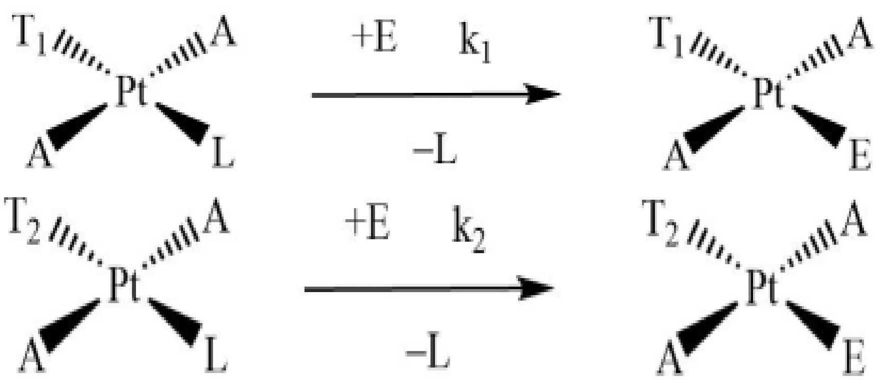


Figure- Kinetic trans-effect in action with k2 >> k1 showing that T2 ligand is having greater trans-effect strength than T1.

The π-trans effect—most pronounced for π-acidic the ligands like CO & CN^- themselves—has a different origin. These the ligands take free electron density from occupied metal d-orbitals in the form of π-

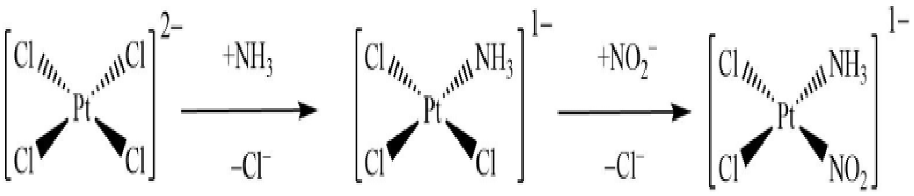
Notes

backbonding, lowering electron density in the metal d-orbital that is populating bonding with the trans ligand. Such depletion weakens the trans bond & allows for its easier substitution. Later theoretical analyses have suggested the trans effect is also a consequence of stabilisation of the trigonal bipyramidal transition state, with the trans-directing ligand taking up equatorial positions in this geometry to lower the activation energy for substitution of the trans group even further. The trans effect is of immense synthetic utility. It gives a comparison of ligand combinations in the assembly of square planar complexes & allows for their regioselective synthesis. For example, the synthesis of cisplatin, $[Pt(NH_3)_2Cl_2]$, harnesses the trans effect using a strategically designed synthetic sequence. Since $K_2[PtCl_4]$ is symmetric, the first ammonia substitution can take place at any location. But the second ammonia will preferentially occupy the trans position relative to a chloride rather than (seat) trans to the first ammonia, because chloride has a greater trans effect than ammonia. This makes the selectivity give predominantly the cis isomer, which exhibits the important biological activity lost in the trans configuration.

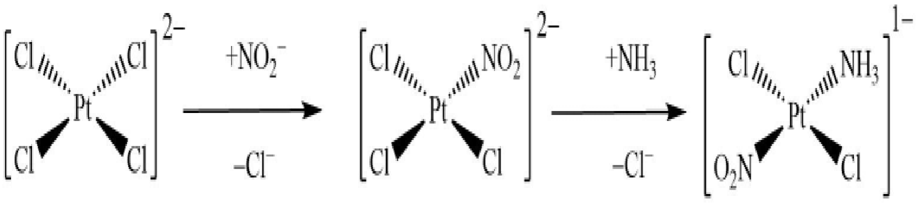
More involved synthetic methods use the trans effect to build intricate architectures with defined arrangements of the ligands. As an illustration, the precise addition of the ligands can be mediated in the synthesis of $[Pt(NH_3)(py)(Cl)(NO_2)]$, where py is pyridine, through the use of the hierarchy of trans effects. Introducing the ligands that exert strong trans effects early in the synthetic sequence allows chemists to focus on substitution at specific positions for regioselectivity that would be difficult or near impossible due to other factors in the system. In addition to being synthetic applications, the trans effect offers mechanistic insights. Observing which ligand is substituted in a specific complex can provide insight into relative trans effects of different the ligands, allowing for further refinement & extension of the known trans effect series. However, mechanistic studies of this type have been especially informative toward elucidating catalytic cycles involving square planar intermediates, in which differences in ligand exchange rate are sometimes a key determinant of catalytic efficiency & selectivity.

Synthesis of the isomers of [Pt(NH3)(NO2)Cl2]1–:

The trans-effect order of the three groups in [Pt(NH3)(NO2)Cl2]1– complex is NO – > Cl– > NH3.



(a)



(b)

Figure - Synthesis route for (a) cis-[Pt(NH$_3$)(NO$_2$)Cl$_2$]1– and trans-[Pt(NH$_3$)(NO$_2$)Cl$_2$]1– complexes.

The trans effect is also significant in computational chemistry, acting as a benchmark for testing theoretical methods. Making a quantitative calculation of trans effect magnitudes is a challenging test for electronic structure calculations, as it involves capturing both σ & π bonding components accurately, which can only be achieved with computational methods. Theoretical investigations have also advanced our appreciate and comprehend ing of the orbital interactions at play in the trans effect, elucidating this fundamental concept in coordination chemistry. In biological systems, & specifically in platinum-based anticancer drugs, the trans effect is critically important in shaping their reactivity profiles with biological nucleophiles such as DNA & proteins. The anticancer activity of cisplatin is due to aquation reactions (the substitution of the chloride by water) & subsequent coordination to DNA, mainly at guanine N7 sites. These substitution kinetics, which are affected by the trans effect, dictate the pharmacokinetic profile of the drug and, eventually, its therapeutic efficacy. Knowledge of these mechanisms has inspired the design of second- & third-generation platinum-based anticancer drugs with more favorable preclinical profiles. As we will summarize here, the trans effect has also been leveraged in catalyst design, particularly in homogeneous catalysis, where square planar complexes are catalysts or catalytic intermediates. In the case of Pd-catalyzed cross-coupling

Notes

reactions, for example, the reductive elimination step can be associated with a square planar intermediate in which the trans influence can impact the rate and selectivity of the process. Catalyst design strategies often take advantage of these effects to increase performance, where the ligands are chosen not only for their electronic & steric characteristics but also for their trans-directing ability.

In recent years, the trans effect has been exploited in dynamic combinatorial chemistry to generate adaptive coordination systems. These systems reorganize upon exposure to environmental cues, where the trans effect directs the course of reorganization to thermodynamically preferred states. Such systems are promising for applications from tunable materials to selective sensing platforms. Trans effect can also be seen in the field of surface chemistry in the adsorption & reaction of the molecules on different metal surfaces. Similar to molecular complexes, trans-directing characteristics arise for surface-bound species, influencing the adsorption energetics & reactivity of nearby sites. These surface trans effects are critical for heterogeneous catalysis & materials science, connecting molecular coordination chemistry to surface phenomena. Considerations of the trans effect in coordination science have been complemented by a considerable body of work on hemilability & chelate effects, leading to increasingly sophisticated molecular architectures with tuned characteristics. Collective aspects of these principles may dictate the design of metal complexes for small molecule activation or molecular recognition and sensing applications.

Even in octahedral & tetrahedral geometry, the trans effect is present, albeit with lower intensity & different selectivity patterns. These discoveries have generalized the conceptual context of directed substitution in coordination complexes, indicating general rules beyond their particular geometries. Thus, square planar complex substitution reactions return a highly multifaceted realm in inorganic chemistry, boasting unique mechanistic routes & kinetics. In contrast to substitutions in other coordination geometries, such as octahedral & tetrahedral, the associative mechanism which these systems conform to indicates the peculiar electronic & steric environment governing the square planar arrangement. The trans effect, which has such a strong influence over substitution regioselectivity, illustrates the overall paradigm for harnessing fundamental mechanistic principles to regain synthetic control, a potential to inform chemical design as well.

These reactions are still the subject of investigations that provide insight with implications throughout the subdisciplines of chemistry ranging from basic coordination chemistry to applied fields such as catalysis, materials science, & medicinal chemistry. Increased characterization of square planar substitutions will occur as analytical techniques improve, as this type of substitution continues to add utility to chemical synthesis & technology. The relevance of coordination chemistry in diverse scientific spheres is illustrated by how experimental findingsalign with theoretical models andguids practical applications. The rich mechanistic detail & utility of square planar substitution chemistry speaks compellingly to the intellectual & practical rigor of inorganic reaction mechanisms.

Unit 16 Redox Reactions in Metal Complexes

Classification of Redox Reactions

Metal complex redox reactions are a cornerstone of coordination chemistry, with far-reaching consequences for catalysis, biological processes, & materials science. These reactions comprise metal centers & the ligands exchanging electrons and altering oxidation states. There are different views on how redox problems in metal complexes can be classified, including different perspectives on mechanisms and of reactivity patterns. One of the fundamental classification schemes for redox reactions of metal complexes is based in the inner-sphere & outer-sphere electron transfer mechanisms. Mechanisms that include inner-sphere processes include generation of a bridged intermediate formed by the oxidant & reductant, where the electron is transferred through a ligand that connects the two metal centers. In this role, the bridging ligand acts as a channel for the electron transfer, leading to greater overlap of the orbitals, & ultimately, higher electron transfer rates. It is fully a view which conjugation, analogous to the bound urban of chlorine on mixed-complex precursor phases, fully extends to solvate frames across cooperative metal–metal links. Outer-sphere mechanisms, in contrast, are not dependent on bridged intermediate formation. Instead, the metal centers conduct the charge directly with minimal coordination-sphere reorganization. These reactions are common between complexes with stable coordinate geometries & they often happen with electron transfer both, via space or through mechanism of weak electronic coupling. Both theory & practice have evolved to vigorously discuss outer-sphere electron transfer in terms of the Marcus theory that incorporates the concept of a reaction barrier in terms of reorganization energy, & whether the reaction is optimized on a thermodynamic driving force scale. Complementary electron transfer (CET) & non-complementary electron transfer (NCET) form yet another classification scheme based on whether electron flow is directional or multidirectional. CET is described as the transfer of an electron from a filled orbital of the reductant to an empty orbital of the oxidant of similar symmetry characteristics, enabling good orbital overlap & efficient electron transfer. NCET, in contrast, is mediated by electron transfer between orbitals having different symmetry characteristics, leading to slower rates due to poor overlap between the orbitals. This delineation emphasizes the role of orbital symmetry & electronic structure in characterizing the kinetics of ET reactions.

Notes

Depending on the type of electron transfer, the redox reactions in metal complexes can also be categorized into homogeneous & heterogeneous. In solution, both the oxidant & reductant are typically in the same phase, & this is called homogeneous electron transfer. These reactions are largely characterized by well-known kinetic models that follow a predictable rate law. These include heterogeneous electron transfer, where the reactants are in two different phases, for instance an electron transfer event between a solution-phase species & an electrode surface. Other factors affect these reaction including surface modify, adsorption, and electrical double-layer effect. Second, the the ligands participate in the redox process, & this gives rise to a second classification of metal versus ligand-centered redox reactions. Redox reactions centered on a metal pertain to the oxidation state transition of the metal center with retaining the coordination environment. The reactions are prevalent in transition metal complexes with stable the ligands and are usually associated with large modulations of electronic & magnetic behavior. Ligand-centered redox processes, on the other hand, transfer an electron to or from the ligand, without changing the formal oxidation state of the metal. Such reactions are common in the complexes with redox-active or so-called non-innocent the ligands, such as quinones, dithiolenes & some nitrogen-containing heterocycles. Ligand-centered redox processes are key to biological electron transfer chains & to the design of molecular switches & sensors. Another classification scheme is to categorize redox reactions with respect to the number of electrons transferred. These transformations are commonly mediated by radical intermediates that can be probed by electron paramagnetic resonance (EPR) spectroscopy. Two-electron transfer reactions—the concerted or sequential transfer of two electrons—are common in complexes of metals with accessible multiple oxidation states, especially copper & iron. Multi-electron transfer reactions, where three or more electrons are transferred, are less common but are important in some catalytic processes like nitrogen fixation or water oxidation.

One-Electron Transfer Reactions Mechanism

One-electron transfer reactions are the most apparent type of redox process in metal complexes; however, they are surprisingly complicated in mechanistic details. To comprehend these mechanisms, one must take into account thermodynamic, kinetic, & structural factors, in addition to the implementation of several theoretical frameworks & experimental techniques. Rudolph A. Marcus' theory for outer-sphere one-electron transfer based on Marcus theory. This theory states that the rate of electron transfer is controlled by 3 major parameters, these being the thermodynamic driving force ($\Delta G°$), the reorganization energy (λ) & the electronic coupling between the donor & acceptor (HAB). The reorganization energy is the energy needed to distort the nuclear configurations of the reactants to fit the configurations of the products without transferring any electron. This parameter captures variations in inner-sphere (bond lengths & angles) & outer-sphere (solvent) coordinates. The Marcus theory is then used to relate these parameters to the various factors that govern the electron transfer characteristics of the multiple component polymer matrix. The reaction rate as a function of driving force exhibits a parabolic relationship, which resulted in the counterintuitive prediction of an "inverted region" in which increasing driving force results in a slower reaction. This phenomenon, experimentally confirmed decades after its theoretical inception, has important ramifications for designing efficient electron transfer systems, in artificial photosynthesis & other energy conversion systems. The electronic coupling term (HAB) accounts for the extent of overlap between donor & acceptor orbitals, & is dependent on the distance between the reactants, on the characteristics of the intervening medium, & on symmetry characteristics of the relevant orbits. For outer-sphere reactions, this coupling generally decreases exponentially with distance according to the relationship $HAB \propto e - \beta R$, where β is the medium-dependent attenuation factor.

Inner-sphere one-electron transfer mechanisms result in a more intimate approach of the reactants' coordination spheres, as can be mediated by, for example, a bridging ligand. These mechanisms progress via three distinct steps: (1) a precursor complex is formed in which the oxidant & reductant associate through weak interactions; (2) a bridged intermediate forms where a ligand from one complex forms a bond to the other metal center; (3) electron transfer through the bridging ligand; (4) reorganization of the bridged complex to accommodate the new electron distribution, & (5) the dissociation of the successor complex into separate products. In addition, the bridging ligand can facilitate electron transfer by supporting electronic coupling between the reactants with the pathway being much more effective than that of outer-sphere mechanisms. The bridging the ligands can be halides, hydroxide, cyanide, or other anionic the ligands that can coordinate to both metal centers at the same time. Differentiating between inner-sphere and outer-sphere mechanisms can be done experimentally by a range of different techniques. Detailed kinetic studies are informative since inner-sphere mechanisms commonly show more complex rate laws due to the intermediacy of the bridged intermediate. The statistical analysis is complemented by stereochemical evidence as inner-sphere mechanisms often generate transfer of the ligand or stereochemical changes on the metal centers. Transient intermediates characteristic of inner-sphere pathways are detectable by spectroscopic techniques including time-resolved spectroscopy. Moreover, distinguishing between these mechanisms can be achieved through effects of systematic ligand variations on reaction

Notes

rates, since the identity & characteristics of the bridging ligand are critical to inner-sphere rates, while they influence outer-sphere processes far less.

Solvent effects are important in the one-electron transfer of metal complexes. In outer-sphere mechanisms, the solvent reorganization contribution to the total reorganization energy may dominate, especially for complexes with rigid coordination geometries. The dielectric constant of the solvent modifies the stabilization of charge-separated states, which in turn affects the thermodynamics & kinetics of electron transfer. Organized structures in solvents can be formed that promote or inhibit electron transfer due to hydrogen bonding & specific solvent-solute interactions. In protic solvents, proton coupled electron transfer (PCET) mechanisms can become important, where one transfers electrons along with protons to yield more nuanced kinetic behavior & solvent isotope effects. In one-electron transfer reactions, the thermodynamic driving force modulates kinetics according to Marcus theory relationships. For small driving force reactions ($|\Delta G°|\ \lambda$), higher driving forces decrease reaction rates thanks to an activation barrier related to the (re)organization of nuclear coordinates. This surprising behavior has been experimentally demonstrated for a variety of systems including intramolecular electron transfer in donor-bridge-acceptor molecules & electron transfer quenching of excited states. The temperature dependence studies give useful information about the activation parameters for the one-electron transfer reactions. Both Arrhenius & Eyring analyses of temperature-dependent rate constants yield activation energies, entropies, & volumes that are directly related to the reorganization energy & mechanism of reaction. Such processes usually have positive activation energies, which is consistent with the energy needed to reorganize the nuclear coordinates. Activation entropies assist in appreciate and comprehend ing whether the system tends to order/disorder in the formation of the transition state. Negative activation entropies imply increased ordering in the transition state, which is typical either in the context of a bridged intermediate through an inner-sphere mechanism or due to significant solvent reorganization. The activation volumes which are determined from pressure dependence studies can differentiate between mechanisms that exhibit large (significant structural change) & small (minimal structural reorganization) activation volumes.

The presence of multiple metal centers having redox potential complicates the mechanism of electron transfer in polynuclear complexes. These systems can display cooperative effects, such that electron transfer at one center alters the redox behavior of another center via electronic coupling or an altered geometrical arrangement. Mixed-valence compounds, in which their metal centers are at

Notes

different oxidation states, are excellent models for studying intramolecular electron transfer phenomena. These complexes are further classified using the Robin-Day scheme, where Class I compounds have no electronic coupling between the various metal centers, Class II compounds exhibit moderate coupling resulting in partial delocalization of the electron, & Class III compounds show strong coupling and, hence, complete delocalization & averaging of oxidation states. Spectroscopic methods, & in particular intervalence charge transfer (IVCT) spectroscopy, affords experimental tools to differentiate between these classes & to quantify the extent of electron coupling. Another significant class of one-electron transfer reactions involves metal-ligand electron transfer. For instance, these processes interface electron transfer at the metal center with a coordinating ligand as opposed to between two metal centers. This kind of electron transfer is especially significant for complexes with redox-active or "non-innocent" the ligands, including quinones, semiquinones, dithiolenes, & nitrogen-containing heterocycles. Ligand-centered radicals generated through metal-ligand electron transfer possess unique spectroscopic signatures & reactivity profiles. These processes can be understood within the framework of frontier molecular orbital theory, which highlights the relative energies of the metal d orbitals & ligand π^* orbitals. Strong mixing takes place when the energy of these orbitals are comparable by producing molecular orbitals which have significant contributions from both metal & ligand. This orbital mixing can obscure the distinction between metal-centered & ligand-centered redox processes & can introduce ambiguities in the assignment of formal oxidation states.

For redox reactions, coordination unsaturation opens up more mechanistic pathways for electron transfer reactions. In these instances, electron transfer may be coupled to ligand binding or dissociation events. For example, before electron transfer, a reductant can coordinate to a free site at the oxidant, or electron transfer can lead to ligand dissociation, owing to the metallacycle through bond reorganization of the metal's electronic configuration and binding preferences. These processes are particularly relevant for many catalytic cycles involving redox-active metal complexes, where such coordination unsaturation is frequently necessary for substrate activation. Electron transfer coupled to ligand exchange processes can be kinetically complex & may necessitate more advanced analytical approaches to elucidate mechanism. These include effects of quantum mechanics such as tunneling & non-adiabatic processes which are important for some of the one-electron transfer reactions. At low temperatures or for systems with weak electronic coupling a quantum mechanical process known as electron tunneling can dominate where the electron transfers by virtue of tunneling through a potential energy barrier rather than above it. This results in reaction rates that are

Notes

temperature-independent, or show only weak temperature dependence at low temperatures. However, when the electronic coupling between donor & acceptor is weak, the probability of electron transfer is low even if the nuclear configurations (i.e., the relative positions) are favorable, which is known as non-adiabatic electron transfer. These quantum effects become particularly relevant for long-distance electron transfer in biological systems & in some inorganic systems with rigid structures that avoid close approach of the redox centers.

Advances in experimental techniques to investigate one-electron transfer pathways have become more sophisticated, yielding progressively greater details of these processes. Reactions on millisecond to nanosecond timescales can be probed using stopped-flow & flash photolysis techniques to detect transient intermediates & measure elementary rate constants. In this method, reactive species are formed through radiolytic reduction or oxidation, allowing the examination of the reactions that are challenging to trigger with traditional approaches. Electrochemical techniques (cyclic voltammetry & spectroelectrochemistry) yield information on the thermodynamics & kinetics of electron transfer processes at electrode interfaces. Advanced spectroscopic techniques including time-resolved absorption & emission spectroscopy, electron paramagnetic resonance (EPR), & Mössbauer spectroscopy provide fine details regarding the electronic structures of reactants, products, & intermediates. Ultrafast spectroscopic techniques have also now made it possible to observe electron transfer at femtosecond timescales that allow us to glean previously hidden details of these processes. Computational techniques are now essential tools for the study of one-electron transfer mechanisms. Metal complexes' electronic structures, redox potentials, & reorganization energies were obtained from density functional theory (DFT) calculations. Our molecular dynamics simulations shed light on solvent dynamics and conformation changes along the path to electron transfer. Combined quantum mechanical/molecular mechanical (QM/MM) methodologies facilitate accurate handling of the immediate environment of the redox centers while including the influence of the extended system. These computational techniques supplement experimental studies, & are often able to access aspects of the reaction mechanism not readily probed experimentally.

One-electron transfer reactions in metal complexes have applications in a variety of fields. In biological systems, electron transfer chains in e.g. respiration & photosynthesis consist of sequential one-electron transfer events between metalloproteins. These mechanisms are relevant to developing artificial photosynthetic systems & bioelectronic devices. One-electron transfer processes often initiate or terminate catalytic cycles in homogeneous catalysis, impacting both activity & selectivity. Kinetics & thermodynamics of electron transfer in the design of efficient catalysts For example, one-electron transfer reactions play a fundamental role in how electroactive materials operate, such as those used in electrochemical batteries, supercapacitors, & electrochromic devices. The principles of electron transfer also guide efforts to create molecular electronics, which use the electrons in single molecules as parts of electronic circuits. The leading research frontiers into the one-electron transfer mechanisms involve to a significant degree the investigation of processes that entail coupling electron & proton transfer (PCET), which are of fundamental importance in myriad biological & catalytic processes. These processes then couple electron transfer with proton transfer to avoid these high-energy intermediates, leading to better energetics. An additional area of activity is the study of ultrafast electron transfer reactions using high-time resolution spectroscopy methods, which sheds light on the initial steps in these reactions. These theoretical approaches, including quantum mechanical effects & explicit treatment of the environment, are being further developed to quantitatively predict electron transfer rates & mechanisms. Moreover, using these fundamental principles to inform the design of improved catalysts, energy conversion devices, & molecular devices remains an active challenge at the boundary between basic & applied research.

Feature Article One-electron transfer reactions: from fundamentals to materials and biology. These reactions may occur along inner-sphere or outer-sphere pathways, with the involvement of different levels of electronic coupling & nuclear (re)organization. The concept of electron transfer as referenced by the Marcus theory underpins many of these processes, encapsulating thermodynamic driving force, reorganization energy, & electronic coupling. From traditional kinetic approaches to state-of-the-art experimental spectroscopic & computational methods, new tools and techniques are advancing our appreciate and comprehend ing of these fundamental processes. With further development of kinetic & thermodynamic theories as well as experimental techniques, the appreciate and comprehend ing of one-electron transfer reactions & their unique kinetics will clearly spark new applications in energy transfer/catalysis, electrochemical energy conversion, & molecular electronics, among others, solving challenges for the society.

Unit 16 Outer-Sphere & Inner-Sphere Reactions

Electron transfer processes in coordination compounds are proposed to follow one of two mechanistic pathways: outer-sphere reactions or inner-sphere reactions. These mechanisms differ drastically in the electron transfer, & the extent of coupling between the coordination spheres of the re-, & the charge-transfer (or red) state, following the approach & how fast the interaction occurs, & are known as electron hopping or electrostatic attractionhicht to their red state scientists are

Notes

still studying the rate where electrons can intercalate between metal centers. These mechanisms are key to appreciate and comprehend ing both the kinetics, thermodynamics, & stereochemical outcome of redox reactions involving transition metal complexes.

Outer-Sphere Reaction Mechanism

Outer-sphere electron transfer reactions are among the simplest, yet most elegant mechanisms in coordination chemistry. In these reactions, electron transfer between two reactants occurs with little change in their primary coordination spheres during the course of the reaction. Even in this afterstate, the donor & acceptor complexes retain their structural identity, & their binding the ligands are unchanged from the reaction. Outer-sphere mechanisms are characterized by little to no orbital overlap between the reactants, with the electron needing to tunnel through space from one metal center to another, above a barrier generated by the surrounding the ligands. Specifically, Marcus receive the Nobel Prize in Chemistry in 1992 for his pioneering work that lays the theoretic foundation of external sphere electron transfer. However, the Marcus theory establishes a quantitative relationship between the reaction rate of electron transfer and the thermodynamic driving force of the reaction. The theory depicts the reaction coordinate in terms of rearrangement of the reactants & of surrounding solvation molecules to settings that favor attempts to transfer electrons. This reorganization is necessary because the electron transfer must follow the Franck-Condon principle, which states that electronic transitions happen without adjusting the positions of the atomic nuclei. The outer-sphere mechanism is usually stepwise in nature. Imports come together in solution to form a precursor complex. This stabilization of the complex occurs via weak intermolecular forces that includes hydrogen bonding, van der Waals interactions, or electrostatic attractions, based on the nature of the ligands & the overall charges of the complexes. In this precursor complex, the electron donor & acceptor are located within a distance at which electron transfer is probable, usually 10-20 Å.

The electron transfer event itself is the rate-determining step in the majority of outer-sphere reactions. The rate of this step depends on multiple factors, such as the reorganization energy, the free energy change of the reaction, and the electronic coupling of donor & acceptor. Reorganization energy is the energy needed to push the reactants & surrounding solvent molecules away from their equilibrium positions into the positions needed for electron transfer. This parameter is especially relevant, as it includes the contributions from both the inner-sphere reorganization (the changes in bond lengths/angles within the coordination spheres) & the outer-sphere reorganization (the rearrangement of solvent molecules). After electron transfer, the precursor complex dissociates to form the products, which then relax to their new equilibrium structures. The Marcus equation relates the overall reaction rate of an outer-sphere electron transfer reaction to the rate constant for the transfer event, & through ΔGet, λ, & Hm for the reacting species, all of which can be computed. Because of this, there is actually what Marcus theory calls an "inverted region", where above a critical driving force, increasing that driving force results in decreasing reaction rates. The true shape of this dependency, a counterintuitive prediction that has been proved experimentally, reflects the complexity of electron transfer processes.

Notes

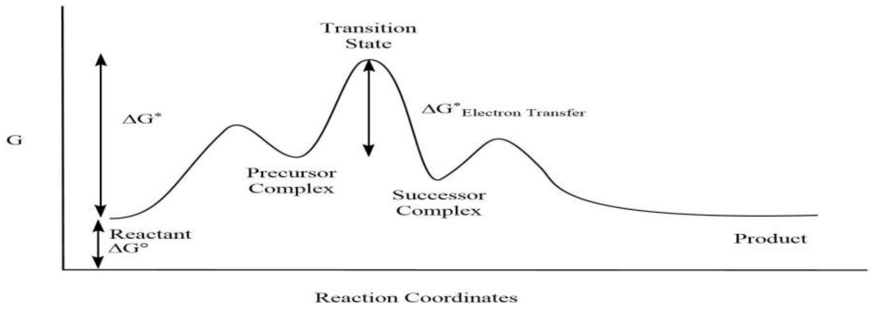


Figure - The general reaction coordinate diagram for the mechanism involved outer-sphere electron transfer reactions.

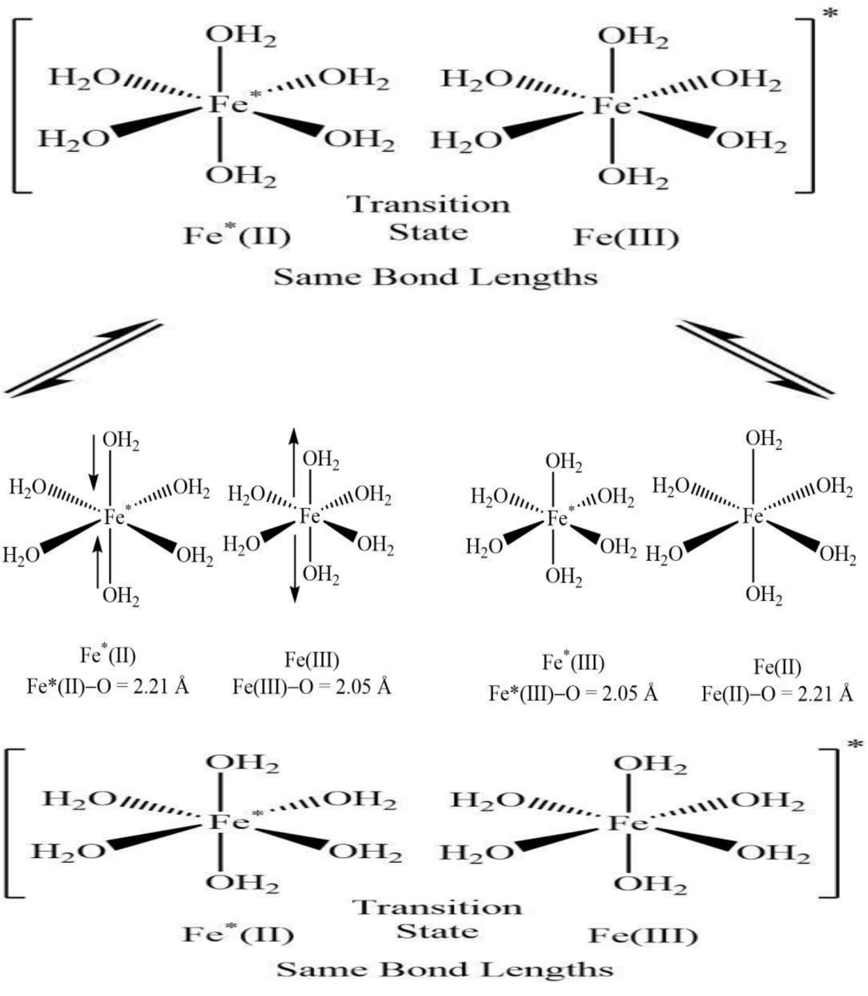


Figure- Formation of (a) internal reorganization and (b) corresponding ligand field splitting.

Outer-sphere mechanisms are then often found in reactions of complexes with stable coordination spheres, especially those with full d-electron shells or strong field the ligands which produces kinetically inert complexes. A staple of electrochemical studies are the transfer of electrons between hexacyanoferrate(II) & hexacyanoferrate(III) ions, as well as the reduction of tris(bipyridine)ruthenium(III) by an assortment of reducing agents. The frequency of these processes is generally dependent on the architecture and arrangement of the the ligands, as they dictate the value of the reorganization energy & the strength of electronic coupling between the products. Quite a lot of techniques have been applied for studying outer-sphere electron transfer reactions, including UV-visible, infrared and electron paramagnetic resonance spectroscopies. Such techniques yield useful information about the electronic structures of the reactants & products, & the kinetics of the electron transfer process. Thermodynamic parameters relevant to these reactions, particularly the standard reduction potentials of the complexes involved, have also been established using electrochemical techniques such as cyclic voltammetry.

Certain key features of outer-sphere electron transfer reactions differentiate them from inner-sphere mechanisms. These include the lack of bridging the ligands interconnecting the reactants, the lack of ligand exchange during the reaction, & that the reaction rate does not depend on the nature of the bridging groups or steric factors that would influence ligand exchange. Moreover, outer-sphere mechanisms maintain the stereochemistry of the reactants due to the absence of significant rearrangements of the coordination spheres. Outer-sphere electron transfer has applications beyond subfundamental coordination chemistry. These types of reactions are commonplace in biological systems, especially in electron transport chains during photosynthesis & respiration. Outer-sphere mechanisms have shaped an appreciate and comprehend ing that, among other applications, has guided artificial photosynthetic elements & electron transfer catalysis as well as informed the design of molecular electronics. Researchers have written further textbooks on the topic, & insights gained from studying outer-sphere electron transfer have been utilized in designing molecular switches, sensors, & other functional materials that hinge upon controlled electron transfer processes.

Mechanism of Inner-Sphere Reactions

Inner-sphere electron transfer reactions demonstrate a more elaborate mechanistic pathway compared to outer-sphere processes. In these reactivities, the reactants' coordination spheres are directly involved in electron transfers featuring the emergence of a bridged intermediate complex during which both metals share one or more the ligands. 【7†source】 The bridging ligand can be defined as the molecule through which electrons can pass, allowing overlap by their orbitals between the donor & acceptor metal centers, rendering the electron transfer process more efficient. Henry Taube, Nobel Laureate in Chemistry 1983, first proposed the concept of inner-sphere electron transfer based on his pioneering work. Taube's work helped to clarify the role of bridging the ligands in electron transfer reactions & to establish the underlying principles that rule inner-sphere mechanisms. His work on cobalt(III) & chromium(II) etal complexes gave strong evidence for the nature of bridged intermediates & the metal to ligand transfer that followed inner-sphere electron transfer. Inner-sphere mechanism generally happens through well-defined steps of processes. As in the case of outer-sphere reactions, the first step is the formation of a precursor complex. In the case of inner-sphere mechanisms, however, this complex is transformed into a bridged intermediate when a ligand is transferred from one coordination sphere to another. At least one of the reactants must involve a complex that is labile enough that it has a coordination site that a bridging ligand can easily occupy during the substitution process.

The bridging ligand facilitates inner-sphere electron transfer by providing a pathway for electronic communication. This communication is only effective if the bridging ligand is of a certain nature, which can promote orbital overlap & electron delocalization. Halides, cyanide, thiocyanate, & carboxylates are among the most effective binding motifs & act as π-donors or acceptors, which allow them to engage in π-bonding interactions with the metal centers. After the formation of bridged intermediate the electron transfer between donor & acceptor metal center takes place via bridging ligand. Such electron transfer is commonly paired with substantial changes in the electronic structures of the metal centers, which can result in variations in their coordination preferences & ligand binding strengths. Therefore, the bridged intermediate can further undergo ligand exchange, rearrangement, or dissociation for the formation of the final products. One example of an inner-sphere electron transfer reaction is the reduction of pentaamminechlorocobalt (III) by chromium (II) aqua ions. The aforementioned chloride ligand acts as a bridge between a cobalt (III) & a chromium (II) centre in this process. Chromium (II) is oxidized to chromium (III) with electron transfer through a chloride bridge to produce cobalt(II) aqua ions & a chloride-coordinated chromium(III) complex. The observation that chloride is transferred from cobalt to chromium served as strong evidence for Taube's proposed inner-sphere mechanism. The kinetics for inner-sphere electron transfer reactions are dependent on this multiple factors that include lability of the complexes, nature of the bridging ligand,

Notes

thermodynamic driving force of the reaction & the reorganization energy associated with the electron transfer. In contrast to outer-sphere reactions, in inner-sphere mechanisms the rate-determining step is usually the formation of a bridged intermediate, rather than the electron transfer itself. In such reactions, especially those of kinetically inert complexes, the divisions stem from the considerable configuration changes required for bridged intermediate formation.

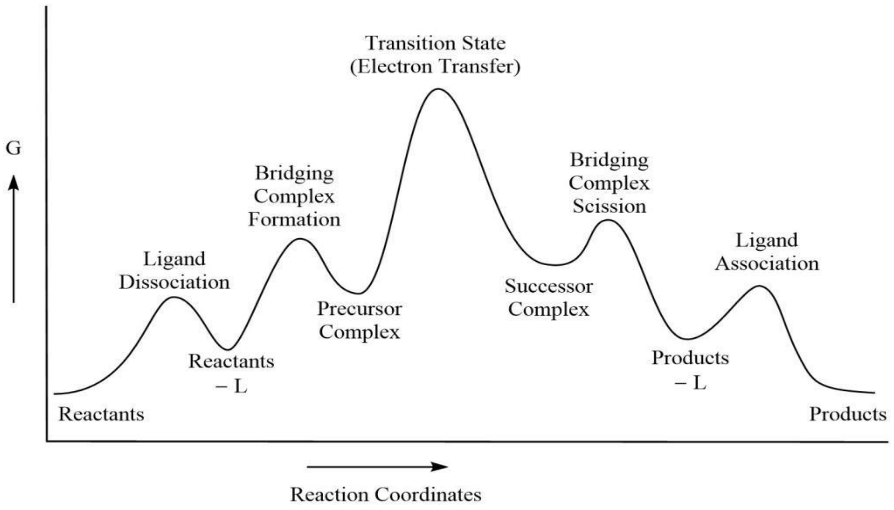


Figure- The reaction coordinate diagram for inner sphere electron transfer mechanism.

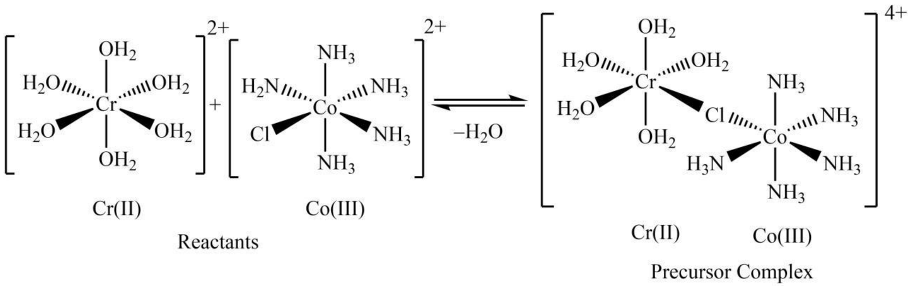


Figure- The formation of precursor complex, successor complex and the state of electron transfer in inner-sphere electron transfer mechanism.

Inner-sphere electron transfer reactions often give us information about the reaction mechanisms through their stereochemical results. The geometry of the bridged intermediate & the ligand transfer pathway can be mapped from the retention or inversion of configuration at the metal centers. The detection of bridged intermediates or observation of ligand transfer are also diagnostic for inner-sphere mechanisms. Inner-sphere electron transfer reactions are ubiquitous in synthetic & biological systems. In synthetic chemistry, such reactions are used for the synthesis of mixed-metal compounds, small-molecule activation, &

Notes

different catalytic processes, among others. Inner-sphere mechanisms in biological systems: As mentioned, inner-sphere mechanisms are involved in metalloenzyme functions in biological systems, particularly substrate oxidation & reduction. These enzymes often include bridging the ligands that can be derived from amino acid residues or cofactors that mediate electron transfer between the metal centers. Various, stopped-flow kinetics, electrochemistry & several spectroscopic techniques have been developed to study inner-sphere electron transfer. Computational approaches, such as density functional theory, have also offered an important appreciate and comprehend ing of the electronic structures of reactants, intermediates, & products in addition to energy profiles of inner-sphere electron transfer reactions.

Note that the distinction between inner-sphere & outer-sphere mechanisms is not always clearly defined, with some reactions showing both pathways. Depending on the nature of the metal centers and the ligands, the reaction conditions, & if the driving force is thermodynamic, different mechanisms predominate in a particular reaction. Identifying these counterbalancing forces is paramount to predicting the mechanism of electron transfer reactions, as well as the designing of catalysts & functional materials based on orchestrated electron transfer processes. Concluding Remarks: Inner-sphere vs outer-sphere electron transfer reactions are two of the fundamental mechanistic manifestations in coordination chemistry & with opposite characteristics & operational meaning. Notably, despite being a rather broad concept, it has already been elucidated how these mechanisms dictate redox processes in transition metal complexes as well as having guided the development of numerous applications in catalysis, materials science, & biochemistry. Insights gleaned from studies of inner-sphere & outer-sphere mechanisms underpin current rationalization of new classes coordination compounds with attribute redox characteristics & functionalities.

PRACTICAL APPLICATION

Practical Applications of Square Planar & Redox Chemistry in Everyday Life

The chemistry of square planar complexes & redox reactions may appear to be esoteric academic knowledge; nonetheless, these concepts subtly influence numerous facets of our daily existence. The mechanisms that regulate these reactions significantly influence technology, medicine, & environmental activities we frequently encounter. Platinum-based anticancer agents exemplify a prominent practical application of square planar chemistry. Medications such as cisplatin function by a meticulously regulated substitution process, wherein the square planar platinum complex enters the bloodstream almost unaltered, yet experiences ligand substitution events within

Notes

cancer cells. The trans effect—where specific the ligands enhance the substitution of groups positioned opposite to them—is meticulously utilized in these pharmaceuticals to guarantee their reaction occurs at the appropriate moment & location within the body. The longevity of a cancer patient undergoing chemotherapy relies on the regulated kinetics of square planar substitution processes, which enable platinum to bind to DNA, inducing apoptosis in cancer cells while reducing harm to healthy tissue.

The catalytic converters in modern automobiles depend significantly on the redox chemistry of metal complexes. These devices employ platinum, palladium, & rhodium in different oxidation states to enable electron transfer processes that transform toxic pollutants such as carbon monoxide & nitrogen oxides into less hazardous molecules. Inner-sphere electron transfer mechanisms, in which a bridging ligand momentarily links two metal centers during electron exchange, are essential to the operation of these catalysts. Every time you use your vehicle, you are utilizing advanced metal complex redox chemistry that safeguards air quality & public health via meticulously engineered electron transfer pathways. Contemporary rechargeable batteries that energize our smartphones, laptops, & electric vehicles essentially rely on regulated redox reactions involving metal complexes. Lithium-ion batteries employ transition metal oxides, often comprising cobalt, nickel, or manganese, which participate in reversible one-electron transfer processes during charging & discharging cycles. The Marcus-Hush hypothesis aids engineers in comprehending & optimizing the energy barriers associated with electron transfers, so directly affecting the charging speed of devices & their endurance in recharge cycles prior to degradation. The smartphone in your pocket & the electric vehicle on your street exemplify the application of metal complex redox chemistry refined by the principles discussed in this chapter. Many towns employ water filtration methods that leverage the redox characteristics of metal complexes to remove dangerous chemicals. Iron-based coagulants function via meticulously regulated redox & substitution reactions to eliminate contaminants from potable water. Simultaneously, advanced oxidation techniques employed to eliminate persistent organic contaminants in wastewater frequently depend on iron or copper complexes that produce hydroxyl radicals via electron transfer pathways. Outer-sphere electron transfer processes—where electrons travel between metal centers without direct contact—facilitate the effective degradation of pollutants into innocuous constituents. The purity of the clean water emanating from your tap is likely attributable to these implemented redox principles. The vivid hues in several commonplace objects—from textile dyes to LCD displays—originate from metal complex chemistry that entails particular electronic transitions. Metal-complex dyes utilized in textiles depend on the exact energy gaps between molecular orbitals, which are directly affected by ligand field stabilization & the electron transfer characteristics of the metal centers. The stability of these colorants under different settings relies on their resistance to unwanted substitution & redox processes. Likewise, the pixels of electronic displays frequently employ transition metal complexes, whose optical characteristics are dictated by the principles of electron transfer & ligand field theory discussed in this chapter.

Notes

Agricultural fertilizers & soil amendments often contain chelated metal nutrients, whose efficacy relies on regulated substitution reactions. Micronutrients such as iron & zinc are frequently provided in square planar or octahedral complexes engineered to release these vital elements at rates commensurate with plant absorption. The stability constants & substitution mechanisms of these metal complexes dictate the consistency of nutrient availability for crops, influencing the occurrence of deficiency & toxicity cycles. The food on your plate probably benefited from applied metal complex chemistry, which enhanced nutrition delivery through coordination chemistry & substitution kinetics concepts. Photographic techniques, despite the growing prevalence of digital technology, continue to employ silver-based chemistry in numerous applications that depend on meticulously regulated redox reactions. Conventional film photography relies on the photoreduction of silver ions to metallic silver, however some developing procedures entail intricate redox chemistry with defined electron transfer mechanisms. Despite the digital era, silver nanoparticles—whose characteristics are determined by the redox chemistry of silver complexes—are utilized in antimicrobial coatings & specialized electronic components. The images that safeguard your family memories have likely profited from these concepts of metal complex redox chemistry. Industrial catalysis, essential for the production of several everyday products such as plastics & pharmaceuticals, extensively employs square planar complexes & their replacement processes. Palladium-catalyzed cross-coupling processes, awarded the 2010 Nobel Prize in Chemistry, depend on the distinctive reactivity of square planar palladium complexes & their capacity for regulated oxidative addition & reductive elimination sequences. These reactions are employed to produce several goods, including pharmaceuticals, electronic materials, & specialized polymers. The synthetic materials you meet daily, such as the plastic in household utensils & the active chemicals in pharmaceuticals, frequently derive from industrial processes refined via the comprehension of square planar substitution mechanisms & redox chemistry.

Multiple-Choice Questions (MCQs)

1. Substitution reactions in square planar complexes generally follow:

Notes

a) Associative (A) mechanism

b) Dissociative (D) mechanism

c) SN1 mechanism

d) Concerted electron transfer

2. The trans effect in square planar complexes influences:

a) The rate of ligand substitution

b) The oxidation state of the metal

c) The formation of high-spin complexes

d) The paramagnetism of the complex

3. Which of the following the ligands exhibits a strong trans effect?

a) NH_3

b) Cl^-

c) CO

d) H_2O

4. Outer-sphere electron transfer is characterized by:

a) Direct bonding between reactants

b) No covalent bond formation between metal centers

c) Ligand substitution before electron transfer

d) Metal-metal bond formation

5. Inner-sphere electron transfer occurs via:

a) Electron hopping through solvent molecules

b) Formation of a bridging ligand between two metal centers

c) Direct tunneling of electrons

d) No interaction between metal complexes

6. Which of the following is an example of an outer-sphere reaction?

a) $[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+}$ → electron transfer

b) $[CoCl(NH_3)_5]^{2+} + [Cr(H_2O)_6]^{3+}$ → Cr-bound Cl^- transfer

c) Oxidation of $[Cr(H_2O)_6]^{2+}$ via ligand substitution

d) Reductive elimination in square planar complexes

Notes

7. The Marcus-Hush theory explains:

a) Kinetics of ligand exchange

b) Mechanism of electron transfer reactions

c) Color changes in transition metal complexes

d) Inner-sphere ligand substitution

8. According to Marcus theory, the rate of electron transfer reactions depends on:

a) Ligand exchange rates

b) The reorganization energy of the reactants

c) Metal-ligand bond strength

d) pH of the reaction medium

9. A key assumption of Marcus Theory is that:

a) Electron transfer occurs instantaneously

b) Electron transfer depends on nuclear reorganization

c) The rate is independent of solvent polarity

d) Redox reactions do not involve charge distribution changes

10. Cross reactions in electron transfer refer to:

a) Electron transfer between two identical metal ions

b) Electron transfer between different metal ions

c) Ligand exchange between transition metals

d) Magnetic coupling in metal complexes

Short Answer Questions

1. What is the trans effect, & how does it influence ligand substitution in square planar complexes?

2. Differentiate between outer-sphere & inner-sphere electron transfer mechanisms.

3. Explain why the ligands like CO & CN^- have a strong trans effect.

4. Describe the mechanism of electron transfer in an outer-sphere reaction.

5. What is the role of bridging the ligands in inner-sphere redox reactions?

Notes

6. What are the key factors influencing the rate of electron transfer reactions?

7. Define the reorganization energy in the Marcus-Hush theory.

8. Why do cross-reactions in electron transfer sometimes have different kinetics than self-exchange reactions?

9. How does the oxidation state of a metal center influence ligand substitution rates?

10. Explain the kinetics of substitution reactions in square planar complexes.

Long Answer Questions

1. Explain the mechanism of ligand substitution in square planar complexes, highlighting the trans effect & its applications.

2. Discuss the classification of redox reactions in metal complexes, including examples of each type.

3. Compare & contrast outer-sphere & inner-sphere electron transfer reactions, including their mechanisms & factors affecting their rates.

4. Explain Marcus-Hush electron transfer theory, including how it predicts reaction rates.

5. Discuss the role of solvent dynamics & ligand environment in controlling electron transfer rates.

6. How does ligand substitution affect the reactivity of metal complexes in catalytic cycles?

7. Explain reorganization energy in the context of Marcus Theory & its impact on redox reaction rates.

8. Discuss the factors affecting cross-reactions in electron transfer & how they relate to reaction feasibility.

9. Describe the kinetic & thermodynamic factors governing redox reactions in transition metal complexes.

10. How do spectroscopic techniques help in studying electron transfer mechanisms in transition metal complexes?

Notes

MODULE- 5

METAL π COMPLEXES

Objectives

- To delineate metal π complexes & comprehend their importance in coordination chemistry & catalysis.
- To examine the structure, bonding, spectroscopic characteristics, synthesis, & reactivity of metal carbonyl complexes.
- To investigate the bonding, production, & reactivity of transition metal-nitrosyl complexes.
- To examine the synthesis, coordination, & utilization of dinitrogen & dioxygen metal complexes in biological & industrial applications.
- To investigate the function of tertiary phosphines as the ligands, their bonding characteristics, & their applications in catalysis & synthesis.

5.1 Introduction to Metal π Complexes

One of the most intriguing & vital class of compounds in modern chemistry Metal π complexes. Bonds between the π electrons of unsaturated organic the ligands & metal atoms result in unique chemical entities that exhibit unique structures & reactivity patterns. In contrast to metal complexes that make σ bonds with metal through lone pairs of electrons, metal π complexes interact with the π electron clouds of alkenes, alkynes, aromatic molecules, & other unsaturated organic molecules. Because the bonding is so fundamentally different, this leads to rich structural diversity and chemical functionality with significant implications across a range of chemistry disciplines. Much more than just an academic interest, metal π complexes underpin myriad industrial processes, synthetic methodologies, and biological systems. The mid-20th century was the era of discovery for organometallics, with the elucidation of the structure of ferrocene in 1952 representing a paradigm shift in organometallic chemistry that challenged existing theories of chemical bonding. This porcelain-doll breakthrough paved the way for a Nobel Prize to Geoffrey Wilkinson and Ernst Otto Fischer in 1973 & launched him into a whole new frontier in the study of the interactions of metals with organic compounds.

The unusual electronic & structural features of metal π complexes afford them a versatility not present in other classes of compounds. π-bonds formed between metals & unsaturated the ligands afford

Notes

electron-rich neighbourhoods amenable to chemical manipulation. The metal center serves both as electron donor & acceptor, which allows it to mediate reactions that would otherwise be thermodynamically unfavorable or kinetically hindered. The ability of metal π complexes to serve as Lewis acid or Lewis base, depending on reaction requirements, make them especially potent catalysts for many organic transformations such as hydrogenation, carbonylation, polymerization & cross-coupling reactions, which constitute the foundation of contemporary chemical production. Metal π complexes are essential components in catalytic systems used in the industrial production of everyday materials from pharmaceuticals & agrochemicals to polymers & fine chemicals. Which enables guidance of reaction pathways, increasing yields & minimizing waste while promoting green chemistry. Examples of these metallic π acids can be seen in the 2005 Nobel prize winning ruthenium π complexes, which are used in olefin metathesis; & in reactions involving rhodium complexes which are used in hydroformylation to form aldehydes, then also with cross coupling using nickel & palladium catalysts to form carbon-carbon bonds.

Metal π complex formation is premised on overlap of unsaturated the ligands filled π orbitals with empty orbitals on the metal (and back-donation of filled metal d orbitals to empty π* antibonding orbitals on the ligand). As typically described using the Dewar-Chatt-Duncanson model, this orbital interaction generates a synergistic bonding arrangement that stabilizes the complex & impacts the ensuing reactivity. Not only are the strength & nature of these interactions widely variable depending on the metal electronic configuration, oxidation state, & ligand structural features, but this variability gives chemists a large number of parameters available to manipulate the characteristics of these complexes for specific applications. The construction of π complex chemistry of metals: A historical overview & theoretical pursuit Although simple π complexes (such as Zeise's salt ($K[PtCl_3(C_2H_4)]•H_2O$)) were first prepared in the 1820s, their true nature a scientific curiosity until the mid-20th century. The discovery of ferrocene ($Fe(C_5H_5)_2$) by Pauson & Kealy in 1951 (reported as a structure that was later shown to be incorrect), & its correct structural elucidation by Wilkinson & Woodward revolutionized organometallic chemistry. This "sandwich" compound, containing an Fe atom "sandwiched" between two cyclopentadienyl rings, showed unprecedented stability & aromatic character, running contrary to established views of chemical bonding, and led to the production of many analogous structures.

Metal π complexes exhibit remarkable architectural structural diversity. ranging from just simple monometallic complexes with a single π-bound ligand to elaborate multinuclear systems with bridging the ligands, the structural possibilities appear almost infinite. The most common ligand types are alkenes, alkynes, dienes (including cyclic systems such as cyclooctadiene), arenes (e.g. benzene & its derivatives), & cyclopentadienyl & related ring systems. These bonding modes can be represented systematically using haptic notation (η^n, where n is the number of contiguous atoms in the ligand bonded to the metal). For example, in the η^2 case, ethylene typically binds, & in the η^5 case, cyclopentadienyl. Similar diversity & fascinating electronic characteristics of metal π complexes are observed. The interaction alters the relative contributions of the ops, and therefore they are related to changes of electron density within the whole complex that affect its stability, reactivity, & spectroscopic characteristics. This can create a variety of electronic environments, where electron rich metal centers can donate electron density to electron-withdrawing substituents on the ligands & where electron-poor metals can accept electron density from the electron rich the ligands. Such electronic tunability is one of the reasons for the excellent catalytic activity of many metal π complexes in stabilizing reaction intermediates & enabling electron transfer processes.

The metal π systems also show fascinating magnetic & spectroscopic behaviours that give important information on their electronic structure & bonding. Nuclear magnetic resonance (NMR) spectroscopy, for instance, shows well-defined ligand proton shifts when coordinated with metals, which are a reflection of changes in electron density & shielding. Likewise, infrared spectroscopy can sense changes in stretching frequencies of the bonds of π-bound the ligands, indicating a change in bond strength & electron density. The role of these spectroscopic methods, complementing X-ray crystallography, has been crucial to our appreciate and comprehend ing of the structures & bonding in metal π complexes. Metal π interactions in biological systems: Potential role in protein function & enzyme catalysis For example, through their π nutrient proteins often interact with aromatic amino acid residues like histidine, tryptophan, & tyrosine metal ions in metalloproteins, contributing to protein stability and function. These interactions can affect protein folding, substrate binding, & catalytic activity. The detailed correlations between these natural metal π interactions have led to the design of biomimetic catalysts aiming to recapitulate enzymatic reactivity with high efficiency & selectivity. Metal π complexes can be classified from different viewpoints, such as the nature of the metal center, the kind of π-bonding ligand, & the overall structure of the complex. A typical classification system is as follows: half-sandwich complexes (the metal binds to one face of a π-system), sandwich complexes (the metal is located between two π-systems that are in a parallel formation), and multidecker sandwich complexes (where multiple alternating species of metals & π-the ligands exists). Alternatively, these complexes were

Notes

classified according to the oxidation state of the metal or electronic configuration, emphasizing the correlation between electronic structure & reactivity.

Various strategies have been reported for the synthesis of metal π complexes depending on the targeted structure. One straightforward route is through direct complexation of metal precursors with π-donor the ligands, typically resulting in the substitution of more labile the ligands (e.g., carbon monoxide or phosphines). Redox-controlled syntheses take advantage of the correlation between the oxidation state of the metal & its interaction with various ligand types. Another versatile synthetic route involves transmetalation reactions, in which the ligands are transferred from one metal to another. The synthetic method is often guide by parameters like stability of the necessary complex, functional groups compatibility & precursors availability. The reactivity motifs of metal π complexes are representative of the significant impact of metal coordination on the characteristics of unsaturated the ligands. Coordination to a metal center typically promotes π bonds to be activated toward nucleophilic attack, which differs markedly from the electrophilic reactivity typically observed with free alkenes & alkynes. This activation stems from the redistribution of electron density that occurs upon coordination, which instills partial positive charges on carbons that formerly resided in electron-rich environments. In contrast, back-donation from the metal can increase the observed nucleophilicity of coordinated the ligands in some scenarios as dictated by the intricate electronic interplay that defines such systems. Besides altering the reactivity of the ligands, π coordination with metals can stabilize reactive intermediates that would be fleeting or invisible under normal state of affairs. Also reactive species such as metallocycles, carbonium ions, etc. can be solubilized & stabilized through coordination to appropriate metal centers for subsequent isolation & characterization. This stabilizing influence has proven quite valuable in elucidating reaction mechanisms & materials behavior in reactive intermediates during a number of transformations.

Metal π complexes have arguably made their most significant contribution to practical chemistry through catalytic applications. These complexes serve as precursors to homogeneous catalysts that drive a myriad of transformations with high efficiency & selectivity. Hydrogenation catalysts $[RhCl(PPh_3)_3]$ (Wilkinson's catalyst) & $[Ir(cod)(PCy_3)(py)]PF_6$ (Crabtree's catalyst) allow for the step-wise addition of hydrogen at unsaturated bonds at ambient temperature. Olefin metathesis catalysts, & specifically those based on ruthenium (Grubbs catalysts) & molybdenum (Schrock catalysts), have transformed the way in which we form carbon-carbon bonds. The development of cross-coupling catalysts, especially palladium or nickel π complexes, has revolutionized synthetic strategies to forge complex molecular architectures. The mechanistic principles that govern these types of catalytic processes often imply elementary steps in which π complexation is a critical feature. Common mechanistic patterns include:

- Formation of activated π complexes through coordination of unsaturated substrates
- CO-Insertion into Metal–Hydride or Metal–Carbon Bonds
- New bond formation and regeneration of the catalyst via reductive elimination
- -β-hydride elimination as an important step in many catalytic cycles
- Ligand exchange mediated metathesis processes

The comprehension of these mechanistic fundamentals has allowed for the rational engineering of new catalysts with superior activity, selectivity, & stability parameters, thus propelling ongoing innovation within this domain. Metal π complexes find relevance beyond conventional catalysis, with significant implications in the domains of materials science, medicinal chemistry, & energy conversion. It qualified metallocene derivatives in materials science to act as precision catalysts in polyolefin production, achieving control over parameters such as molecular weight distribution, branching & stereochemistry with high precision. Ferrocene & its derivatives are employed in electrochemistry as redox-active components for sensors, batteries, & other electrochemical devices. Metal π complexes are also used as building blocks in building molecular machines, switches & other functional materials owing to their unique structural & electronic characteristics.

Metal π complexes have been built up as a candidate for drug candidates in medicinal chemistry. Compounds that contain ferrocene display notable biological activities such as antimalarial, anticancer, & antimicrobial activity. This reductive process not only removes functional groups, protecting some sensitive groups, but also retains more than one coordination pair split in the target molecules & thus enhances the lipophilicity and membrane involvement, contributing to better targeting & therapeutic efficacy. These applications are underpinned by the interdisciplinary field of bioorganometallic chemistry, which aims to exploit the unique characteristics of metal π complexes & their potential applications in biomedicine. Metal π complex chemistry also has another frontier in energy-related applications. Ruthenium polypyridyl complexes are commonly used as photosensitizers in dye-sensitized solar cells, where they absorb light energy & generate electron transfer processes. Electrocatalysts for

Notes

water splitting, carbon dioxide reduction, and other energy conversion processes also rely heavily on metal π complexes. The capacity for multi-electron transfers, along with the ability to activate small molecules, highlights their importance to problems in energy storage & conversion.

Since their discovery, the theoretical appreciate and comprehend ing of metal π complexes has evolved substantially, mirroring advancements in both experimental techniques & computational methods. The Dewar-Chatt-Duncanson model is a qualitative representation of metal-ligand π interactions, however, more advanced theories based on molecular orbital theory & density functional theory provide deeper appreciate and comprehend ing of electronic structure & bonding. Computational studies today can predict binding energies, structural parameters, & spectroscopic characteristics at an unprecedented level of accuracy, paving the way for informed experimental studies & mechanistic exploration. However, there is notable vitality & innovation in the field of metal π complex chemistry, as shown by recent developments. Development of first-row transition metals for applications as alternatives to precious metals addresses concerns surrounding sustainability and reveals reactivity patterns that are new for precious metals. Chiral, alkyl-substituted π metallic complexes can be employed in asymmetric catalysis, allowing for the enantiospecific synthesis of enantiopure groups that merit great interest for the pharmaceutical & agrochemical industries. Metal π complex-configured photochemical systems utilize mild energy input to facilitate diverse chemical transformations. The study of cooperative effects in multinuclear complexes demonstrates emergent functionalities unavailable within monometallic systems.

Another exciting frontier includes metal π complexes with unconventional the ligands. Heterocyclic the ligands, boron-containing π systems, & other unorthodox architectures – beyond the classical carbon-based π systems – significantly enrich the structural & electronic diversity of these compounds. Likewise, metal π complexes contribute to supramolecular assemblies, polymer materials, & extended materials that introduce hierarchical structures & unique functionalities. Thus, the environmental & sustainability features of metal π complex chemistry are primarily acknowledged to current research. Although these complexes have typically depended on metals such as platinum, palladium, & rhodium, the escalating focus on sustainable chemistry has brought forth the study of alternatives founded on earth-abundant elements including iron, cobalt, & nickel. Not only do these first-row transition metals decrease reliance on scarce resources, but they also frequently show complementary or superior reactivity patterns relative to their heavier congeners. Such research on recyclable catalysts, more efficient processes with less byproduct formation, and the development of biodegradable metal π complexes merges with the ideals of green chemistry & our environmental problems.

Metal π complexes in extreme environments may be regarded as a niche, albeit interesting, area of research. Studies of how these complexes perform at high pressure, extreme temperatures, or in non-conventional solvents yield insights into fundamental characteristics & possible uses in specialized settings. Examples of such metal π complexes retain catalytic activity in supercritical carbon dioxide, which opens up greener processing methods for industrial applications. Others display improved stability or unique patterns of reactivity in ionic liquids, leading to potential new transformations. In addition to their natural metalloprotein role, synthetic metal π complexes can be used as probes of biological processes, diagnostic tools, & therapeutic agents. Reinforcing with metal π complexes via biomolecule conjugation can yield hybrid systems with complementary characteristics, e.g., targeted delivery of catalytic functionality to specific cellular compartments. Metal π complexes exhibit recognition characteristics toward DNA, proteins, & other biomolecules that can be used in sensing, imaging, & therapeutic intervention.

The educational opportunities of metal π complex chemistry should not be overlooked to train the next generations of chemists. Such compounds offer pedagogic case studies to learn basic concepts in bonding, symmetry, reactivity, & catalysis. Their visual interest — many sport bright colors and unusual shapes — makes them a lively topic for introducing students to the principles of chemistry. Contemporary pedagogical methodologies more frequently involve computational modeling of these complexes, helping students visualize orbitals, electron density distributions, & other abstract concepts in a more intuitive way. Several trends & challenges are likely to define the future evolution of metal π complex chemistry. The implementation of artificial intelligence & machine learning methods holds great potential for streamlining discovery by predicting favorable structures, optimizing reaction conditions, & identifying structure-property relationships. The advent of operando spectroscopic techniques will allow unprecedented access to the behavior of metal π complexes during reaction conditions, identifying transient intermediates & dynamic processes. The use of metal π ensembles within spatial confinement — in the interior of proteins, zeolite pores or metal-organic framework channels — will unravel how steric constraints can modulate reactivity & selectivity. Field specific challenges include developing even more efficient synthetic methods for complex multinuclear systems or for systems that utilize exotic the ligands. The ability to stereodirect metal centers is limited in many contexts,

Notes

especially in asymmetric synthesis applications. Metal π complexes in general face persistent limitations for practical applications due to the stability of their reaction products, especially considering the harsh environments or potentially coordinating functionalities (such as amines) that may be present6.

The broad connections of metal π complex chemistry with various scientific and technological domains reflect its multidisciplinary past. Innovation & application in this area is driven by collaborative interaction between synthetic chemists, spectroscopists, theoreticians, materials scientists & biologists. The meet of viewpoints & strategies from these domains trains the realization & capitalization of the distinctive attributes of metal π complexes. As a final point, π complexes of metals are a central pillars of contemporary chemistry bridging between organic & inorganic realms & allowing for transformative technologies spanning disciplines. From their unique bonding modalities, structural diversity, & reactive adaptability, the field of science & industry alike is continually stirred by the petri dish ingenuity of plasmatic intelligence. Both their historical roots in academic curiosity & modern challenges of energy, health, & sustainability demonstrate how even mundane chemical principles can serve as the foundation for the most technologically advanced & scientifically relevant innovations. As the field continues to uncover new emergent behavior & applications from these compounds, metal π complexes will surely remain central to tomorrow's chemistry, with answers to tomorrow's medicine, materials science, photovoltaics & environmental protection.

Metal π complexes provide educational opportunities outside of mainstream chemistry curricula into multidisciplinary learning. These compounds are extremely illustrative for discussions related to the structure–property relationship, the relevance of quantum mechanical principles to real-world systems, & how foundational scientific research can lead to technology. Their historical development demonstrates how scientific knowledge grows through a synthesis of experimental observation, theoretical insight, & technological development — an important teaching message for students in all scientific disciplines. We should also call attention to the aesthetic dimension of metal π complexes. Many of these compounds shine with vibrant colors & crystallize into spectacular shapes that have transfixed chemists & non-chemists alike. The orange crystals of ferrocene, the yellow needles of ruthenocene, & the deep green color of some of the chromium arene complexes highlight the esthetic beauty of these compounds. These aesthetic features have rendered metal π complexes popular themes in chemical art & visualization, adding to their scientific significance by better communicating the beauty of chemistry to wider audiences. For this reason, such compounds made of π-metal species are named as π-metal clusters & classification is implemented to recognize crystal types. η^n is the classical haptic notation, specifying the span of contiguous atoms in the ligand that interacts with the metal, although when the coordination is more complex hyphenation becomes less helpful & one must use other descriptors. In the particular case of multinuclear complexes with bridging π the ligands it may be necessary to specify multiple coordination modes simultaneously. Extensive structural diversity of these complexes requires a systematic approach for their naming/labeling to facilitate effective communication among the science community.

Advances in analytical techniques have improved profoundly the characterization of metal π complexes. Employing them alongside classical methods such as NMR & infrared spectroscopy, special methods like X-ray absorption spectroscopy, Mössbauer spectroscopy or electron paramagnetic resonance can give comprehensive information on the electronic structure & the bonding. State-of-the-art mass spectrometry methods provide data on complex mixtures & facilitate identification of reaction intermediates. These experimental approaches are complemented through computational techniques to predict spectroscopic signatures & to aid experimental data interpretation. Indeed, the industrial relevance of metal π complexes is booming — the use cases reach far outside conventional sectors. Also in electronics, these compounds are used to make organic light-emitting diodes, conducting polymers, & other materials. In environmental technology, they are used as sensors for pollutants & in catalytic processes for remediation. They assist in hydrogenation & other changes in production of edible oils & other food industry objects. This growing range of applications illustrates the diverse fields of application that these compounds enter across a plethora of technological fields. Metal π complex-based technologies have a significant economic impact. Catalytic-mediated reactions facilitated by these entities produce billions of dollars of valuable products per year, including polymers, medicine, and fine chemicals. This translates to significant cost savings & environmental benefits given the efficiency improvements & waste reduction wrought by metal π complex catalysis relative to related methodologies. As these advances in technology continue to advance, the economic impact will only escalate, especially in high value sectors such as precision medicine, advanced materials and sustainable energy technologies.

Metallo π complex chemistry is distributed globally with both established & new trends (patterned after the development of the field) being reflected in the work produced worldwide & reviewed here. Although North America, Europe, & Japan have historically been leading countries in this field, much of the research is now also being

Notes

conducted in China, South Korea, India, & other emerging scientific countries. By reaching out to new locations, this geographical diversity brings fresh ideas, techniques & usability, which fosters advancement & exploration. Much of the progress made in this area is made by international collaboration that combines complementary expertise & resources. The context of culture & society in which metal π-complex chemistry develops is also relevant. Public attitudes to chemistry, environmental expectations, frameworks for regulation, & even funding priorities all influence the direction & speed with which research can proceed in this field. For example, the growing focus on sustainability has spurred increased interest in earth-abundant metals & environmentally harmless processes. Likewise, health-related applications have emerged in the wake of societal needs & the challenges facing the healthcare sector. These larger contexts will be helpful in placing the evolving landscape of metal π complex chemistry (or lack thereof 2). Metal π complex chemistry also carries philosophical import, as it forces us to consider what we mean by chemical bonding, how structure relates to characteristics, & where the borderlands of chemical disciplines lie. These results upset simple models of bonding & reactivity, elucidating the intricate details as the factors that drive chemical behavior. They are also a classic example of emergent characteristics, which emerge in specialized arrangements of atoms & electrons & how complex functions can emerge from simple physical rules.

Teaching of metal π complex chemistry is an evolving field, elaborating with new educational technologies & concepts arising from cognitive science. Virtual & augmented reality tools help visualise and manipulate three-dimensional structures aiding in intuition for spatial relationships & bonding patterns in students. One pedagogic route whereby students are tasked to transfer the principles of metal π complex chemistry through real life examples, honing critical thinking & analytical skills, is through problem-based learning approaches. In a collaborative learning environment, discussion & peer teaching can reinforce appreciate and comprehend ing, promote retention & provide invaluable formative assessment. appreciate and comprehend ing the history of metal π complex discoveries provides insight into the human aspects of science. The serendipitous finding of ferrocene is a good example of how science often involves surprises, missteps, & rethinking. The social dynamics of groups of scientists has been elucidated through studies of the competitive & collaborative relationships between research groups focused on metal π complexes. These different historical contexts inform our appreciate and comprehend ing of how chemical knowledge is produced & changes over time.

Similarly, the judiciousness regarding the research & implementation of metal π complexes can also be pondered on ethical grounds. Concerns regarding resource consumption, environmental consequences & potential misapplications of these technologies are raised in different contexts. Ethical questions around, & hence the responsible development & use of metal π complex technologies must recognize the trade-off between actors that may be exploited for profit & the altruism that scientists have to partake on an equal basis with respects stemming from harmful consequences, whether practical or not. Transparent engagement on both the capabilities & limitations of these technologies help further ethical decision-making.

5.2 Metal Carbonyl Complexes

Metal carbonyl complexes are one of the most significant & oldest classesunder the umbrella of organometallic compounds. Complexes of transition metals with bonded carbon monoxide the ligands have widespread applications in industrial catalysis, synthetic organic chemistry, & the pathway towards fundamental bonding theory. In this chapter, we investigate the construction of metal carbonyls, focusing on their structural characteristics, bonding characteristics, spectroscopic characteristics, synthetic strategies & important chemical reactions.

1. By direct reaction: Some of the mononuclear carbonyls can be prepared by the direct reaction of carbon monoxide with metal powder.

$$Ni + 4CO \xrightarrow[1\ atm]{25^\circ C} Ni(CO)_4$$

$$Fe + 5CO \xrightarrow[200\ atm]{200^\circ C} Fe(CO)5$$

$$2Co + 8CO \xrightarrow[35\ atm]{150^\circ C} Co2(CO)8$$

2. By reduction: One of the most widely used methods to synthesize metal carbonyls is the reduction of corresponding metal salts in the presence of carbon monoxide.

$$CrCl_3 + Al + 6CO \xrightarrow[benzene]{AlCl3} Cr(CO)_6 + AlCl_3$$

$$VCl_3 + 4Na + 6CO \xrightarrow[high\ pressure]{diglyme,\ 100^\circ C} [(diglyme)_2Na][V(CO)_6] + 3NaCl$$

Notes

200°C
$2CoI_2 + 4Cu + 8CO$ →——————————→ $Co_2(CO)_8 + 4CuI$
200 atm
120 − 200°C
$2CoCO_3 + 2H_2 + 8CO$ →——————————————→ $Co_2(CO)_8 + 2H_2O + 2CO_2$
250 − 300 atm
250°C
$Re_2O_7 + 17CO$ →——————————→ $Re_2(CO)_{10} + 7CO_2$
350 atm

In the last reaction, carbon monoxide is the reducing agent on its own.

2. By reduction: One of the most widely used methods to synthesize metal carbonyls is the reduction of corresponding metal salts in the presence of carbon monoxide.

$CrCl_3 + Al + 6CO$ →———$AlCl_3$ ———→ $Cr(CO)_6 + AlCl_3$

benzene

diglyme, 100°C

$VCl_3 + 4Na + 6CO$ →————————————————→ $[(diglyme)_2Na][V(CO)_6] + 3NaCl$

high pressure

200°C

$2CoI_2 + 4Cu + 8CO$ →——————————→ $Co_2(CO)_8 + 4CuI$

200 atm

120 − 200°C

$2CoCO_3 + 2H_2 + 8CO$ →——————————————→ $Co_2(CO)_8 + 2H_2O + 2CO_2$

250 − 300 atm

250°C

$Re_2O_7 + 17CO$ →——————————→ $Re_2(CO)_{10} + 7CO_2$

350 atm

In the last reaction, carbon monoxide is the reducing agent on its own.

Notes

3. From iron pentacarbonyl: Carbon monoxide ligands in $Fe(CO)_5$ are labile and therefore can be used to synthesize other metal carbonyls.

110°C

$MoCl_6 + 3Fe(CO)_5$ →——————————→ $Mo(CO)_6 + 3FeCl_2 + 9CO$

ether

110°C

$WCl_6 + 3Fe(CO)_5$ →——————————→ $W(CO)_6 + 3FeCl_2 + 9CO$

ether

4. From metathesis reaction: Mixed-metal carbonyls can successfully be prepared via a metathesis reaction route as:

110°C

$MoCl_6 + 3Fe(CO)_5$ →——————————→ $Mo(CO)_6 + 3FeCl_2 + 9CO$

ether

110°C

$WCl_6 + 3Fe(CO)_5$ →——————————→ $W(CO)_6 + 3FeCl_2 + 9CO$

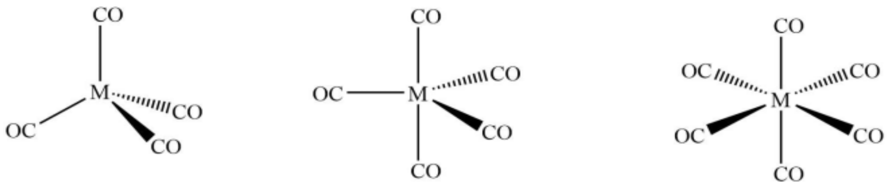
ether

5. From metathesis reaction: Mixed-metal carbonyls can successfully be prepared via a metathesis reaction route as:

$KCo(CO)_4 + [Ru(CO)_3Cl_2]_2$ →————————→ $2RuCo_2(CO)_{11} + 4KCl$

The " Structure and Bonding in Metal Carbonyls "

Carbon monoxide molecules are coordinated to transition metal centres in metal carbonyl complexes. The unprecedented nature of these compounds has been pivotal in our appreciate and comprehend ing of chemical bonding, notably the synergistic interaction between metals & the ligands. The metal-carbonyl bond consists of two individual action that act simultaneously: a sigma donation from the carbon monoxide to the metal & a pi donation from the metal to the carbon monoxide. The CO molecule has a lone pair on the carbon. The lone pair then coordinates to an empty orbital on the metal center, forming a sigma bond in the sigma bonding component. This donation renders more electron density at the metal, resulting in a partial negative charge. At the same time metal d-orbitals fill & overlap the CO π* antibonding empty orbital causing the pi back donation. This back-donation reinforces the metal-carbon bond, but loosens the carbon-oxygen bond. This is a synergistic bonding model, & it is often called the Dewar-Chatt-Duncanson model, & it explains many of the characteristics of the metal carbonyls that we have observed. The extent of back-donation can have a profound impact on the strength of the C−O bond, as demonstrated by infrared spectroscopic studies. The frequency of C-O stretching in pure carbon monoxide is about 2143 cm^{-1}. Nonetheless, for carbonyl complexes with metals, this frequency is often lower (1850 <Ψ 2120 cm^{-1}) due to the weakening of the C−O bond resulting from the metal-to-ligand back-donation.



$M(CO)_4$
M = Ni, Pd

$M(CO)_5$
M = Fe, Ru, Os

$M(CO)_6$
M = V, Cr, Mo, W

Figure-. The structures of some mononuclear metal carbonyls.

Metal carbonyls display a wide range of geometrical arrangements, which are mainly dictated by the electronic and steric characteristics of the metal atom at the centre. Common geometric shapes of simple mononuclear carbonyls, such as $Ni(CO)_4$, $Fe(CO)_5$, & $Cr(CO)_6$ reveal tetrahedral, trigonal bipyramidal, & octahedral configurations, respectively. These are apparently all consistent with the so-called 18 electron rule of organometallic chemistry, which proposes that transition metal complexes have a tendency to approach total electrophytic configurations with 18 valence electrons (like the noble gases). This additional structural complexity is achieved in binuclear & polynuclear metal carbonyls by the presence of metal–metal bonds & bridging carbonyl the ligands. In such systems, carbonyl the ligands assume terminal, doubly-bridging (μ_2) or triply-bridging (μ_3) conformations. For example, $Fe_2(CO)_9$ has three bridging carbonyls & six terminal carbonyls, while $Fe_3(CO)_{12}$ has both terminal & bridging carbonyls in its triangular metal framework. Metal carbonyls are good model systems to get information about the nature of bonding from the bond length. Typical M-C bond lengths in terminal carbonyl the ligands range from 1.8 to 2.0 Å, whereas C-O bond lengths are ca. 1.15 Å (this is somewhat longer than the 1.128 Å length seen in free CO). The corresponding bridging carbonyls have longer M-C bonds (2.0–2.3 Å) & even longer C-O bonds (1.16–1.20 Å), indicating less pi back-donation to each CO ligand.

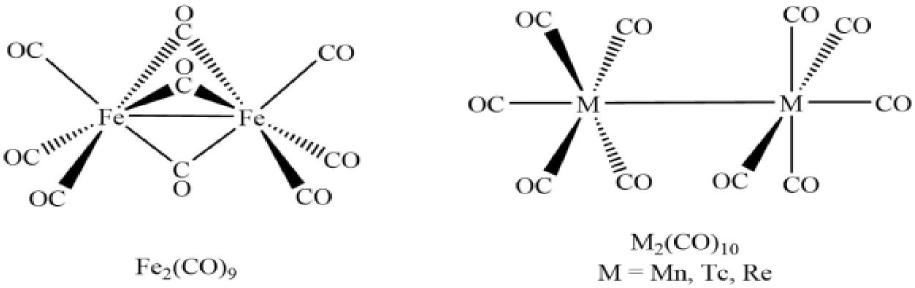


Figure- . The structures of some binuclear metal carbonyls.

The stability and reactivity of metal carbonyl complexes are chiefly determined by electronic factors. Carbonyls of metals in low oxidation states (especially d^6, d^8 & d^{10} configurations) are the most stable because of their highest ability for pi back-donation. This is a significant limitation, in that higher oxidation states generally impart lower stability on carbonyl complexes, due to decreasing electron richness of the metal centers, & therefore, lower ability for back-donation. Coordination numbers in metal carbonyls are nicely described by the 18-electron rule. The coordination number is varied to achieve the 18-electron configuration, since each CO ligand donates 2 electrons to the metal's valence shell. That means Ni(0) (10 valence electrons) coordinates with four CO the ligands (8 e−) → 18 e−, Fe(0) (8 valence electrons) needs five CO the ligands (10 e−). However, there are exceptions to the 18-electron rule, especially for the early transition metals & out for some of the 2nd & 3rd row transition elements. So for example, $V(CO)_6$ is a 17-electron complex that is remarkably stable despite being a radical. Such deviations emphasize the intricate balance of electronic & steric influences on the stability of metal carbonyls.

The bonding model in metal carbonyls (for the bonded species detailed in eqs 3 & 5) also applies to other π-acceptor the ligands (e.g., isocyanides (RNC), carbon disulfide (CS_2), & nitric oxide (NO)), which also participate in such synergistic bonding interactions. This paradigm has been enormously useful in interpreting a wide variety of organometallics, well beyond simple carbonyls. Another way to describe appreciably bonding interactions is through crystal field theory. Since these the ligands are strong field the ligands, they may greatly split d-orbitals, leading to low-spin complexes for most of the metal carbonyl complexes. The use of such electronic arrangement is a necessary condition for exhibiting the diamagnetic property in many of these metal carbonyls, so that they can be examined by nuclear magnetic resonance spectroscopy.

Notes

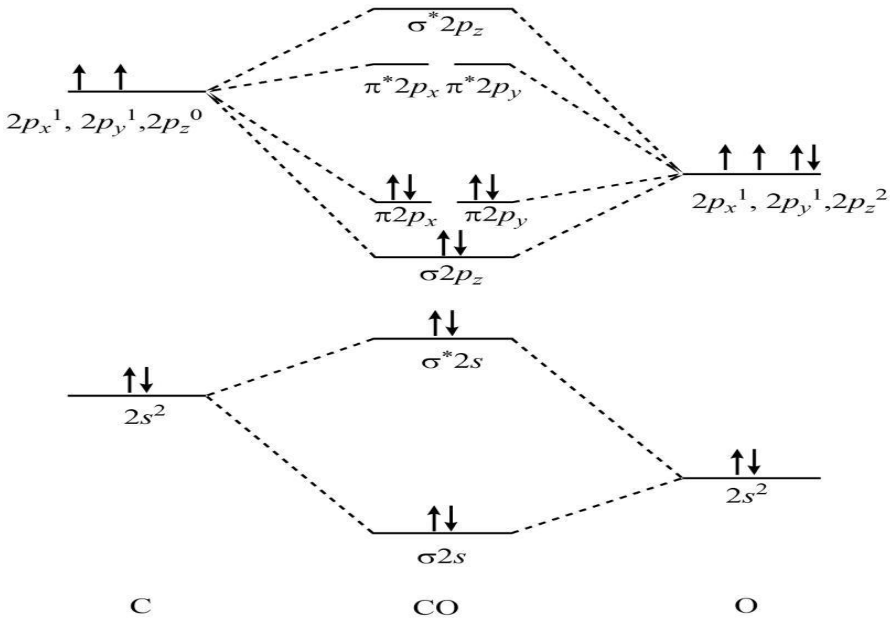


Figure - The first generation molecular orbital diagram of carbonyl ligan

Spectroscopy of Metal Carbonyls in Different Ways

Infrared spectroscopy is an invaluable analytical tool for characterising carbon complexes of transition metals. Due to the unique characteristics of the carbon-oxygen stretching vibrations in these compounds, these typically give rise to strong absorption bands at 1850-2120 cm^{-1} in the infrared spectrum, which are clearly distinguished from other common functional groups. This spectroscopic signature facilitates screening of carbonyl the ligands & reveals important information regarding their bonding environment. The position of the CO stretching frequency provides direct evidence of the degree of the metal-to-ligand back-donation. Increasing donation causes back-population of the π* antibonding orbitals of CO, weakening the C-O bond & lowering the stretching frequency. This relation enables infrared spectroscopy to probe the electronic characteristics of the metal center. Thus, electron-rich centers are capable of good back-donation & corresponding lower CO stretching frequencies, whereas electron-poor metals have frequencies increased towards that of free CO.

There are many factors affecting the CO stretching frequency in metal carbonyl complexes. The oxidation state of the metal has a strong influence on the back-donation ability—lower oxidation states will typically show lower stretching frequencies as a consequence of the increased back-donation. The influence of other the ligands on CO stretching bands via electronic & steric effects is also a known fact.

Electron donating the ligands increase electron density at the metal center, thus promoting back-donation to CO and reducing the stretching frequency. In contrast, electron-withdrawing the ligands have an opposite effect. Terminal & bridging carbonyl the ligands boast unique spectroscopic signatures. Terminal COs generally show stretch frequencies from 1850 to 2120 cm^{-1}, whereas bridging carbonyls absorb at lower frequencies (1700−1860 cm^{-1}) where decreasing bond order leads to lower force constants. Triply-bridging carbonyl the ligands exhibit even lower stretching frequencies sometimes below 1700 cm^{-1}. These spectroscopic distinctions allow for structural elucidation of intricate polynuclear metal carbonyls. With the new quantum numbers defined & the related symmetries imposed, we turn to group theory, which gives a very powerful framework to analyse the vibrational spectra of the metal carbonyls. The frequency & number of CO stretching bands provide information on the symmetry of the molecule, enabling the symmetry of carbonyl the ligands to be deduced. For instance, octahedral $M(CO)_6$ complexes have only a single IR-active band due to their high symmetry (Oh point group), in contrast with the ligands of lower symmetry, e.g. $Fe(CO)_5$ (D3h) leading to multiple bands.

Raman spectroscopy, that is primarily sensitive to changes in polarizability, complements infrared analysis in that it detects vibrations that are, for symmetry reasons, infrared-inactive. This is the so-called mutual exclusion rule; vibrations that are active in Raman spectroscopy must be inactive in infrared spectroscopy, & vice versa, in centrosymmetric molecules. Yes, combined infrared & Raman studies permit an exhaustive vibrational analysis & are particularly useful for high-symmetry metal carbonyls. Variable-temperature infrared spectroscopy allows monitoring of dynamic processes in metal carbonyl complexes. For example, intramolecular carbonyl exchange in $Fe(CO)_5$ is an example of fluxional behavior, which leads to temperature-dependent spectroscopic changes. At low temperatures, separate absorption bands are observed from distinct CO environments, while at higher temperatures exchanges speed up & bands coalesce. Additional structural information is obtained from isotopic labeling experiments in which ^{13}C- or ^{18}O-enriched carbon monoxide has been used. Replacing ^{12}C by ^{13}C results in a downshift of the CO stretching frequency by about 40 cm^{-1} (to lower frequencies), given the increase of the reduced mass of the oscillator. These isotopic changes assist in assigning complicated vibrational spectra & clarifying reaction mechanisms involving carbonyl the ligands.

The force constant of the C-O bond (obtained with the stretching frequency) measures the strength of a bond & is related to the extent of back-donation of π electrons from the metal atom to the carbinol group. Typical force constants vary from 16-17 $\times 10^5$ dyne/cm for

Notes

terminal carbonyls up to 14-15 ×10^5 dyne/cm for bridging carbonyls, compared to (18.5 × 10^5 dyne/cm for free CO. These are quantitative measures of back-donation effects. Metal carbonyl complexes where more than one carbonyl acts as a ligand show coupling of individual CO stretching vibrations, leading to symmetric & antisymmetric stretching modes. These coupled vibrations create distinctive patterns of bands that depend on the geometric arrangement of the carbonyl the ligands. For example, cis-$M(CO)_2$ fragments usually show two bands, whereas trans-$M(CO)_2$ units show a single band. Calculations of metal carbonyls via density functional theory have also gained prominence in predicting & interpreting vibrational spectra. Such computational methods often closely match experimental frequencies & assist in the assignment of difficult spectra, particularly for new or unstable carbonyls that are difficult to characterize experimentally.

Infrared spectroscopy is also useful in following certain reactions with metal carbonyls. Substitution reactions, for example, result in signature changes in the CO stretching pattern as the symmetry & electronic characteristics of the complex change. These allow for interrogation of mechanistic evolution & tracking of reaction progress. SEIRAS & ATR methods have pushed vibrational methods to the domains of metal carbonyls adsorbed on surfaces. Such approaches are especially useful for the study of heterogeneous catalysts and surface-bound intermediates within CO activation catalytic contexts.

Preparations and Significant Reactions

The synthesis of metal carbonyl complexes takes place using a variety of methods from direct carbonylation of metals to reduction of metal salts in the presence of CO at high pressure. Over decades of investigation, these preparative avenues have been honed, providing reproducible methods to obtain a diverse range of carbonyl complexes. One of the earliest & simplest synthetic methods is the direct reaction of finely powdered metals with carbon monoxide at high temperature & pressure. Nickel tetracarbonyl, $Ni(CO)_4$, was initially synthesized by Ludwig Mond in 1890 by the direct carbonylation of metallic nickel under atmospheric pressure & relatively moderate temperature. This process, called the Mond process, became the basis for the industrial purification of nickel. Similar direct carbonylation methods yield iron pentacarbonyl [$Fe(CO)_5$] & chromium hexacarbonyl [$Cr(CO)_6$], but these often require more rigorous conditions (150-200 °C & 50-200 atm CO pressure). Further, reductive carbonylation provides a complementary synthetic pathway that can accommodate metals that are not easily carbonylated via direct reaction. This method depends on the reduction of metal salts or oxides in the presence of carbon monoxide but is often supplemented by other reducing agents. One example is molybdenum hexacarbonyl [$Mo(CO)_6$], which can be prepared by reducing molybdenum chloride with aluminum powder at

CO pressure. Manganese carbonyl compounds are typically prepared by reduction of manganese(II) compounds in the presence of CO and a suitable reducing agent.

Notes

Milder synthetic alternatives for delicate systems are photochemical & thermal carbonylation approaches. Ultraviolet irradiation of transition metal complexes in the presence of carbon monoxide (CO) allows for ligation of CO to the complex by promoting ligand substitution, a common route to the formation of other carbonyl the ligands, which was previously only low yielding or inaccessible. To show the effectiveness of these methods, preparation of mixed-ligand carbonyl complexes such as (η^5-C_5H_5)Mn$(CO)_3$ is highlighted in section E, where photolysis of manganese pentacarbonyl bromide in the presence of cyclopentadienyl anion generates the resulting compound. 5965 Metal carbonyl anions, commonly known as carbonylate anions, are an important class of reactive intermediates in carbonyl chemistry. Example compounds, namely $[Fe(CO)_4]^{2-}$ & $[Mn(CO)_5]^{-}$, can be synthesized from the respective neutral carbonyls by reduction with strong reducing agents such as sodium metal or sodium naphthalenide. Functionalized carbonyl complexes & heteronuclear metal clusters can also be obtained by chemical oxidation of carbonylate anions which act as ubiquitous nucleophiles. Mononuclear precursors in controlled thermal decomposition24 or photolysis25 procedures have also been used to prepare both binuclear & polynuclear metal carbonyls. For instance, the reactive iron species formed by the photolytic decomposition of iron pentacarbonyl is trinuclear $Fe_3(CO)_{12}$, whereas controlled thermolysis provides $Fe_2(CO)_9$. These processes generally happen via CO ligand loss leading to coordinatively unsaturated metal centers that cluster to yield metal–metal bonds.

Insertions of carbon monoxide are a foundational reaction in metal carbonyl chemistry with important consequences for industrial processes. In these processes CO condenses with metal-element bonds, giving rise to new functionalized carbonyls. CO insertion into metal-alkyl bonds, for example, forms acyl complexes, which are important intermediates in hydroformylation catalysis. CO can similarly insert into metal-hydrogen bonds to give formyl complexes, a central theme in syngas conversion chemistry. Another important class of transformations is the substitution reactions of metal carbonyls. Various donor the ligands appropriate for coordination like phosphines, amines, or N-heterocyclic carbenes can selectively replace carbonyl the ligands. Such substitutions usually occur through one of several dissociative mechanisms, especially for 18-electron species, where initial CO dissociation generates a reactive 16-electron complex. Both the electronic and steric characteristics of the incoming ligand, & the electron density at the metal center determines the rate & selectivity of substitution. The migratory insertion reaction, which involves the

Notes

combining of a CO ligand & another ligand on the metal center, features prominently in many catalytic cycles. In the canonical case, a metal-alkyl entity performs migratory insertion with a neighboring CO ligand, resulting in a metal-acyl complex. This fundamental change underlies industrial reactions such as Monsanto acetic acid synthesis & hydroformylation catalysis.

The reactivity of low-valent metal carbonyls is greatly broadened by oxidative addition reactions. In these conversions, at the reaction of a substrate that contains a covalent bond (H-H, C-H, C-X, etc.), the metal center increases its oxidation state, coordination number, & electron count by two. For instance, with halogens they yield halocarbonyl species, whereas hydrogen can produce metal hydride species if appropriate conditions are met. Reductive elimination is the microscopic reverse of oxidative addition as two the ligands come together and leave the metal center, lowering the metal oxidation state & coordination number in the process. Such transformations are central to catalytic cycles, typically comprising the product-forming step. For instance, metal acyl complexes can reductively eliminate a hydride ligand to liberate aldehydes or ketones. Metal carbonyls are pivotal to catalysis, stoichiometric activation of small molecules. Low-valent metal carbonyls activate dihydrogen, oxygen, alkenes, alkynes & carbon dioxide under mild conditions. The most common activation steps involve an initial coordination of the substrate to a coordinatively unsaturated metal center, followed by a bond cleavage or rearrangement. Hydroformylation (oxo synthesis) is among the most industrially relevant reactions catalyzed by metal carbonyls. The process transforms alkenes, carbon monoxide & hydrogen into aldehydes that have a carbon atom added. Hydroformylation was first discovered with cobalt carbonyls, & now that modern industrial hydroformylation processes generally utilize rhodium carbonyl catalysts to access increased selectivity & activity in milder conditions with the assistance of phosphine the ligands.

Metal carbonyl-catalyzed water-gas shift reactions show their promise for producing hydrogen & utilizing CO. In this process carbon monoxide reacts with water to generate carbon dioxide & hydrogen. Iron carbonyls are active for this transformation, especially in basic media & for the applications in hydrogen economy or the upgrading of synthesis gas. A wide range of carbonylation reactions are exhibited by the metal carbonyls, imparting groups of CO into organic substrates. In industrial settings, the Monsanto acetic acid process, in which methanol is carbonylated to acetic acid in the presence of a rhodium carbonyl catalyst, is often cited as an example. Related carbonylation chemistry can be extended to generate carboxylic acids, esters, & amides from a range of organic substrates. Electrophile reactivity of metal carbonyls leads to functionalized organometallics. For example, acylium ions react with metal carbonyls to give acylmetal products. Likewise, alkylation of the carbonylate anions affords alkyl metal carbonyl complexes, which may be precursors to further transformations.

Another relevant reaction pathway is nucleophilic attack on coordinated CO the ligands. The back-donation from the metal-insert center increases the electrophilicity of the CO carbon atom, & thus yields this active intermediate, which can easily undergo nucleophilic attack. Using this reactivity, one can generate metalloacyl species and, subsequently, C-C bond forming reactions of relevance to organic synthesis. Decarbonylation reactions are the removal of CO from organic substrates, usually aldehydes, by transition metal catalysts. Rhodium & iridium carbonyls are especially effective for this reaction, which has been utilized in the assembly of complex molecules. The reverse process—carbonylation—frequently uses the same catalytic systems in the presence of a pressure of CO. Reactions of coordinatively unsaturated intermediates formed via CO dissociation from metal carbonyls are photochemical in nature. The photogenerated species can take part in a wide variety of transformations, such as ligand substitution, oxidative addition, & small molecule activation. Photochemistry allows for detailed access to reactive intermediates under mild conditions & selective transformations inaccessible, or at least nontrivial, thermally. Metal carbonyl clusters exhibit a rich space of structural rearrangements and transformations. These processes can be classified into core expansion & contraction processes, which involve the addition or loss of metal atoms to the cluster(s) & skeletal rearrangements, which involve a geometrical rearrangement of metal atoms retaining the same nuclearity. Such dynamic behavior underscores the weaker bonding in metal clusters, as well as their potential for catalysis.

Controlled thermochemical reduction of metal nanocrystals are accessible via metal carbonyls. This method, called metal-organic chemical vapor deposition (MOCVD), is used in materials science & microelectronics. Many metal carbonyls are highly volatile, thus providing an ideal source for metals that can be deposited at a controlled rate to produce high-purity deposits. Reactions of Metal Carbonyls with Alkenes/Alkynes: π-complexes & metallacycles These conversions frequently generate catalytic cycles for alkene hydrogenation, isomerization, & polymerization processes. The Pauson-Khand reaction is also an example of synthetic utility; using a metal carbonyl (usually $Co_2(CO)_8$), cycloaddition between an alkyne, an alkene, & carbon monoxide give cyclopentenones. The metal carbonyls exhibit addition reactions with dihydrogen leading to metal carbonyl hydrides that are key intermediates in hydrogenation & hydroformylation catalysis. Such hydride complexes can participate in

Notes

further reactivity including the insertion of unsaturated substrates as well as reductive elimination processes that close catalytic cycles for the functionalization of organic substrates. Most metal carbonyls are protonated to give hydride complexes and, at least in some cases, molecular hydrogen. 2 & 3: in metal carbonyl complexes, the basicity of metal centers is directly proportional to their electron density, which varies depending on the metal & co-the ligands involved. The well known acid-base reactions outline the electronic characteristics of metal carbonyl complexes, as well as their possible catalytic action.

It has also been observed that metal carbonyls can participate in electron transfer reactions resulting in radical species with unique reactivity. For example, one-electron reduction can lead to 19-electron radical anions, whereas oxidation may give rise to 17-electron radical cations. Odd-electron species often show increased substitution kinetics compared to the 18-electron precursors, known as the radical mechanism of substitution. Beyond terminal and bridging modes of bonding, carbon monoxide coordination in metal complexes leads to semi-bridging interactions & to uncommon bonding geometries. Semi-bridging carbonyls where the CO ligand predominantly interacts with a single metal center, but in addition has a weaker bond to a second metal. These subtle bonding variations control reactivity & are prominent in the mechanisms of reaction involving multinuclear species. Introduction 3 Surprisingly, metal carbonyls are precursors for organometallic reagents such as iron carbonyl diene complexes. The formation of complexes such as $Fe(CO)_3$(diene) by the reaction of $Fe(CO)_5$ with conjugated dienes have been used as stoichiometric reagents in organic synthesis, especially for stereoselective transformations of unsaturated systems.

appreciate and comprehend ing surface interactions of metal carbonyls is important for heterogeneous catalysis. The surface chemisorption of CO on metals shows many similarities with these molecular metal carbonyls, having essentially the same modes of binding & infrared spectroscopic characteristics. These surface-bound species can be probed in detail using surface science techniques, providing a connection to homogeneous & heterogeneous catalysis. The metal carbonyls reactivity with CO_2 has drawn attention as a way of CO_2 utilization. Some low-valent metal carbonyls are known to activate CO_2 in reactions that result in insertion into metal-element bonds or reduction to carbon monoxide, formate, or methanol. Such transformations present promising routes to valorize this greenhouse gas into value-added chemicals. The C-H activation processes, which involve cleavage of unreactive C-H bonds at the metal center, occurs for metal carbonyls. This addressable reactivity provides a route to hydrocarbon functionalization & has important consequences for synthetic methodology & studies of fundamental bond activation mechanisms. Metal carbonyls are also readily photolytically activated to produce very reactive fragments that readily insert into C-H bonds.

This indicates that the metal carbonyls undergo fluxional behavior that can also inform on their dynamic structures. However, intramolecular rearrangements, such as the Berry pseudorotation in $Fe(CO)_5$, make certain positions equivalent on the NMR timescale, even though they are geometrically distinct. & that interplay impacts reactivity patterns & spectroscopic characteristics, particularly in variable-temperature NMR experiments. In summary, metal carbonyl complexes lie at the foundation of organometallic chemistry, displaying abundant structural diversity, unusual spectroscopic characteristics, & diverse reactivity. Their distinctive bonding characteristics have deepened our fundamental knowledge of chemical bonding, whereas their reactions underpin many industrially important catalytic processes. These compounds range from simple homoleptic carbonyls that were first discovered in the late 19th century to complex mixed-ligand & cluster species that are studied to this day, motivating innovations in catalysis, materials science, & synthetic methodology. Through the interlinked study of metal-carbonyl species by experiment & theory, the complexity & richness of such interactions have been revealed, making metal-carbonyls a paradigmatic archetype for the constantly adapting & sophisticated field of coordination chemistry.

5.3 Transition Metal-Nitrosyl Complexes

Bonding & Structure of Nitrosyl Complexes

IntroductionTransition metal-nitrosyl complexes comprise one of the most intriguing & thoroughly explored aspects of coordination chemistry, with important implications ranging from the elementary theories of chemical bonding to technological applications in catalysis, materials science, & biology. One of the most versatile the ligands in terms of coordination chemistry is the nitrosyl ligand (NO) with respect to transition metals, owing to its dynamic coordination behaviour, which poses a persistent challenge to classical bonding concepts. The conflicting electronic attributes of the NO group, & in particular, its non-innocent nature, engender unique structural & reactivity trends that set metal-nitrosyl chemistry apart from other branches of coordination chemistry. Metal-nitrosyl complexes have been the focus of extensive theoretical and experimental studies of bonding since the advent of coordination chemistry. The initial description of IVCDR was relatively simple, but the astronomical development of spectroscopic techniques & computational power has allowed to thoroughly investigate the IVCDR region. The nitrosyl ligand, with its unpaired electron, is capable of several different coordination modes to transition metals, with varying geometric & electronic parameters. The two main coordination modes are linear (M-N-O) & bent (M-N-O)

Notes

geometries, with essentially distinct electronic interactions between the metal & the NO ligand. In the linear geometry characteristic of {M-NO}^6 complexes (in accordance with Enemark-Feltham nomenclature), the metal-nitrogen-oxygen angle is near 180° & the bonding is commonly described in terms of a formalism wherein NO^+ (nitrosonium ion) donates to a metal center. This gives rise to a configuration where filled orbitals dπ of the metal interact with empty π* antibonding orbitals of NO^+, leading to a synergy such as that which exists in metal complex carbonyls. This π-acceptor strength of the NO^+ ligand induces substantial electron density back donation to the metal, resulting in stabilization of lower oxidation states of metals in complexes. Linear nitrosyl complexes consistently exhibit shorter M-N bond distances than the corresponding bent complexes in X-ray crystallographic studies, consistent with the stronger binding elements associated with multiple bond character in these systems.

In contrast, bent nitrosyl complexes, analogous to {M-NO}^8 systems, commonly exhibit metal-nitrogen-oxygen angles between 120° & 140°. In such complexes, the metal has more complicated bonding than just the metal reacting with NO^- (and NO2^-). The observed bent geometry results from the electron-withdrawing functionalization of the ligand nitrogen atom, which favors population of the 9* antibonding orbitals of the NO ligand & consequently lowers the bond order of the N−O bond & generates a lone pair on the nitrogen atom. The electronic nature gives rise to a almost exclusive σ-donation from the nitrogen lone pair to the metal and a weaker π-acceptor capacity than that of the linear coordination mode. Bent nitrosyl complexes are therefore more common in complexes with a metal centre in an oxidation state that is higher than unity, which is able to accommodate the additional electron density from a NO^- ligand. The difference between the linear and bent geometries, however, is an idealized view of metal-nitrosyl bonding. Most importantly however, many complexes do have an intermediate angle which manifests a continuum of electronic states between the NO^+ & NO^- formulations. The Enemark-Feltham notation, where metal-nitrosyl complexes are termed {M(NO)x}^n (in which case, n is equal to the sum of the metal d electrons & the π* electrons contributed by the NO the ligands), has proven to be the most effective way to conceptualize the electronic structure without forcing a formal assignment of oxidation states to the metal & nitrosyl portions of the molecule. Emphasizing the total electron count of the metal-nitrosyl unit, this approach recognizes the lack of a well-defined oxidation state in such elaborate ligand coordination spheres. In addition to the simple linear & bent coordination modes, nitrosyl the ligands can bond via more complex arrangements. Bridging nitrosyls, in which the NO group tethers two or more metal centers together, are structurally diverse with μ-η1:η1-NO (bound through N to both metals), μ-η1:η2-NO (bound through N to one metal & side-on to the other), & μ-η2:η2-

NO (side-on bound to both metals) geometries. This bridging behavior is important in polynuclear metal complexes & cluster compounds & can be a significant structural contributor in catalytic intermediates.

Notes

Advanced spectroscopic techniques play an important role in the characterization of metal-nitrosyl complexes. Infrared spectroscopy gives insights into the nature of the M-NO bonding, & the NO stretching frequency (νNO) is a sensitive probe of the electronic state of the nitrosyl ligand. TheoOrganic Nitrosyl ComplexesThe chemical structure of a nitrosyl complex consists of one or more nitrosyl the ligands (NO+), a N + O bond, which forms when N, O- from a nitrogen atom in a nitrosyl ligand donate oxygen to the nitrogen atom of another nitrosyl ligand, & the N-O bond length of nitrosyl complexes are characteristic of these complexes. Linear nitrosyl complexes generally show higher ν_NO values (1650-1900 cm^-1) than bent nitrosyl complexes (1400-1650 cm^-1) due to the N-O bond strength in the former being stronger than in the latter. X-ray crystallography is still the gold standard for elucidating the geometric parameters of metal-nitrosyl complexes, though the electronic structure & oxidation states can also be deduced using complementary techniques such as electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), & X-ray absorption spectroscopy (XAS). DFT computations, & more elaborate ab initio methods, have greatly aided in the appreciate and comprehend ing of metal-nitrosyl bonded interactions. These theoretical tools have yielded insight into the factors influencing preference for linear vs.bent geometries, the characteristics of the metal-nitrosyl bonding orbitals, & the energetics of different coordination modes. Similarly, recently, computational studies have highlighted the importance of relativistic effects & spin-orbit coupling in heavy metal-nitrosyl complexes which add further complexity to their electronic structure. The coordination sphere of meta-nitrosyl complexes can be further diversified structurally following coordination of other the ligands6. Although this influence is attributed primarily to the nitrosyl ligand trans through its scope effect, the linear geometry of the nitrosyl moiety also plays a substantial role in binding behavior & is responsible for the elongation of metal to ligand bonds within the metal–nitrosyl complex, even resulting in complete loss of the ligands bound trans to the nitrosyl ligand. In contrast, the electronic & steric characteristics of alternative the ligands have been shown to tune the binding mode of the nitrosyl group, & thus provide a way to control the reactivity & characteristics of the complex. The versatility of this system originates from the interaction between the nitrosyl ligand & the chemical surroundings in the coordination environment, which can also be tuned to optimize almost any desired functional property.

Synthesis & Reactivity

Notes

The methods for the preparation of transition metal-nitrosyl complexes are extremely diverse, reflecting the varying coordination preferences of the nitrosyl ligand in the transition metal series. Direct reactions with nitric oxide gas are the simplest & most straightforward method, & this or similar routes have been primarily employed for metal complexes with open coordination sites or labil the ligands. For example, the classical synthesis of sodium nitroprusside, $Na_2[Fe(CN)_5NO]$ is performed by reacting sodium hexacyanoferrate(II) with sodium nitrite in an acidic environment, producing NO in situ that subsequently coordinates to the iron center. This direct methodology has been adopted in a range of metal systems, providing important information regarding the kinetics & thermodynamics of NO coordination. Other synthetic approaches rely on the use of nitrosyl transfer agents, which are able to transfer the NO group to a metal center without needing gaseous NO: the most widely used nitrosyl transfer reagents are nitrosonium salts (NO^+X^-, where X^- are BF_4^-, PF_6^-, SbF_6^-), organic nitrites (RONO), nitrosyl halides (NOX, where X is a halogen) or nitrous acid (HNO_2). This access provides a milder, more controlled route to introduce the nitrosyl group compared to NO gas reactions, & generally increased selectivity. For instance, the reaction of ruthenium complexes with nitrosonium tetrafluoroborate in acetonitrile gives a convenient access to ruthenium-nitrosyl species that act as general precursors for further synthetic elaboration.

A second important class of synthetic methods for metal-nitrosyl complexes involves redox-based approaches. These protocols either rely on the reduction of nitrogen oxides (e.g., NO_2^-, NO_3^- or N_2O) bound to a metal center, or the oxidation of nitrogenous the ligands (e.g., NH_3, NH_2OH or N_2H_4) co-ordinated to the metal. A common touchpoint on the reduction pathway is the reaction of metal complexes with nitrite salts under suitable conditions—where nitrite gets reduced to NO, which stays coordinated to the metal. In contrast, the oxidation route is exemplified by the conversion of coordinated hydroxylamine to nitrosyl in some iron & ruthenium complexes. These redox-based strategies frequently access metal-nitrosyl species with unique oxidation states or coordination geometries that may be difficult to obtain through simple coordination of NO. Another level of complexity—and opportunity—arises in the synthesis of polynuclear metal–nitrosyl complexes. In many cases, bridging nitrosyl the ligands can be accessed by way of controlled oligomerization involving the respective mononuclear precursors, frequently aided by partial metallation reduction. Another approach is the selective coordination at certain metal sites of NO or nitrosyl transfer agents to preformed polymetallic frameworks. The formation of heterometallic systems with bridging nitrosyls can be a challenging task, as control over the reaction conditions must be exerted to prevent disproportionation or rearrangement, but will grant access to materials with novel electronic

& magnetic characteristics resulting from metal-metal interactions mediated by the NO bridge.

In recent years, synthetic approaches to metal-nitrosyl complexes have increasingly focused on controlling the secondary coordination sphere—that is, the non-covalent environment that encompasses the metal-nitrosyl unit. These hydrogen bonding, π-stacking, & other supramolecular interactions can drastically alter the geometric & electronic characteristics of the coordinated nitrosyl, which can in turn affect its reactivity. The introduction of hydrogen bond donors which are positioned to interact with the oxygen atom of the nitrosyl ligand can for instance stabilize the bent coordination mode by accepting electron density from N-O π* orbitals. These approaches are inspired by metalloenzymes containing metal-nitrosyl sites, where the protein microenvironment modulates the characteristics of the metal-NO unit for particular biological functions. The reactivity of transition metal-nitrosyl complexes is remarkably diverse, involving nitrosyl ligand-centered transformations & metal-centered reactions modulated by the electronic characteristics of the nitrosyl. Indeed, as the NO ligand is redox non-innocent, much of this reactivity was underpinned by the ability of the nitrosyl to shuttle between NO^+, NO•, & NO^- forms to suit the electronic needs of the reaction. This versatility allows metal-nitrosyl complexes to exhibit both one- & two-electron behavior to function as useful reagents in organic synthesis, catalysis, & materials chemistry. A direct nucleophilic attack at the nitrogen atom of the coordinated nitrosyl is a basic pattern of reactivity, particularly common for M-N-O complexes having a linear arrangement & with nitrosyl bearing substantial NO+ character. Nucleophiles including alcohols, amines, & hydride donors can add to the electrophilic nitrogen, forming derivative the ligands in the form of N-alkoxy, N-amino, or N-hydroxy nitrosyls. For example, the transitions have been explored in-depth for nitroprusside and its related iron-nitrosyl systems, in which the nucleophilic addition products frequently exhibit unique spectroscopic features, showing greater stability than their parent nitrosyl complexes. The nucleophile reactivity is tunable by metal center & cothe ligands, granting spatial & kinetic control over the addition process.

Less common is electrophilic attack at the oxygen atom of the nitrosyl ligand in complexes that favor the bent coordination mode, in accord with having a partial negative charge on the oxygen in the NO^- formulation. This pattern of reactivity is seen for some late transition metal complexes in which Lewis acids or proton donors can coordinate to nitrosyl oxygen to facilitate N-O bond cleavage in suitable conditions. Susceptibility to electrophilic attack is directly proportional to the metal-nitrogen-oxygen angle, with more acute angles generally correlating with increased electrophile reactivity. Redox

Notes

transformations of metal-nitrosyl complexes represent an especially fertile realm of reactivity. A reduction can be more favorable towards the metal center or the nitrosyl ligand depending on their frontier orbitals relative energy levels. The classic coordination mode switches from linear to bent & is associated with a large red shift in the N-O stretching frequency upon nitrosyl ligand reduction. Coordinated nitroxyl (HNO), or even hydroxylamine (NH_2OH) derivatives can be formed upon multiple reductions. Alternatively, oxidation processes can induce the conversion from bent to linear nitrosyls, & in more extreme cases induce nitrosyl dissociation or conversion into coordinate nitro (NO_2^-) or nitrito (ONO^-) the ligands. Interconversion between these different species of nitrogen oxides at metal centers provides strong models for biological nitrogen oxide metabolism & chemical nitrogen oxide abatement processes in industry.

When it comes to the photochemical reactions of metal-nitrosyl complexes, they have been greatly focused, especially toward the construction of photoactive materials & phototherapeutic agents. For example, irradiation with the right wavelengths can induce the dissociation of NO from the metal center, which has been applied in photodynamic therapy, where controlled release of NO in biological systems can initiate desired physiological responses. The photochemistry of metal-nitrosyls is strongly influenced by the type of excited states accessible upon irradiation, with markedly different outcomes depending on whether MLCT, LMCT or IL transitions are the primary driving forces of the chromophore. Although time-resolved spectroscopic methods brought important information on the dynamics of these photochromic transformations, including details on short-lived intermediates along the respective reaction pathways & spin crossings confirmed by intersystem crossing between different spin states. Owing to their redox characteristics, metal-nitrosyl complexes can undergo reactivity toward small molecules such as dioxygen (O_2), carbon monoxide (CO), & olefins, making them relevant in a number of catalytic applications. Interaction with O_2 results in nitrosyl oxidation to coordinated nitrite or nitrate, yet the resulting species in some cases is more complex due to N-O bond cleavage & reassembly. In this case, the coordination site for the metal is under competition with CO in those reactions, & the relative binding strengths of NO & CO dictate the winner. Such competitive binding has been harnessed in CO sensing platforms predicated on metal-nitrosyl complexes whose CO-M displacement of NO is accompanied by a measurable spectroscopic or electrochemical signal. From olefins, we would expect simple coordination competition or more complex transformations involving either nitrosylation of the olefin, or modifications thereafter mediated by the metal-nitrosyl unit.

Notes

Nitrosyl ligand transfer reactions involving migration of the NO group between metal centers constitute an important class of transformations with implications for synthetic applications & biological processes (1–3). These metal-to-metal transfers maybe direct, & mediated by multinuclear intermediates formed when the nitrosyl bridges between the donor and acceptor metals prior to transfer completion. Or the transfer could also occur by dissociation of the NO followed by recapture of NO at a separate metal site, (for example for systems in which the metal–nitrosyl bond is fairly labile). The thermodynamics & kinetics of nitrosyl transfer are governed by factors such as the relative NO affinities of the metals involved, the geometric constraints of the coordination environments, & any auxiliary the ligands that can stabilize or destabilize the metal-nitrosyl bonds. Metal-nitrosyl complexes have found applications in catalysis across fields, such as organic synthesis, environmental remediation, & energy conversion. In organic synthesis, metal-nitrosyls act as either catalysts or reagents for nitrosylation reactions, whereby the NO group is introduced into organic substrates with a certain degree of selectivity. In particular, ruthenium & iron nitrosyl complexes have emerged as efficient catalysts for the nitrosylation of aromatic compounds, olefins & activated C-H bonds. More specifically, in environmental settings metal-nitrosyl entities also play a significant role as intermediates during catalytic denitrification of nitrogen oxides (NO_x) to harmless products (e.g., N_2), a paradigm contributing to air pollution abatement. Electrocatalytic nitrite reduction to ammonia, an environmentally & energetically relevant transformation, is often associated with reduced metal–nitrosyl intermediates & their stability/reactivity determines the efficiency & selectivity of the overall transformation. More recently, the biological chemistry of metal-nitrosyl complexes has become a focus area since nitric oxide has been identified as an important signal transduction molecule in other physiological processes. Bacterial natural metalloenzymes (e.g nitric oxide synthase (NOS) & soluble guanylate cyclase (sGC)) as well as heme proteins (e.g myeloperoxidase (MPO), cytochrome P450, & guanylate cyclase) in higher eukaryotes interact with NO to yield metal-nitrosyl species that mediate NO's biological action or are involved in its metabolism. Thus, synthetic metal-nitrosyl complexes are important models for these biological systems & can shed light onto the structural & electronic requirements which dictate NO binding & activation in the protein milieu. Furthermore, metal-nitrosyl complexes built to liberate NO upon the application of certain physiologically relevant conditions (for example, low pH, changed redox atmosphere, & irradiation with light) can be considered as a promising class of NO donor drugs which potentially could serve as therapeutics for diverse diseases from cardiovascular diseases to malignancies.

Notes

Metal-nitrosyl complexes interact with biological targets beyond simple NO delivery. Some metal–nitrosyl complexes undergo transnitrosylation reactions, whereby the NO^+ equivalent is transferred to biological thiols to generate S-nitrosothiols (RSNOs), which can function as endogenous NO carriers & storage reservoirs. The functional consequences of such reactivity are relevant to the therapeutic utility of metal-nitrosyl complexes, as well as to their potential toxicity, because excessive S-nitrosylation of protein thiols can alter normal cellular physiology. Metal-nitrosyl complexes represent an invaluable class of bioactive molecules that allow the specific targeting, regulation, & manipulation of endogenous - & postsynthetically modified - metal:sulfur clusters whose intrinsic affinity for NO lies in the low micromolar range and thus can be readily modulated, making them excellent candidates for specific mediators of NO-dependent signaling pathways. The advances in the chemistry of metal-nitrosyl complexes during the past decades have been greatly facilitated by new development of characterization techniques & theoretical frameworks. Methods like X-ray absorption spectroscopy (XAS) or nuclear resonant vibrational spectroscopy (NRVS) based on synchrotron radiation can give accurate insight into the electronic structure and vibrational characteristics of metal-nitrosyl units even embedded in complex matrix such as proteins or heterogeneous catalysts. Direct observation of the dynamics of photoinduced processes taking place in metal-nitrosyl systems (including reaction intermediates & energy dissipation pathways) is obtained using time-resolved spectroscopic techniques such as femtosecond infrared & ultraviolet-visible (UV-vis) spectroscopy. Computational studies, especially those involving multiconfigurational & relativistic calculations, have been increasingly employed to refine current knowledge on bonding & reactivity in metal-nitrosyl species & predict spectroscopic characteristics & mechanisms.

Turning to future directions in metal-nitrosyl chemistry, there are several promising paths forward. Multinuclear metal-nitrosyl complexes with tunable electronic coupling between metal centers may provide both a platform for buildings such high-performance materials & a new class of compounds with unusual magnetic, optical, or conductive characteristics. Metal-nitrosyl units incorporated in metal-organic frameworks (MOFs) or covalent organic frameworks (COFs) would allow new strategies for gas separation, sensing & heterogeneous catalysis. * Biocompatible scaffolds (proteins, peptides, nanoparticles, etc)) can be paired with metal-nitrosyl complexes to allow for specific targeting of NO release in therapy, potentially addressing the shortcomings of current NO donor systems. Despite this direct manifest, it also highlights the needs of investigating metal-nitrosyl chemistry not only in axiomata transition metals, but also in main group elements, lanthanides & actinides, which will yield unique bonding settings & reactivity trends. Overall, transition metal-nitrosyl complexes are a vibrant & dynamic area of research at the nexus of inorganic chemistry, materials science, catalysis, & biochemistry, These last finalized reactivity instincts when bonded to a nitrosyl ligand which may also represent a redox non innocent ligand & exhibit a non classical density of binding modes proving to showcase both basic & applied studies. Over recent years, our comprehension of the fundamental principles governing metal-nitrosyl systems has benefited from new synthetic methodologies, characterization techniques, & theoretical frameworks, opening new opportunities for the application of metal-nitrosyl systems in addressing issues from sustainable chemistry to human health. The new developments in metal-nitrosyl chemistry make an intriguing combination of scientific, technological & biomedical relevance, reflecting modern-day challenges.

Notes

5.4 Dinitrogen & Dioxygen Complexes

Two of the most predominant gases in the atmosphere of Earth are molecular dinitrogen (N_2) & dioxygen (O_2), which together comprise nearly 99% of dry air. Notwithstanding their prevalence, these gases are strikingly unreactive at ambient conditions owing to their stable triple (N≡N) & double (O=O) bonds. The inherently stable N_2 (bond dissociation energy 941 kJ/mol) & O_2 (bond dissociation energy 498 kJ/mol) do by nature have longer lifetime. Such stability represents a major hurdle for biological systems & industrial processes that wish to use these molecules as feedstocks. Nature has honed specialized metalloenzymes to trigger these molecules under soft conditions often used in the industry, however, tends to demand also high temperature & pressure. Investigating how these abundant but kinetically inert molecules can be coordinated, activated, & converted by transition metal complexes has been at the forefront of coordination chemistry, through which both fundamental science & practical applications have been significantly enabled.

Dinitrogen Complexes

The first dinitrogen complexes, the compound $[Ru(NH_3)_5(N_2)]^{2+}$, was reported by Allen & Senoff in 1965 & is considered a landmark event in coordination chemistry. Many techniques have since been developed to prepare these metal-dinitrogen complexes, illustrating that transition metals can indeed bind N_2 in a variety of modes. These methods include:

Direct Coordination of N_2: Many low-valent, electron-rich transition metal complexes are capable of directly binding of diatomic atmospheric N_2. This result usually requires the generation of a coordinatively unsaturated metal centre that is capable to bind N_2. For instance, $[RuCl_2(PPh_3)_3]$ reacts with N_2 in the presence of reducing

Notes

agents to afford $[Ru(N_2)(PPh_3)_4]$. Displacement Reactions (N_2 Displaces Weakly Bound The ligands): Solvents, ethylene, or dihydrogen are weakly bound the ligands that can be displaced by N_2. A canonical example of this behaviour in the context of a complex of Shilov comes from the displacement of coordinated solvent: upon the addition of N_2 to [Mo(THF)(dppe)$_2$] the solvent THF can be replaced, to yield [Mo(N_2)$_2$(dppe)$_2$].

Decomposition under N_2 atm: Metal complexes can indeed be reduced under N 2 to bind N 2 at the reduced metal center. An example given is the reduction of [$MoCl_4$(phosphine)$_2$] with sodium amalgam under N_2 to produce [Mo(N_2)$_2$(phosphine)$_2$]. Protonation of azide complexes: N_2 complexes can be prepared from protonation of metal azide complexes known from the literature, with loss of N_2H_4. By using solid N_2 rather than gasphase N_2, this provides a route to N_2 complexes without directly using gasphase N_2.

Photochemical Methods: Contains precursors that can undergo photolysis in the presence of N_2 to produce N_2 complexes. Photolysis of [$Mn_2(CO)_{10}$] under N_2 produces [$Mn(CO)_4(N_2)Mn(CO)_4$]. Such synthetic methodologies have afforded a broad range of transition metal N_2 complexes, particularly well-developed for Group 6 (Cr, Mo, W), Group 7 (Mn, Re) as well as Group 8 (Fe, Ru, Os) metals across transition metals. The stability & reactivity of the resulting N_2 complexes is strongly dependent on the choice of ancillary the ligands. In particular, phosphines bearing donating substituents are excellent at increasing metal center electron density & backbonding to the N_2 ligand to stabilize M-N_2 bonds.

Bonding in Dinitrogen Complexes

Metal-dinitrogen complexes exhibit a beautiful interplay between σ-donation & π-backbonding interactions in their bonding. In contrast to CO in which excellent π-acceptor character, N_2 is a poor σ-donor & weak π-acceptor, rendering its coordination to metals less energetically favored. The bonding model can be defined in the following way:

- σ−Donation: The filled σ-symmetry lone pair orbital on the nitrogen atom donates electron density to an empty metal d-orbital of appropriate symmetry. This donation is weak comparatively to other donor the ligands.

- π-Backbonding: Occupied metal d-orbitals of π-symmetry donate electron density to the empty π* antibonding orbitals of N_2. This backbonding serves the purpose of strengthening the M-N bond while weakening the N-N bond that is essential for activation.

The strength of these interactions governs the coordination mode of N_2, which can bind to metals in multiple fashions:

• End-on Terminal (η^1): The most frequently observed mode where N_2 coordinates through one nitrogen atom only resulting an M-N-N carbon between N_2. NNO ligand types: $[Ru(NH_3)_5(N_2)]^{2+}$ $[Fe(N_2)(dppe)_2]$.

• End-on Bridging (μ-η^1:η^1): N_2 connects the two metal centers via its terminal nitrogen atoms. This is similar to what is seen with $[(CO)_5Mn(N_2)Mn(CO)_5]$ & encourages the activation of N_2.

• Side-on (η^2): Both nitrogen atoms bridge to the same metal center in a side-on mode. This rare coordination mode has been reported on some early transition metal complexes & ultimately contributes to the instability of the N-N bond.

• Side-on Bridging (μ-η^2:η^2): N_2 bridges through two metal centers in side-on configurations leading to four-membered rings. Such bonding leads to considerable N-N bond activation.

N_2 activation is quantified by several parameters:

• N-N Bond Length: The N-N bond length in free N_2 is 1.098 Å, which increases upon coordination, with values in the 1.10–1.20 Å range for terminally bound N_2 but >1.40 Å for highly activated side-on complexes.

• N−N stretch: The free N_2 molecule has a stretching frequency of 2331 cm^{-1}. This frequency drops on coordination, to around 1900-2100 cm^{-1} for terminally bound complexes, & to 50 million tons year−1).

• Propylene Oxide Production: Pathways for Propylene Oxide production that rely on O_2 activation includes the chlorohydrin pathway, & direct oxidation pathways.

• Acetaldehyde Production: The Wacker process involves the oxidation of ethylene to acetaldehyde, employing a $PdCl_2/CuCl_2$ catalyst system in the presence of a terminal oxidant (O_2).

• Fine Chemicals & Pharmaceuticals: Selective oxidation is a key reaction in the preparation of numerous high-value products & there is a growing focus on catalytic methods using O_2 as a clean oxidant.

Conventionally, these processes are heavily dependent on heterogeneous catalysts carried out at high temperatures & pressures. Nonetheless, interest in bio-inspired O_2 activation has turned to the development of more selective & energy-efficient catalytic systems.

Biomimetic Methods of Oxidation in the Society

Simplified biological O_2 activation has inspired the design of biomimetic catalysts to be used in industrial oxidation reactions:

Notes

- Metalloporphyrin Catalysts: Synthetic metalloporphyrins, particularly iron & manganese complexes, have been utilized in a variety of oxidation reactions, including alkane hydroxylation, epoxidation, & sulfoxidation.
- Non-Heme Metal Catalysts Complexes of iron & manganese with nitrogen-donor the ligands have been explored as transition metal catalysts for a wide variety of oxidative transformations, particularly in the context of C-H functionalization.
- Copper Systems: Dinuclear copper complexes have been designed & synthesized to hydroxylate phenols (and similar transformations) with inspiration by tyrosinase.

Polyoxometalates have the potential to activate O_2 for selective oxidation reactions with advantages in stability & recyclability.

It is hypothesised that biomimetic catalysts would be more selective & function under milder conditions with less environmental impact than traditional industrial catalytic processes, & they have the potential to work in green solvents. The incorporation of these catalysts in sustainable oxidation technologies is an active & active research direction.

Practical Applications of Metal π Complexes in Chemistry

Metal Carbonyl Complexes

Metal carbonyl complexes are widely utilized in industrial catalysis, especially in hydroformylation processes that generate aldehydes from alkenes, carbon monoxide, & hydrogen. The oxo process is a significant application of homogeneous catalysis in the chemical industry, yielding millions of tons of aldehydes each year, which function as intermediates for plasticizers, detergents, & other vital industrial chemicals. The meticulous regulation of steric & electronic characteristics in altered metal carbonyl catalysts has facilitated exceptional selectivity & efficacy in these reactions. Moreover, metal carbonyls function as important precursors in organometallic synthesis, facilitating the formation of coordinatively unsaturated metal centers via regulated CO dissociation. This feature has been utilized in the creation of catalysts for asymmetric hydrogenation, carbonylation, & C-C bond formation processes, which are essential in pharmaceutical & fine chemical synthesis. The distinctive IR spectroscopic characteristics of metal carbonyls render them excellent molecular probes for investigating electronic effects in metal complexes, offering insights into the nature of metal-ligand interactions that inform catalyst design.

Transition Metal-Nitrosyl Complexes

Notes

Transition metal-nitrosyl complexes have become important in medical chemistry & biochemistry because of their function in the storage & distribution of nitric oxide (NO). These complexes can release nitric oxide under particular physiological situations, prompting their exploration as possible therapeutic agents for cardiovascular disorders, cancer treatment, & antimicrobial uses. The capacity of specific ruthenium & iron nitrosyl complexes to release NO in a regulated fashion has led to their advancement as agents for photodynamic treatment, wherein light-activated NO release can provoke selective cell death in tumor tissues. Nitrosyl complexes in materials science are utilized in the creation of photochromic materials & molecular switches, leveraging the reversible binding of nitric oxide to transition metals. The unique electrical & structural alterations resulting from NO coordination render these complexes significant for investigating fundamental elements of metal-ligand interactions. Moreover, transition metal-nitrosyl complexes have been employed as catalysts in diverse organic transformations, such as the nitrosylation of aromatic compounds & selective oxidation processes, showcasing their versatility beyond biological applications.

Dinitrogen & Dioxygen Complexes

Dinitrogen complexes signify a crucial advancement in sustainable chemistry, having significant ramifications for artificial nitrogen fixation & ammonia production. In contrast to the energy-intensive Haber-Bosch method that now prevails in industrial ammonia synthesis, dinitrogen complexes present prospective pathways for nitrogen fixation under moderate conditions, which could transform fertilizer production & tackle global food security issues. Recent advancements in molecular dinitrogen complexes of molybdenum, iron, & other transition metals have illustrated the viability of N_2 activation & functionalization under ambient circumstances, advancing the development of biomimetic nitrogen fixation systems inspired by nitrogenase enzymes.

Preparation: i) Metal dinitrogen complexes can be prepared via many routes, but direct formation from dinitrogen is very common. For example:

[CoH2(PPh3)3] + N2 → [Co(PPh3)3(N2)] + H2

[RuH4(PPh3)3] + N2 → [RuH2(PPh3)3(N2)] + H2

[CoH3(PPh3)3] + N2 → [CoH(PPh3)3(N2)] + H2

[FeH4(PEtPh2)3] + N2 → [FeH2(PEtPh2)3(N2)] + H2

ii) From compounds containing chains of nitrogen atoms:

Notes

$[Ru(NH_3)_5L]^{n+} + N^- \rightarrow [Ru(NH_3)_5(N_2)]^{2+} + L$

Bonding: In order to rationalize the nature of the bonding between the metal center and the N_2, we must understand the bonding within the dinitrogen ligand first. The molecular orbital diagram for N_2 is given below.

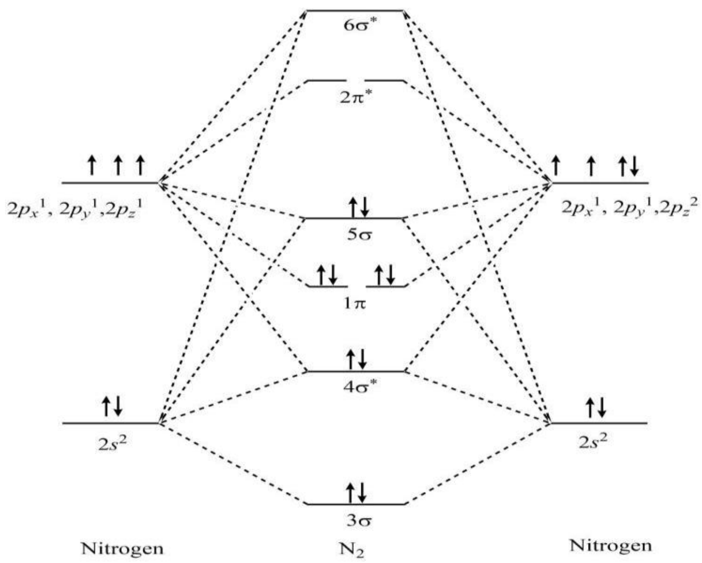


Figure 20. The molecular orbital diagram of dinitrogen molecule.

Reactions: i) The displacement of dinitrogen ligand by some other groups:

trans– $[Mo(N_2)_2(dppe)_2] + 2C_2H_4 \rightarrow$ *trans*– $[Mo(C_2H_4)_2(dppe)_2] + 2N_2$

trans– $[Mo(N_2)_2(dppe)_2] + 2RNC \rightarrow$ *trans*– $[Mo(RNC)_2(dppe)_2] + 2N_2$

trans– $[Mo(N_2)_2(dppe)_2] + 2CO \rightarrow$ *trans*– $[Mo(CO)_2(dppe)_2] + 2N_2$

ii) Reactions of Ligating N_2 with Lewis Acids:

$[ReCl(N_2)(PMe_2Ph)_4] + [Mo(Cl_4)(THF)_2]$

CH_2Cl_2, MeOH [(PMe Ph) ClReN MoCl (OMe)]

→−−−−−−−−−−−−→ 2 4 2 4

[ReCl(N2)(PMe2Ph)4] + [MoCl4(PPh3)2] → [MoCl4{(N2)ReCl(PMe2Ph)4}2]

iii) Formation of metal-hydrazido complxes from ligating N2:

trans– [Mo(N2)2(dppe)2] + 2HCl → [MoCl(NNH2)(dppe)2]Cl + N2

THF

trans– [W(N2)2(dppe)2] + 2HBF4 →−−−−−→ [WF(NNH2)(dppe)2][BF4]

+ BF3. THF + N2

iv) Formation of carbon-nitrogen bonds:

[W(N2)2(dppe)2] + RCOCl + HCl → [WCl(N2HCOR)(dppe)2]Cl

[Mo(N2)(RCN)(dppe)2] + PhCOCl → [MoCl(NNCOPh)(dppe)2]

[Mo(N2)2(dppe)2] + RCOCl + HCl → [MoCl(N2HCOR)(dppe)2]Cl

Dioxygen complexes have significant uses in bioinorganic chemistry, functioning as models for oxygen-transport proteins such as hemoglobin & myoglobin. These complexes have facilitated comprehensive investigations into the mechanics of oxygen activation pertinent to various biological oxidation processes. Dioxygen complexes have been engineered as catalysts for selective oxidation processes in industrial settings, providing ecologically friendly alternatives to conventional oxidation procedures that typically depend on stoichiometric oxidants & produce significant waste. The capacity to regulate the reactivity of coordinated O_2 via ligand design has resulted in advancements in complex oxidative transformations, such as the selective hydroxylation of hydrocarbons & asymmetric epoxidation of olefins.

Preparation: i) Formation of a mononuclear dioxygen adduct with or without displacement of ligands

[IrCl(CO)(PPh3)2] + O2 ⇌ [IrCl(CO)(PPh3)2O2)]

[Co(DMG)2] + O2 + Pyridine → [Co(DMG)2(O2)(Pyridine)]

Notes

ii) Formation of a dimer or a binuclear dioxygen adduct:

$2[Rh(PPh_3)_2Cl] + 2O_2 \rightarrow [Rh(PPh_3)_2(O_2)Cl]_2$

$2[Co(histidine)_2] + O_2 \rightarrow [Co_2(histidine)_4(O_2)]$

iii) Oxidation of ligands with the oxidized ligand remaining coordinated:

$[Ru(PPh_3)_2(CO)_2(SO_2)] + O_2 \rightarrow [Ru(PPh_3)_2(CO)_2(SO_4)]$

iv) Displacement of free oxidized ligand:

$[Pt(PPh_3)_4] + 2O_2 \rightarrow [Pt(PPh_3)_2(O_2)] + 2Ph_3PO$

Bonding: The nature of bonding in metal-dioxygen complexes is usually evaluated by single-crystal X-ray crystallography, focusing both on the overall geometry as well as the O–O distances, which reveals the bond order of the O_2 ligand. However, in order to rationalize the initial idea of the metal-ligand bonding, we must understand the bonding within the dioxygen ligand first. The molecular orbital diagram for O_2 is given below.

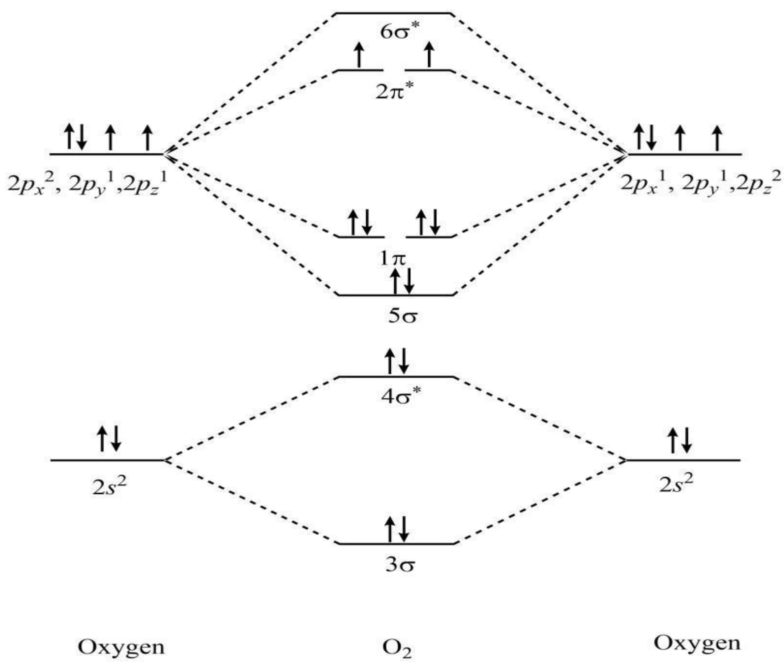


Figure 24. The molecular orbital diagram of the dioxygen molecule.

Tertiary Phosphines as The ligands

Tertiary phosphine the ligands have transformed homogeneous catalysis by their exceptional capacity to adjust the electronic & steric characteristics of transition metal complexes. The pioneering advancement of chiral phosphine the ligands such as BINAP by Noyori marked the commencement of a new epoch in asymmetric catalysis, facilitating the synthesis of single enantiomers of pharmacological intermediates with remarkable selectivity.

Notes

The first phosphine complexes were cis- and trans-[PtCl2(PEt3)2], reported by Cahours and Gal in 1870. Being a L-type ligand, the phosphines do not change the overall charge of the metal complex. These complexes may simply be prepared by the addition of phosphines to a coordinatively unsaturated metal precursor, or by ligand displacement of another L-type complex, such as a solvent molecule acting as a ligand. However, it should also be noted that the replacement of X-type ligand (1-electron donor neutral ligand) can also yield such complexes.

$[PdCl_2]_n + 2nPPh_3 \rightarrow n[PdCl_2(PPh_3)_2]$

$[Cr(CO)_6] + PPh_3 \rightarrow [Cr(CO)_5(PPh_3)] + CO$

$K_4[Ni(CN)_4] + 4PPh_3 \rightarrow [Ni(PPh_3)_4] + 4KCN$

$[Rh(PPh_3)_3Cl] \rightarrow [Rh(PPh_3)_2Cl] + PPh_3$

$[Pt(PPh_3)_3] + MeI \rightarrow [Pt(I)(Me)(PPh_3)_2] + PPh_3$

This innovation has revolutionized pharmaceutical manufacturing methods, enabling more efficient & environmentally sustainable production of several life-saving drugs. Phosphine-modified palladium catalysts have become essential in cross-coupling reactions, enabling carbon-carbon bond forms that were hitherto difficult or unfeasible in organic synthesis. The Buchwald-Hartwig amination, Suzuki-Miyaura coupling, & Negishi coupling processes, all reliant on phosphine the ligands, have significantly enhanced the synthetic chemist's repertoire & are now commonly utilized in the pharmaceutical, agrochemical, & materials sectors. In addition to conventional catalysis, phosphine complexes have been utilized in medicinal chemistry as anticancer drugs, with various molecules demonstrating encouraging efficacy against cisplatin-resistant malignancies. Water-soluble phosphine the ligands, such as TPPTS, have facilitated the creation of biphasic catalytic systems that merge the benefits of homogeneous catalysis with streamlined product separation, tackling a significant difficulty in commercial catalyst application. The ongoing advancement of phosphine ligand design, encompassing the creation of hemilabile phosphines, electron-rich alkylphosphines, & immobilized phosphine

Notes

systems, perpetually unveils new possibilities in sustainable chemical synthesis & green chemistry applications.

Multiple-Choice Questions (MCQs)

1. Metal π complexes are characterized by:

a) σ-bonding interactions only

b) Coordination of the ligands through π-electron systems

c) Ionic bonding between metal & ligand

d) Hydrogen bonding

2. Metal carbonyl complexes exhibit back-donation, which involves:

a) Ligand-to-metal π donation only

b) Metal-to-ligand π back-donation

c) Only σ bonding between metal & ligand

d) Free radical formation in the complex

3. Which spectroscopy is most commonly used to study metal carbonyl complexes?

a) UV-Visible spectroscopy

b) Infrared (IR) spectroscopy

c) NMR spectroscopy

d) Mass spectrometry

4. The M–CO bond strength in metal carbonyl complexes increases when:

a) The metal has a lower oxidation state

b) The metal has a higher oxidation state

c) The metal has no d-electrons

d) π-back donation is weak

5. Transition metal-nitrosyl complexes contain NO the ligands, which can bond as:

a) Linear (M–N≡O) or bent (M–N=O)

b) Only linear (M–N≡O)

c) Only bent (M–N=O)

d) Ionic bonds with metals

6. The metal-dinitrogen (M–N_2) bond is formed due to:

a) Only σ bonding between metal & nitrogen

b) Only π donation from nitrogen to metal

c) Both σ donation & π back-donation

d) Weak van der Waals forces

7. Which metal complex is crucial in biological nitrogen fixation?

a) $[Fe(CO)_5]$

b) $[MoFe_7S_9]$ cluster in nitrogenase

c) $[Cu(NH_3)_4]^{2+}$

d) $[PtCl_4]^{2-}$

8. Dioxygen complexes play an essential role in:

a) Photosynthesis

b) Oxygen transport in biological systems

c) Nucleic acid stabilization

d) Enzyme-free catalysis

9. Tertiary phosphines (PR_3) as the ligands are known for:

a) Strong π-acceptor characteristics

b) Their ability to form stable metal-ligand bonds

c) Weak σ-donor effects

d) Low catalytic activity

10. The Tolman cone angle describes:

a) The electronic effect of phosphine the ligands

b) The steric bulk of phosphine the ligands

c) The oxidation state of the metal

d) The π-back donation of CO

Short Answer Questions

1. What are metal π complexes, & why are they important in coordination chemistry?

2. Describe the structure & bonding in metal carbonyl complexes.

3. How does π-back donation affect the CO stretching frequency in IR spectroscopy?

Notes

4. Explain the difference between linear & bent nitrosyl complexes.

5. How do dinitrogen complexes help in biological nitrogen fixation?

6. What is the role of dioxygen complexes in biological systems?

7. Explain how tertiary phosphines (PR_3) act as the ligands in transition metal complexes.

8. What are the important reactions of metal carbonyl complexes?

9. Describe the spectroscopic methods used to study metal-nitrosyl complexes.

10. What is the Tolman cone angle, & how does it influence catalysis?

Long Answer Questions

1. Explain the structure & bonding in metal carbonyl complexes, including σ-donation & π-back bonding.

2. Describe the vibrational spectroscopy of metal carbonyl complexes, with an emphasis on IR spectroscopy trends.

3. Discuss the bonding, structure, & reactivity of transition metal-nitrosyl complexes.

4. Explain the preparation & bonding in dinitrogen complexes, with their significance in biological nitrogen fixation.

5. Describe the formation, bonding, & applications of dioxygen complexes in biological & industrial systems.

6. Explain the effect of metal oxidation state & ligand electronic characteristics on the stability of metal π complexes.

7. Discuss the preparation & reactivity of metal carbonyls, with reference to important industrial applications.

8. Explain the role of tertiary phosphines in catalysis, & compare their electronic & steric effects.

9. Compare & contrast metal-dinitrogen & metal-dioxygen complexes in terms of structure & bonding.

10. Explain the importance of π-acceptor the ligands (CO, NO, N_2, & O_2) in transition metal chemistry

Reference

Module 1: Theories of Metal Complexes

1. Cotton, F.A., Wilkinson, G., Murillo, C.A., & Bochmann, M. (1999). Advanced Inorganic Chemistry. 6th ed. John Wiley & Sons.
2. Figgis, B.N., & Hitchman, M.A. (2000). Ligand Field Theory and Its Applications. Wiley-VCH.
3. Miessler, G.L., Fischer, P.J., & Tarr, D.A. (2014). Inorganic Chemistry. 5th ed. Pearson.
4. Ballhausen, C.J. (1962). Introduction to Ligand Field Theory. McGraw-Hill.
5. Housecroft, C.E., & Sharpe, A.G. (2012). Inorganic Chemistry. 4th ed. Pearson Education.

Module 2: Spectral and Magnetic Properties of Metal Complexes

1. Drago, R.S. (1992). Physical Methods for Chemists. 2nd ed. Saunders College Publishing.
2. Lever, A.B.P. (1984). Inorganic Electronic Spectroscopy. 2nd ed. Elsevier.
3. Earnshaw, A. (1968). Introduction to Magnetochemistry. Academic Press.
4. Figgis, B.N., & Lewis, J. (1960). The Magnetochemistry of Complex Compounds. In Lewis, J., & Wilkins, R.G. (eds.), Modern Coordination Chemistry. Interscience.
5. Slichter, C.P. (1990). Principles of Magnetic Resonance. 3rd ed. Springer-Verlag.

Module 3: Reaction Mechanisms of Transition Metal Complexes – Part I

1. Tobe, M.L., & Burgess, J. (1999). Inorganic Reaction Mechanisms. Longman.
2. Wilkins, R.G. (1991). Kinetics and Mechanism of Reactions of Transition Metal Complexes. 2nd ed. VCH Publishers.
3. Jordan, R.B. (1998). Reaction Mechanisms of Inorganic and Organometallic Systems. 2nd ed. Oxford University Press.
4. Basolo, F., & Pearson, R.G. (1967). Mechanisms of Inorganic Reactions. 2nd ed. John Wiley & Sons.
5. Langford, C.H., & Gray, H.B. (1965). Ligand Substitution Processes. W.A. Benjamin.

Module 4: Reaction Mechanisms of Transi tion Metal Complexes – Part II

1. Marcus, R.A. (1985). Electron Transfer Reactions in Chemistry: Theory and Experiment. Nobel Lecture.
2. Taube, H. (1970). Electron Transfer Reactions of Complex Ions in Solution. Academic Press.
3. Hush, N.S. (1967). Intervalence-Transfer Absorption. Part 2. Theoretical Considerations and Spectroscopic Data. Progress in Inorganic Chemistry, Vol. 8.
4. Sutin, N. (1982). Nuclear, Electronic, and Frequency Factors in Electron Transfer Reactions. Accounts of Chemical Research.

Module 5: Metal π Complexes

1. Crabtree, R.H. (2014). The Organometallic Chemistry of the Transition Metals. 6th ed. John Wiley & Sons.
2. Elschenbroich, C. (2016). Organometallics. 3rd ed. Wiley-VCH.
3. Cotton, F.A., & Wilkinson, G. (1980). Advanced Inorganic Chemistry. 4th ed. John Wiley & Sons.
4. Collman, J.P., Hegedus, L.S., Norton, J.R., & Finke, R.G. (1987). Principles and Applications of Organotransition Metal Chemistry. University Science Books.
5. Tolman, C.A. (1977). Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis. Chemical Reviews.

MATS UNIVERSITY

MATS CENTER FOR OPEN & DISTANCE EDUCATION

UNIVERSITY CAMPUS : Aarang Kharora Highway, Aarang, Raipur, CG, 493 441

RAIPUR CAMPUS: MATS Tower, Pandri, Raipur, CG, 492 002

T : 0771 4078994, 95, 96, 98 M : 9109951184, 9755199381 Toll Free : 1800 123 819999

eMail : admissions@matsuniversity.ac.in Website : www.matsodl.com