DIRECTORATE OF DISTANCE & CONTINUING EDUCATION
MANONMANIAM SUNDARANAR UNIVERSITY
TIRUNELVELI- 627 012

OPEN AND DISTANCE LEARNING (ODL) PROGRAMMES
(FOR THOSE WHO JOINED THE PROGRAMMES FROM THE ACADEMIC YEAR 2023–2024)

M. Sc. Chemistry
Course Material

Core VIII – Coordination Chemistry – I

Course Code: SCHM32

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Coordination Chemistry – I

Unit I: Modern theories of coordination compounds: Crystal field theory splitting of d orbitals in octahedral, tetrahedral and square planar symmetries, factors affecting 10Dq , crystal field stabilisation energy for high spin and low spin Oh and Td complexes, Applications CFSE, Jahn Teller distortions and its consequences. Ligand filed theory-.Molecular Orbital Theory and energy level diagrams: Sigma and pi bonding in octahedral, square planar and tetrahedral complexes.

Unit II: Spectral characteristics of complexes: Term states for d ions - characteristics of d-d transitions - charge transfer spectra - selection rules for electronic spectra - Orgel correlation diagrams - Sugano-Tanabe energy level diagrams - nephelauxetic series - Racha parameter and calculation of inter-electronic repulsion parameter.

Unit III: Stability and Magnetic property of the complexes: Stability of complexes: Factors affecting stability of complexes, Thermodynamic aspects of complex formation, Stepwise and overall formation constants, Stability correlations, statistical factors and chelate effect, Determination of stability constant and composition of the complexes: Formation curves and Bjerrum's half method, Potentiometric method, Spectrophotometric method, Ion exchange method, Polorographic method and Continuous variation method (Job's method) Magnetic property of complexes: Spin-orbit coupling, effect of spin-orbit coupling on magnetic moments, quenching of orbital magnetic moments.

Unit IV: Kinetics and mechanisms of substitution reactions in coordination complexes: Classification of inorganic reaction and reaction mechanism- Associative SN2, Dissociative SN1,interchange, SN1CB mechanistic pathways for N substitution reactions in octahedral complexes; acid and base hydrolysis of octahedral complexes; Classification of metal ions based on rate of water replacement reaction and their correlation to Crystal Field Activation Energy; Substitution reactions in square planar complexes: Eigen-Wilkins mechanism; Trans effect, theories of trans effect and applications of trans effect in synthesis of square planar compounds; Kurnakov test.

Unit V: Electron Transfer reactions and Photochemistry of coordination complexes: Electron Transfer reactions in octahedral complexes: Outer sphere electron transfer reactions and Marcus-Hush theory; inner sphere electron transfer reactions - nature of the bridging ligand in inner sphere electron transfer reactions. Complementary and Non-Complementary electron transfer reactions. **Photochemistry:** Photochemical excitation in the transition metal complexes: Properties of THEXI states- Photophysical processes: bimolecular deactivation and energy transfer, Photochemical processes: Photo-redox, photo-substitution and photo-isomerisation reactions of Cr (III) and Co (III) complexes Photophysical and photochemical properties of [Ru(bpy)3] 2+. Applications of inorganic photochemistry: photochemical conversion and storage of solar energy-photochemical conversion of N2 to NH3. – TiO2 as a green photocatalyst in removing air and water pollutants.

Text books:

1. 1. J.E. Huheey, E.A Keiter, R.L Keiter and O.K Medhi, Inorganic Chemistry – Principles of structure and reactivity, 4 th Edition, Pearson Education Inc., 2006
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6. Asim K Das and Mahua Das, Fundamental concepts of inorganic chemistry,1st eBook edition, Volume 4, CBS publishers and distributors PVT Ltd,2019
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8. S.K.Agarwal and Keemti Lal, Advanced inorganic chemistry, Pragati Prakashan Educational publication,5th edition,2016.
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Unit – I

Modern Theories of Coordination Compounds

Crystal Field Theory

Crystal Field Theory was proposed by the physicist Hans Bethe in 1929 to describe the bonding in coordination complexes and to rationalize and predict some important properties of coordination complexes (colours, magnetism etc.). This model was based on a purely interaction between the ligands and the metal ion in the complexes with various geometries like octahedral, tetrahedral, square planar etc. Subsequent modifications were proposed by J. H. Van Vleck in 1935 to allow for some covalency in the interactions.

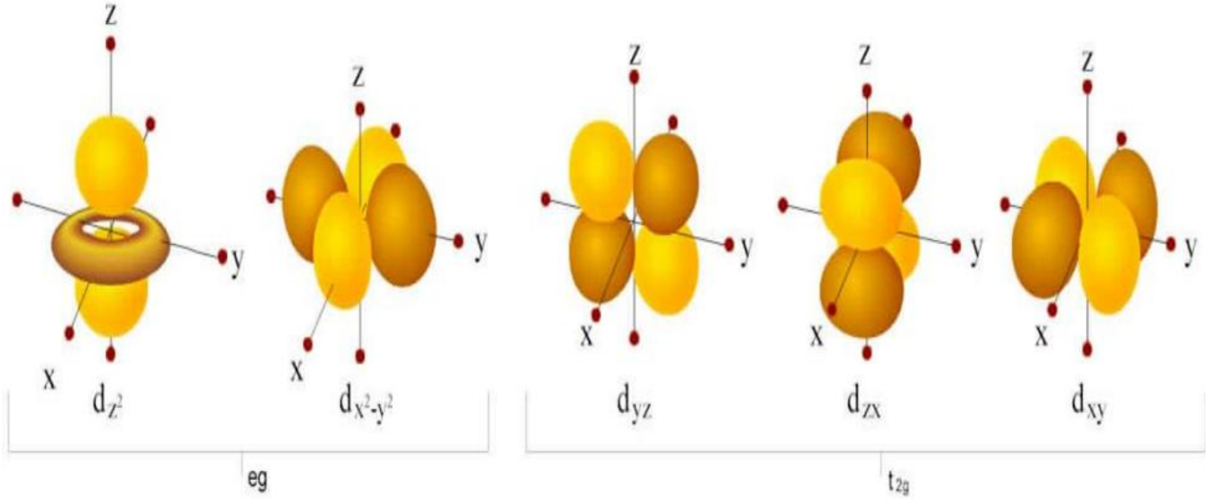
This theory is based on the concept that when the negative charges of the incoming ligands (or the negative ends of dipolar molecules like NH_3 and H_2O) attract the positively charged metal ion, there is also repulsive interaction between d electrons present on the metal ion and the ligands. Certain assumptions are taken while dealing with CFT-

1. The ligands are treated as point charges. In fact, this is not practically true since sometimes the size of ligand particularly when it is sulfur or phosphorus donating ligands, is approximately similar to the size of metal ion.

2. The interactions between metal ion and ligand are treated as purely electrostatic, no covalent interactions are considered. This again is not true, some of the observations cannot be explained without invoking covalent interactions. In isolated gaseous metal ion, all of the five d-orbitals are degenerate.

3. When a hypothetical spherical field of ligand approaches the metal ion, d-orbitals still remain degenerate, but their energy level is raised a bit due to repulsion between the orbitals of metal & ligand. This energy level is called Barycenter. But in the transition metal complexes, the geometry about the metal ions are octahedral, tetrahedral or square planar etc., the field provided by the ligands is not at all spherically symmetrical therefore d-orbitals are unequally affected by the ligands and degeneracy of d-orbitals in metal removed and split into different energy levels (e.g. t_{2g} or e_g).

To understand CFT, it is essential to understand the description of the lobes of d-orbitals



d_{xy}: lobes lie in-between the x and the y axes.

d_{xz}: lobes lie in-between the x and the z axes.

d_{yz}: lobes lie in-between the y and the z axes.

d_{x2-y2} : lobes lie on the x and y axes.

d_{z2}: there are two lobes on the z axes and there is a donut shape ring that lies on the xy plane around the other two lobes.

Shapes of ‘d’ orbitals

In order to have a complete understanding of crystal field theory, it is essential to have a clear picture of the spatial arrangements of the ‘d’ orbital.

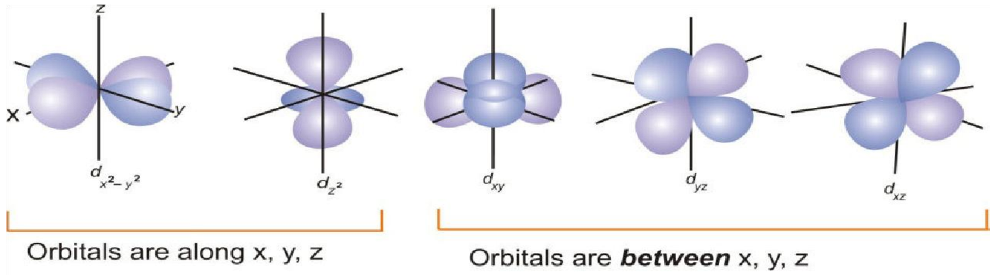
There are five ‘d’ orbitals namely d_{xy}, d_{yz}, d_{xz}, $d_{x2-y2}$and d_{z2}. All these five ‘d’ orbitals are not identical in shape. Four of the five ‘d’ orbitals namely d_{xy}, d_{yz}, d_{xz}, d_{x2-y2} and d_{z2} contain four lobes. But the d_{z2} orbital consists of only two lobes. The four lobes of d_{xy}, d_{yz} and d_{xz} orbitals lie symmetrically between the axes. For example, the lobes of d_{xy} orbital are lying between ‘x’ and ‘y’ axes. Similar is the case with d_{xy} and d_{yz}orbitals.

Therefore, these three orbitals are known as ‘non-axial orbitals’. According to group theory these three orbitals (d_{xy}, d_{yz}, d_{xz}) are known as ‘**t2g**’ orbitals. (t = triply degenerate; g = gerade orbital).

The four lobes of d_{x2-y2} orbital are lying along the ‘x’ and ‘y’ axes. The two lobes of d_{z2} orbital are lying along the ‘z’ axis. Therefore these two orbitals are known as ‘axial orbitals’.

According to group theory these two orbitals (d_{x2-y2} , d_{z2}) are known as “**eg**” orbitals. (e = doubly degenerate; g = gerade orbital).

The d_{xy}, d_{yz}, d_{xz}, d_{x2-y2} orbitals have “clover leaf shaped” structure. The d_{z2} orbitals has “dumb-bell shape“ with a “doughnut shaped” electron cloud in the centre.

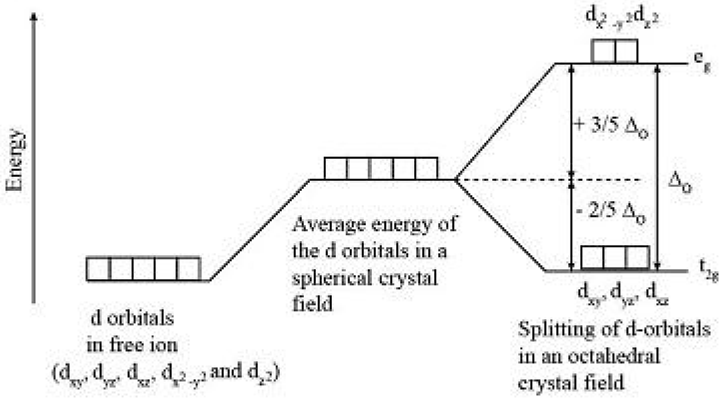


In the absence of magnetic field, all the five ‘d’ orbitals have the same energy. Orbitals having the same energy are called “degenerate orbitals”. This character is known as “degeneracy” . Since the number of ‘d’ orbitals having the same energy is five, these orbitals are said to be “five-fold degenerate orbitals”.

Crystal Field Splitting In Octahedral Complexes ;

In an octahedral complex, the ligands approach the central metal ion along the three cartesian axes. X, Y and z. Since the lobes of two axial e_g orbitals (d_{x2-y2} , d_{z2}) point directly at the path of the approaching ligands, the electrons in these orbitals experience greater repulsion from the ligand. The non-axial t_{2g} orbitals (d_{xy}, d_{yz}, d_{xz}) experience less repulsion.

Hence the energy of the e_g orbitas (d_{x2-y2} , d_{z2}) are increased and the energy of the t_{2g} orbitals (d_{xy}, d_{yz}, d_{xz}) are decreased. Thus the five ‘d’ orbitals which have same energy (degenerate) in the metal ion are split into levels **t2g** and e_g in the metal complex. This splitting is called “Crystal field splitting”. The energy difference between “eg” and “t2g” levels is denoted by $\triangle_{\mathbf{0}}$ or 10Dq and is called the “Crystal field splitting energy” in octahedral geometry.

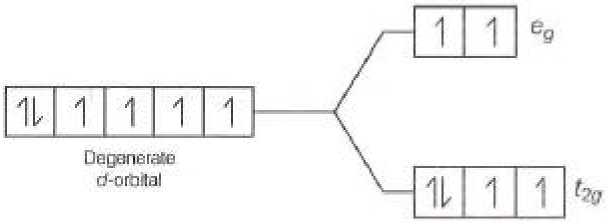


High spin or spin free complexes:

High spin or spin free complexes are those which are formed by "weak field". Under the influence of weak field ligands such as F^-, Br^- etc. The energy difference between the "t_{2g}" and "e_g" orbitals will be smaller. Therefore the distribution of 'd' electrons in the "t_{2g}" and "e_g" orbitals takes place "according to Hunds rule". So such complexes possess maximum number of unpaired electrons and are known as " high spin" or "spin free" complexes. For such complexes $\triangle_0 < P$ ($\triangle_0$ - crystal field splitting energy of an octahedral complexes ; P - average pairing energy).

Examples: $[CoF_6]^{3-}$, $[CoBr_6]^{3-}$,, $[Mn(H_2O)_6]^{2+}$, ,, $[Fe(H_2O)_6]^{2+}$etc.

$[CoF_6]^{3-}$; F^- is a weak field ligand. Therefore $\triangle_0$ is smaller and the distribution of 'd' electrons takesplace according to Hund's rule.



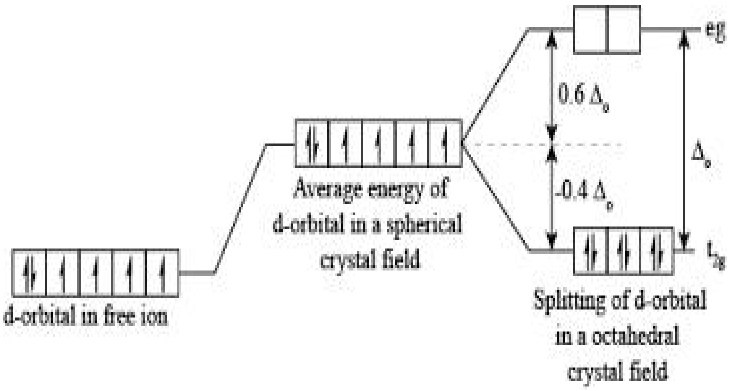
Hence the complex $[CoF_6]$ is paramagnetic (u = 4.90BM; 4 unpaired electrons) and a high spin complex.

Low spin or spin paired complexes:

Low spin or spin paired complexes are those which are formed by “strong field”. Under the influence of strong field ligands such as $NO_2{}^-$, CN^- , CO etc. The energy difference between between the **“t_{2g}"** and **“e_g”** orbitals will be larger. Therefore the distribution of ‘d’ electrons in **“t_{2g}"** and **“e_g”** orbitals takes place “against Hunds rule”. So pairing of electrons takes place in the **t_{2g}"** level and $\triangle_0 >$ P. Such complexes are known as “low spin” or “spin paired” complexes.

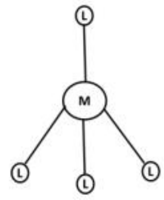
Example: $[Co(NH_3)_6]^{3+}$, $[[Fe(CN)_6]^{4-}$ etc.

$[Co(NH_3)_6]^{3+}$; NH_3 is a strong field ligand. Therefore $\triangle_0$ is large and the distribution of ‘d’ electrons takesplace against Hund’s rule.



Hence the complex $[Co(NH_3)_6]^{3+}$ is diamagnetic (u = 0) and a low spin or spinpaired complex.

Tetrahedral Complexes



In tetrahedral complex ligands approach towards the metal ion between the axes where t_2 set of orbitals feel more repulsion than e set of orbitals. Therefore, in tetrahedral complexes, d_{x2-y2} and d_{z2} orbital have lower energy than d_{xy}, d_{zx} and d_{yz} orbitals. In tetrahedral complex the splitting pattern is reverse of the splitting pattern of octahedral complexes. (Note the lack of a g in the subscripts (t_2, e) because tetrahedral complex does not have a center of symmetry). The energy difference between the two sets of d-orbitals is called crystal field stabilization energy (CFSE) or crystal field splitting energy. It is represented by a symbol Δ_t, where 't' stands for tetrahedral complex. The t_2 level lie $+0.4\Delta_t$ or 2/5 Δ_t above the average level and the e level lie $-0.6\Delta_t$ or $-3/5$ Δ_t below the 'center of gravity,' or 'bary center' so that the total increase in energy of 't_2' electrons is equal to the total decrease in energy of 'e' electron. The difference of energy between two energy levels is $\Delta_t(\Delta_t=4/9\Delta 0)$. Electron don't pair due to this small gap between two energy sets. So tetrahedral complexes have a high spin configuration.

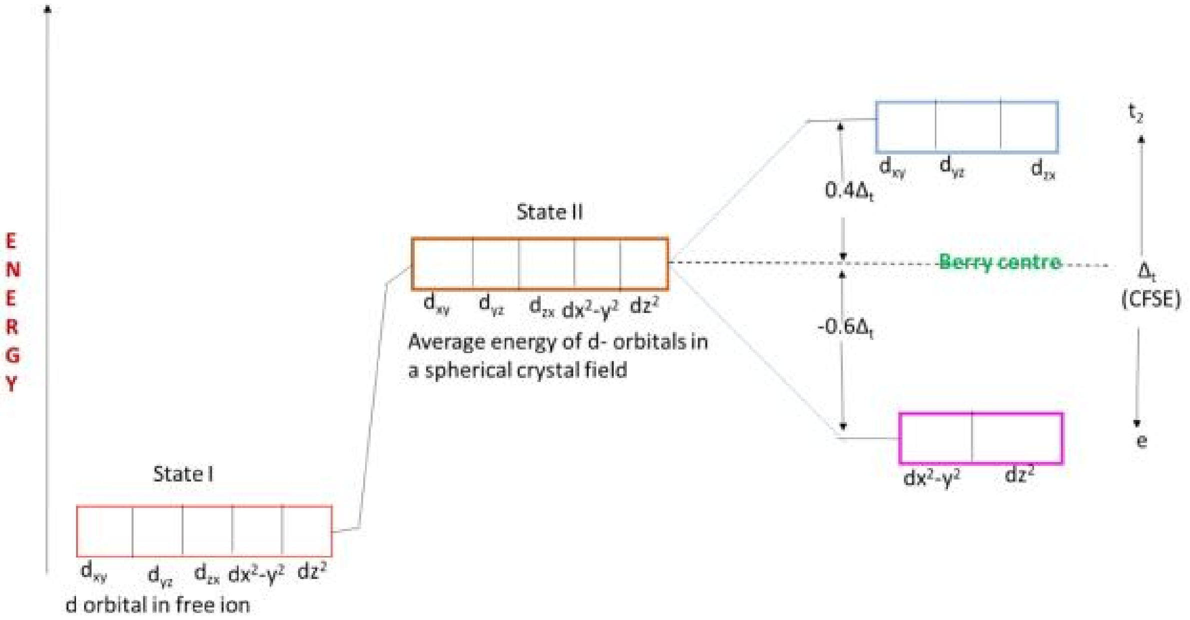


Figure: Splitting of d orbitals in Tetrahedral complexes

Square Planar Complexes

The crystal field splitting diagram for square planar geometry can be derived from octahedral diagram. If two Trans ligands in an octahedral ML_6 complex (based on Z axis) are moved away from the metal ion, then the resulting complex is said to be tetragonally distorted and such distortion favored because of a John teller effect. The removal of two ligands stabilizes the orbitals having z component (i.e., d_{z2}, d_{xz}, and d_{yz}). While the 'non z' orbitals will be raised in energy. As a result, eg set of orbitals split into two level, an upper level b1g (d_{x2-y2}) and a lower a_{1g} (d_Z2), and t_{2g} set is split into b_{2g}(d_{XY}) higher in energy and double degenerate (d_{YZ}, d_{ZX}) lower in energy. As a result, low spin complexes with d8 electrons occupying the low energy d_{xy}, d_{yz}, and d_{xz} orbitals while the high energy d_{x2-y2} orbitals remain unoccupied. Examples; - $[Ni(CN)_4]^{2-}$, $[Ptcl_4]^{2-}$ etc.

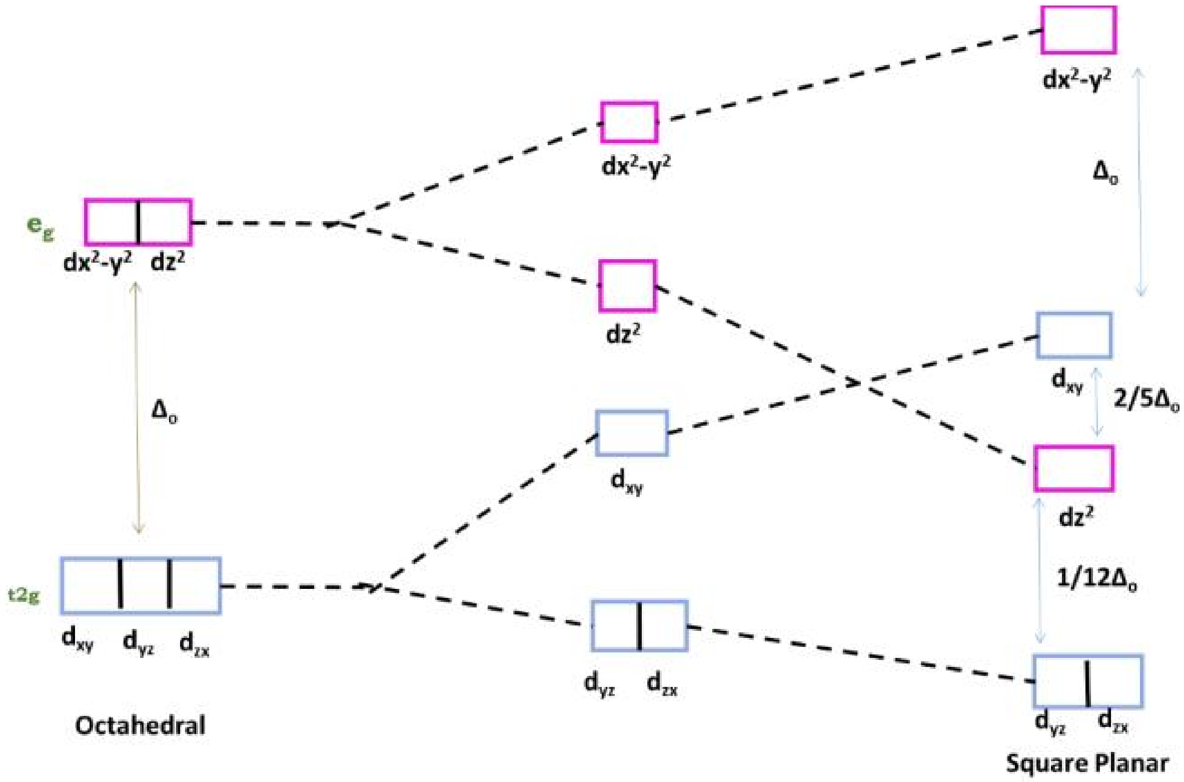


Figure: Splitting of *d* orbitals in Square planar complexes

Measurement of 10Dq Value:

10Dq or Δ_0 is a fundamental concept that represents the crystal field splitting energy between the two sets of d-orbitals (t2g and eg) in an octahedral complex.

The magnitude of 10Dq depends on several factors, including:

1. Metal ion
2. Ligands
3. Coordination geometry
4. Oxidation state

Crystal Field Theory is the distribution of electrons in the d orbitals may lead to net stabilization (decrease in energy) of some complexes depending on the specific ligand field geometry and metal d- electron configurations. It is simple matter to calculate this stabilization since all that is needed is the electronic configuration and knowledge of the splitting patterns. That is crystal field stabilization energy.

In octahedral symmetry the d-orbitals split into two sets with an energy difference, where the dxy, dyz, dzx orbitals will be lower in energy than the $dz^{2,}dx^{2}-y^{2}$, which will have higher energy, because the former group is farther from the ligands than the latter and therefore experience less repulsion.

In tetrahedral geometry, the d-orbitals of a metal ion split into two sets:

1. t2g (triply degenerate): Consisting of dxy, dyz, and dzx orbitals

2. eg (doubly degenerate): Consisting of dx^2-y^2 and dz^2 orbitals

This splitting is due to the tetrahedral ligand field, which is weaker than the octahedral ligand field. As a result, the energy difference between the t2g and eg orbitals is smaller compared to the octahedral case.

The splitting energy in tetrahedral geometry is denoted by Δt, which is approximately 4/9 of the splitting energy in octahedral geometry (Δo).

The ligands are classified into two strong and weak field ligand. For strong field ligand the spin is low and for weak field ligand the spin is high.

CFSE = -0.4 × no. of electrons in t2g level + 0.6 × no. of elerons in eg level + mP

m = No. of pairs of electrons caused by ligands

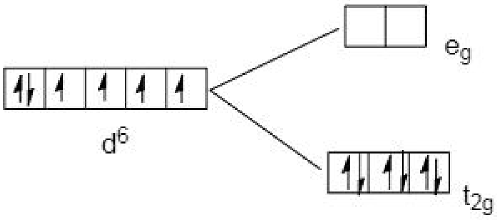
Examples:

Octahedral complex

[Co(NH$_3$)]$_6$

NH$_3$ is strong field ligand so it is low spin complex.

Co^{3+}=$3d^6$



Low spin complex

$t2g^6$ eg^0

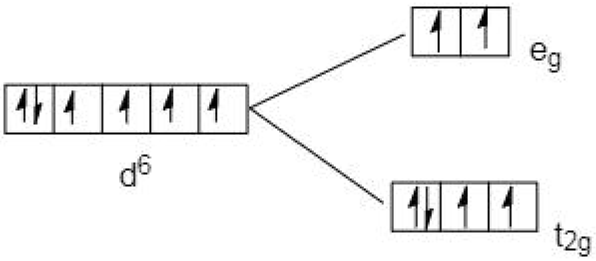
CFSE= $-0.4\times6 + 0.6\times0 + 3P$

$=-2.4\Delta_o+3P$ or $-24Dq+3P$

II. $[Co(H_2O)]_6$

H_2O is weak field ligand so it is high spin complex.

$Co^{3+}=3d^6$



High spin complex

$t2g^4$ eg^2

CFSE=$-0.4\times4 + 0.6\times2 + 1P$

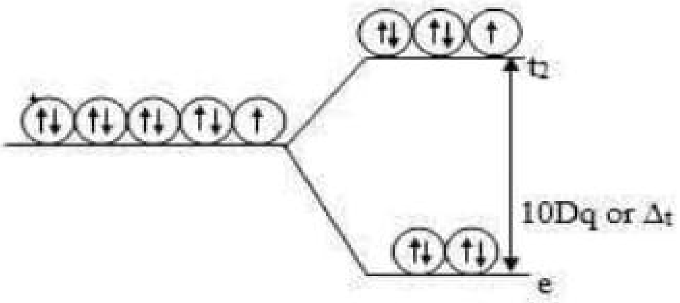
$=-0.4\Delta_o+3P$ or $-4Dq+1P$

Tetrahedral complex

I. $[CuCl_4]^{2-}$

Cl^- is weak field ligand so it is high spin complex.

$Cu^{2+} = 3d^9$



$t2g^5 \ \ eg^4$

CFSE =- 0.4×5 + 0.6 ×4+ 4P

=$0.4\Delta_t$ +4P or 4Dq+4P

Factors affecting the magnitude of Δ_o

I. Valence of the Metal

Increasing the valence of a metal ion has two effects: the radius of the metal decreases, and ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the ligands to interact more strongly with the d-orbitals. Consequently, the magnitude of Δ_o increases as the valence of the metal increases. Typically, Δ_o for a M(III) is about 50% greater than for the M(II) of the same metal; for example, for $[V(H_2O)_6]^{2+}$, $\Delta_o = 11{,}800\ cm^{-1}$; for $[V(H_2O)_6]^{3+}$, $\Delta_o = 17{,}850\ cm^{-1}$.

II. Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ_o (3d) < Δ_o (4d) < Δ_o (5d). The data for hexaammine complexes of the trivalent Group 9 metals illustrate this point:

$[Co(NH_3)_6]^{3+}$: $\Delta_o = 22{,}900\ cm^{-1}$

$[Rh(NH_3)_6]^{3+}$: $\Delta_o = 34{,}100\ cm^{-1}$

$[Ir(NH_3)_6]^{3+}$: $\Delta_o = 40{,}000\ cm^{-1}$

The increase in Δ_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

III. The Nature of the Ligands

Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order F > Cl > Br > I because smaller, more localized charges, such as we see for F, interact more strongly with the d-orbitals of the metal. In addition, a small neutral ligand with a highly localized lone pair, such as NH_3, results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F. The experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series which was presented in a previous section.

IV. Geometry of the complex

In octahedral complex, the splitting of d orbitals is more than twice as strong as in tetrahedral complexes for the same metal ion and ligands. The difference in 10Dq vsalue is because of two factors,

a. In octahedral complexes six ligands are involved while in tetrahedral only four; this results in 33% (i.e. 2/3 rd) decrease in the field strength, provided the other factors remain the same.

b. In octahedral complexes, the ligands are situated exactly in the direction of dz^2 and dx^2-y^2 orbitals while in tetrahedral complexes the ligands are not aimed at any of the d orbitals but exert more influence on the t_{2g}orbitals than on the e_g orbitals. In case of square planar complexes, the degree of splitting is more than in a tetrahedral field.

Spectrochemical series

A spectrochemical series is a list of ligands ordered by ligand "strength", and a list of metal ions based on oxidation number, group and element. For a metal ion, the ligands modify the difference in energy Δ between the d orbitals, called the ligand-field splitting parameter in ligand field theory, or the crystal-field splitting parameter in crystal field theory. The splitting parameter is reflected in the ion's electronic and magnetic properties such as its spin state, and optical properties such as its color and absorption spectrum.

A partial spectrochemical series listing of ligands from small Δ to large Δ is given below.

I− < Br− < S2− < SCN− (S–bonded) < Cl− < NO3− < N3− < F− < OH− < C2O42− < H2O < NCS− (N–bonded) < CH3CN < py (pyridine) < NH3 < en (ethylenediamine) < bipy (2,2'-bipyridine) < phen (1,10-phenanthroline) < NO2− (N–bonded) < PPh3 (Triphenylphosphine) < CN− < CO

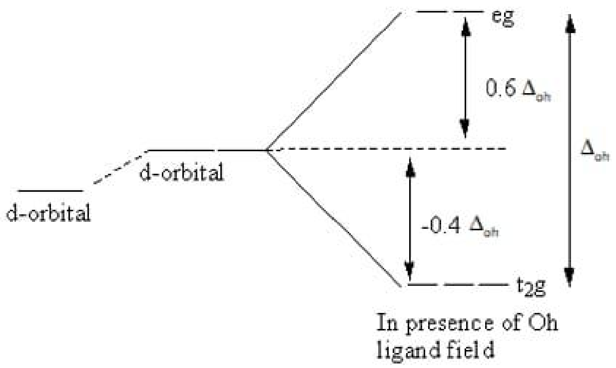
Crystal Field Stabilization Energy

When the ligand approach central metal atom there is repulsion between the ligand electrons there and the d orbital electrons of central metal atom.

The ligand approach the central metal along the axis or between the axis.

When a ligand approach a central metal atom the d orbital splits into two sets e_g and t_{2g}.

The gap between the e_g and t_{2g} is called energy gap or crystal field stabilization energy



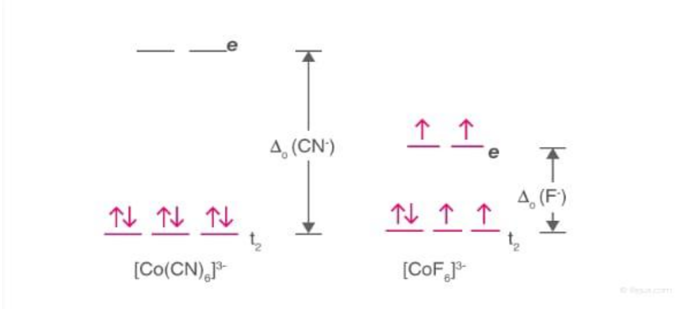
High spin and Low spin Complexes

The complexes with the greater number of unpaired electrons is known as the high spin complexes, the low spin complexes contains the lesser number of unpaired electrons. High spin complexes are expected with weak field ligands whereas the crystal field spiliting energy is small Δ. The opposite applies to the low spin complexes in which strong field ligands cause maximum pairing of electrons in the set of three t_{2g} atomic orbital due to large Δ_0 .

High spin (Weak field) = Maximum number of unpaired electrons.

Low spin (Strong field) =Minimum number of unpaired electrons.

Example: $[Co(CN)_6]^{3-}$ & $[CoF_6]^{3-}$



$[Co(CN)_6]^{3-}$ = Low spin complexes

$[CoF_6]^{3-}$ = High spin complexes

CFSE Calculating Formula

1. CFSE = (-0.4 x No. of electron in t_{2g} level) + (0.6 x No. of electron in e_g level) Δ_0 +Np
2. N = Number of pairing electrons .
3. The negative value of CFSE indicates the higher stability of the complexes.

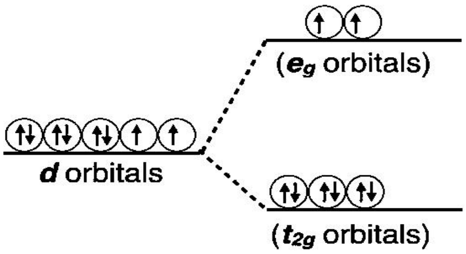
Example:

1. $[Ni(H2O)_6]^{2+}$

Water is a Weak field ligand so High spin formed.

Ni = $4s^2 3d^8$ Configuration

$Ni^{+2} = 3d^8$



CFSE = (-0.4 x 6) + (0.6 x 2) Δ_0 + 3P

= -2.4 + 1.2 Δ_0 + 3P

= -1.2 Δ_0 + 3P

Paramagnetic – Two unpaired electron

The number of unpaired electrons in a complexes can be calculated using the vale of magnetic moment by the formula

$\mu_s = nn+2$ B.M

$= 22+2$

$= 8$

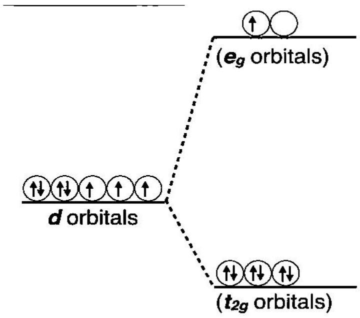
= 2.82 B.M.

2. $[Co(CN)_6]^{2+}$

CN strong field ligand so low spin formed.

Co = $4s^2$ $3d^7$ Configuration

$Co^{+2} = 3d^7$



CFSE = (-0.4 x 6) + (0.6 x 1) Δ_0 + 3P

= -2.4 + 0.6 Δ_0 + 3P

= -1.8 Δ_0 + 3P

Paramagnetic – one unpaired electron

The number of unpaired electrons in a complexes can be calculated using the vale of magnetic moment by the formula

$\mu_s = nn+2$ B.M

$= 11+2$

$= 3$

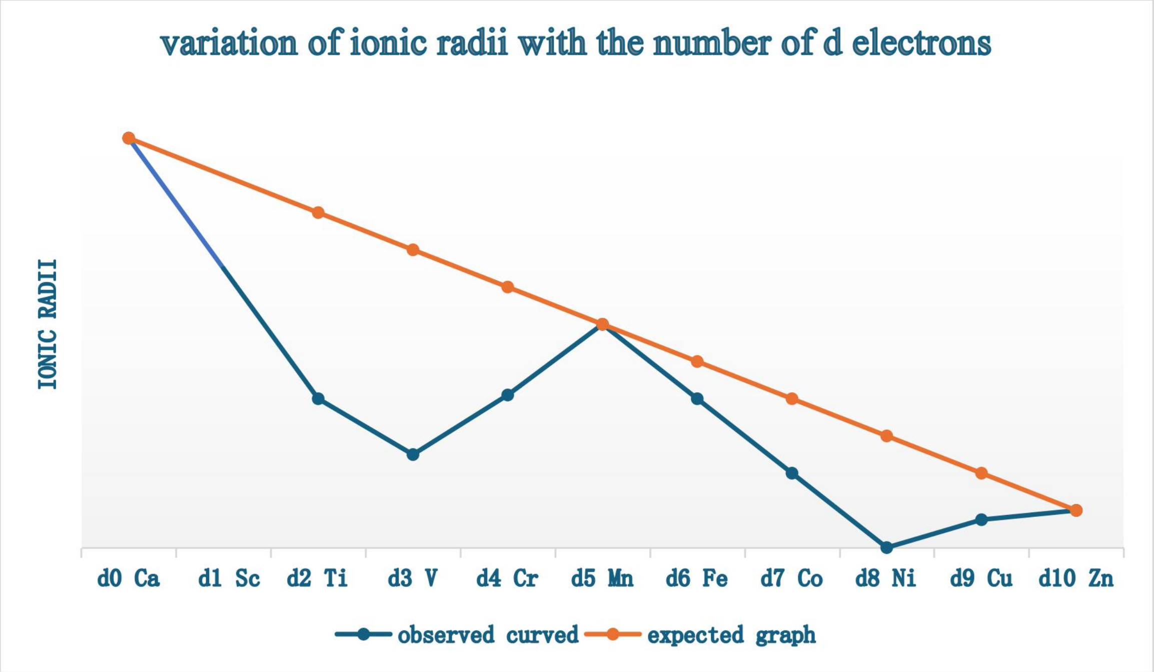
= 1.73 B.M.

Evidences For Crystal Field Splitting

1) Ionic Radii of Transition Metal Ions:

In ionic radii of divalent cation of first transition metal series in their crystalline compounds, where each metal ion is octahedrally surrounded by 6 ligands. In absence of CFSE due to d orbital splitting, the Ionic radii of TM ions decrease gradually with increasing nuclear charge M^2+ ion expected to decrease smoothly from Ca^{2+} to Zn^{2+} due to increased nuclear charge, but the change in size is not regular.

Ca^{2+}, Mn^{2+}, Zn^{2+} which have d^0, d^5, d^{10} configuration. These configuration develop almost spherical field around the nucleus. They have zero CFSE.

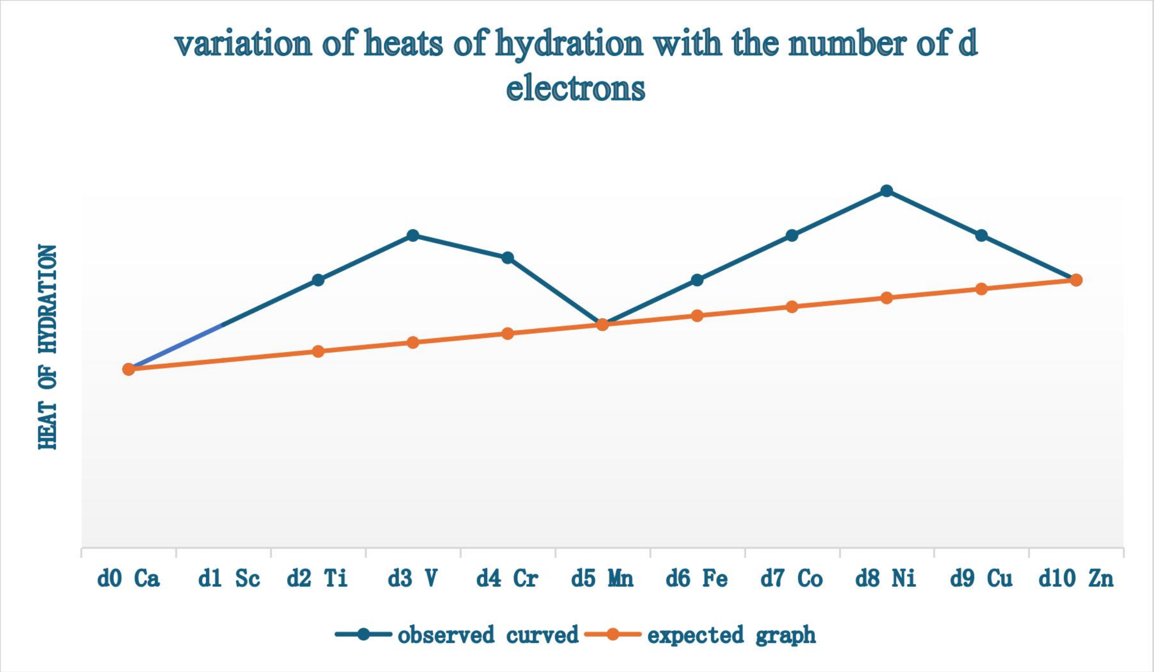


2) Heat of Hydration of Bivalent Ions of Transition Series:

The heat of hydration is heat evolved in the hydration process.

$$M^{2+}_{(g)} + 6\,H_2O_{\,(l)} \longrightarrow [M\,(H_2O)_6]^{2+} + \text{Heat of hydration}$$

Experimental values of heat of hydration of ions increases regularly Ca^{2+} to Zn^{2+} due to the decrease in ionic radii values brings the ligand (water molecules) closer to the metal. Hence the increased electrostatic attraction between the cation and ligands but expected graph doesn't occur.



Ca, Mn, Zn have d0, d5(high spin), d10 which have zero CFSE so fall on the straight line. The distance of other points above this line corresponds to the CFSE.

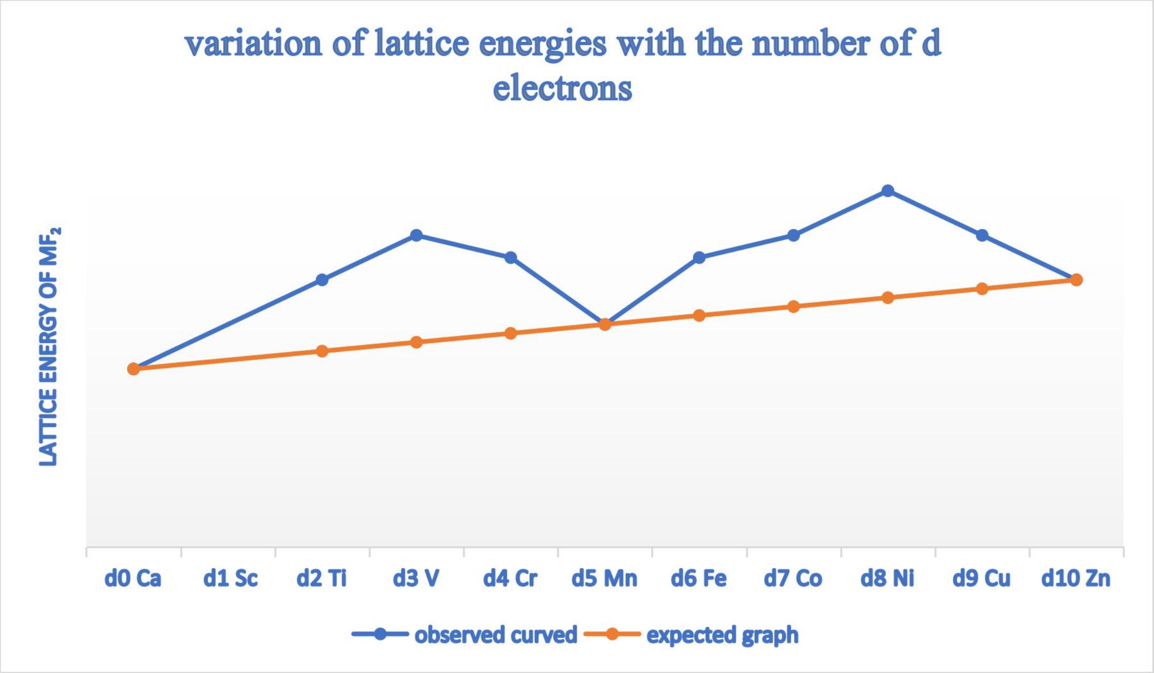
V and Ni show at maxima, Ca, Mn, Zn show at minimum

For high spin complexes CFSE is minimum(zero) for d0,d5 and d10 and they show minima in graph. And maximum for d3 and d8 so they are maxima in graph.

If there was no crystal field splitting then a smooth graph would have been obtained

3) Lattice Energy and CFSE:

Consider difluorides CaF_2 to ZnF_2 , the IR is expected to decrease gradually , their lattice energies should increase gradually. An almost straight line could have drawn through the points which indicates the lattice energies of CaF_2, MnF_2, ZnF_2 due to the absence of any CF effects. Where all the other bivalent metal fluorides follow irregular variation due to the CFS



4)Spectroscopy: Experimental techniques such as UV-VIS spectroscopy reveal absorption bands corresponding to electronic transitions. These transitions provide evidence for CFSE

5)Colour of complexes: The colour of coordination complexes results from electronic transitions due to CFSE. For example, Octahedral complexes with high CFSE appear colourful

6)Magnetic properties: High spin and low spin complexes exhibit different magnetic behaviours due to CFSE. Magnetic susceptibility measurements provide evidence

Site Selections In Spinels And Antispinels

The **spinels** have the general chemical formula **AB_2X_4**.

Where:

A^{II} = a divalent cation like Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn

B^{III} = a trivalent cation like Al, Ga, In, Ti, V, Cr, Mn, Fe, Fe, Co, Ni

X = O, S, Se etc.

Examples of Normal Spinels: $MgAl_2O_4$ (known as spinel), Mn_3O_4, $ZnFe_2O_4$, $FeCr_2O_4$ (chromite) etc.

A spinel unit cell is made up of 8 FCC cells. The anions (usually oxide ions: O^{2-}) occupy the FCC lattice points. The divalent A^{II} cations occupy 1/8th of the tetrahedral voids, whereas the trivalent B^{III} cations occupy one half (1/2) of octahedral voids. We know that in one FCC lattice unit cell, the effective number of atoms (or ions) occupying the lattice points is 4. At the same time, the effective number of tetrahedral voids (holes) = 8 and that of octahedral voids = 4. That means, in a normal spinel, The number of anions occupying the lattice points of 8 FCC unit cells = 8 x 4 = 32. Whereas, the number of divalent A^{II} cations occupying 1/8th of tetrahedral voids = 8 x 1/8 x 8 = 8 and the number of trivalent B^{III} ions occupying the half of octahedral voids = 8 x 1/2 x 4 = 16. i.e. The ratio of $A^{II} : B^{III} : O^{2-} = 8 : 16 : 32 = 1:2:4$ which confirms with the formula of normal spinels. Thus a normal spinel can be represented as: $\mathbf{(A^{II})^{tet}(B^{III})_2{}^{oct}O_4}$

Structures of Inverse spinels ($\mathbf{B(AB)O_4}$): The A^{II} ions occupy the 1/4th of octahedral voids, whereas one half of B^{III} ions occupy the 1/8th of tetrahedral voids and the other half occupy 1/4th of octahedral sites. It can be represented as: $(B^{III})^{tet}(A^{II}B^{III})^{oct}O_4$.

anions occupying the lattice points of 8 FCC unit cells = 8 x 4 = 32 .

divalent A^{II} cations occupying 1/4th of octahedral voids = 8 x 1/4 x 4 = 8

trivalent B^{III} ions occupying the 1/4th of octahedral voids = 8 x 1/4 x 4 = 8.

trivalent B^{III} ions occupying the 1/8th of tetrahedral voids = 8 x 1/8 x 8 = 8.

i.e. The ratio of $A^{II} : B^{III} : O^{2-} = 8 : (8+8) : 32 = 1:2:4$ which confirms with the formula of inverse spinels. Thus an inverse spinel can be represented as: $\mathbf{(B^{III})^{tet}(A^{II})^{oct}(B^{III})^{oct}O_4}$

Examples of Inverse spinels: Fe_3O_4 (ferrite), $CoFe_2O_4$, $NiFe_2O_4$ etc.

The above inverse spinels can also be written as:

$Fe_3O_4 = Fe^{III}(Fe^{II}Fe^{III})O_4$

$CoFe_2O_4 = Fe^{III}(Co^{II}Fe^{III})O_4$

$NiFe_2O_4 = Fe^{III}(Ni^{II}Fe^{III})O_4$

The number of octahedral sites occupied may be ordered or random. The random occupation leads to **defected spinels**.

E.g. $NiAl_2O_4$ for which the formula can be written as $(Al_{0.75}Ni_{0.25})^{tet}\ [Ni_{0.75}Al_{1.25}]^{octa}O_4$.

Another defected spinel is γ-Al_2O_3

1) The relative sizes of A and B: In general, the smaller cation prefers to occupy the site of lower coordination i.e., tetrahedral site.

However, in the spinel, $MgAl_2O_4$ itself this factor is outweighed by greater lattice energy of smaller cation, Al^{3+}, which occupies the octahedral site and thus by giving normal spinel structure. Otherwise the "spinel" will have the inverse spinel structure!

2) The Madelung constants for the normal and inverse structures: It is observed that the Madelung constants are same for both normal and inverse spinels and hence are not that much important in arriving at the type of spinels.

3) Ligand-Fleld Stabilization Energies: Applicable whenever there are transition metal ions and is discussed below.

The structures of spinels are affected by the relative LFSE values of metal ions**. The ion with** more LFSE value in octahedral geometry when compared to the LFSE in tetrahedral geometry tends to occupy octahedral sites. The difference between the LFSE values in octahedral and tetrahedral geometries is referred to as Octahedral Site Stabilization Energy (OSSE). “If the B^{III} ion has more CFSE gain in octahedral site than that of A^{II} ion, a normal spinel structure is expected.” “Whereas an inverse spinel is formed whenever the divalent A^{II} ion has comparatively more CFSE gain in octahedral geometry than the trivalent B^{III} ion.”

- A normal spinel structure is assumed if both the divalent and the trivalent metals are non transition metals since no CFSE is involved.
- There is a tendency of formation of inverse spinel structure in some cases (not all the cases) which contain transition metal ions. This is because, the transition metal ion may get extra stability (LFSE) in octahedral geometry, prefers octahedral voids over tetrahedral ones.
- The d^0; high spin d^5, d^{10} ions have no preference between tetrahedral and octahedral coordination since the LFSE is zero.
- Usually d^3 & d^8 ions have strongest preference for octahedral geometry.
- Other ions with d^1, d^2, d^4, d^6, d^7, d^9 too have slightly more preference for octahedral symmetry.
- That means, if **A^{II} has d^3 or d^8 configuration** and the B^{III} ion has configuration other than these, then the **spinel is inverted**.
- If the divalent A^{II} is a transition metal (with configurations other than d^0; highspin d^5 & d^{10}) and the B^{III} ion is a non transition metal, there is a tendency to form inverse spinel.
- But there are exceptions like $FeAl_2O_4$ which has normal spinel structure.

- Above generalizations are valid for high spin systems as the oxide ion is expected to be a weak field ligand.

For example, Co^{3+} is a low spin system even in presence of oxo ligands due to high charge on the ion.

A^{II}	B^{III}	**Structure**
Non transition metal or d^0 or d^5 or d^{10} transition metal	Non transition metal	Spinel structure
Non transition metal or d^0 or d^5 or d^{10} transition metal	A transition metal with d^1 or d^2 or d^3 or d^4 or d^6 or d^7 or d^8 or d^9 configurations	Spinel structure
A transition metal with d^1 or d^2 or d^3 or d^4 or d^6 or d^7 or d^8 or d^9 configurations	Non transition metal or transition meta with d^0 or d^5 or d^{10} configurations	Inverse spinel
Transition metal with higher CFSE value	Transition metal with lower CFSE value	Inverse spinel

1) **$MgAl_2O_4$ has normal spinel** structure since both the divalent and trivalent ions are non transition metal ions. There is no question of CFSE.

2) **Mn_3O_4 is a normal spinel** since the Mn^{2+} ion is a high spin d^5 system with zero LFSE. Whereas, Mn^{3+} ion is a high spin d^4 system with considerable LFSE.

3) **Fe_3O_4 has an inverse spinel structure** since the Fe(III) ion is a high spin d^5 system with zero CFSE. Whereas the divalent Fe(II) is a high spin d^6 system with more CFSE.

4) **$NiFe_2O_4$ is again an inverse spinel** since the divalent Ni^{2+} (a d^8 ion) has more CFSE than the trivalent Fe^{3+} (a d^5 ion).

5) **$FeCr_2O_4$ is a normal spinel** since the divalent Fe^{2+} is a high spin d^6 ion with CFSE = 4 Dq and the trivalent Cr^{3+} is a high spin d^3 ion with CFSE = 12 Dq. Hence Cr^{3+} gets more OSSE while occupying octahedral sites.

6) **Co_3O_4 is a normal spinel**. Even in the presence of weak field oxo ligands, the Co^{3+} is a low spin d^6 ion with very high CFSE. It is due to high charge on Co^{3+}. Hence all the Co^{3+} ions occupy the octahedral sites.

7) **$NiAl_2O_4$ show random or defected inverse spinel**. The CFSE of Ni^{II} is greater in octahedral than tetrahedral coordination. But Al^{3+} also has strong preference for octahedral sites due to high lattice energy. This leads to almost complete randomization of all the cations on all the available sites. Its formula can be written as $(Al_{0.75}Ni_{0.25})^{tet}\,[Ni_{0.75}Al_{1.25}]^{octa}O_4$.

The spinels can be ferromagnetic or anti ferrimagnetic depending on the structure and nature of metal ions. The unpaired spins of metal ions are coupled through shared oxide ions by super exchange process. In ferrite spinels, the spins of electrons at tetrahedral sites have one orientation, whereas the spins of electrons at octahedral sites have opposite orientation. If the number of spins in these two types of sites is equal, then that spinel will be antiferromagnetic. Otherwise, it will be ferromagnetic.

E.g. The inverse spinels - Fe_3O_4, $NiFe_2O_4$ and $CoFe_2O_4$ are ferrimagnetic. In these cases, the spins of trivalent ions are cancelled out since half of them belong to tetrahedral sites and the other half belong to octahedral sites. However, the spins of divalent ions are not cancelled. Hence they show ferrimagnetism.

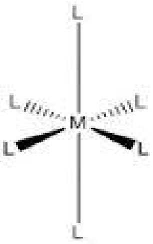
In case of $FeCr_2O_4$ - a normal spinel, the number of spins of high spin Cr^{3+} (d^3) ions is equal to the number of spins of high spin Fe^{2+} (d^6) ions. Hence it is antiferromagnetic. $MgAl_2O_4$ is diamagnetic since all the electrons in the metal ions are paired up. Note: Antiferro magnetic substances show weak magnetism, whereas diamagnetic substances show no magnetism at all.

Jahn Teller Distortions and its Consequences

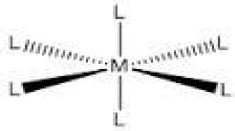
In 1937, John and teller put forward a remarkable theorem to explain why some six coordinated complexes(ocatahedral) undergo distortion and have distorted octahedral geometry.This theorem states that if a molecule/complex possessing any shape(excepting linear shpe)has an unsymmetrically filled set of degenerate orbitals is unstable and hence undergoes distortion.This distortion takes place such a way that the symmetry and energy of the molecule /complex.Thus,accorind to this theorem ,If the electrons in d-orbitals of the central metal ion of a regular ocathedral of a complex are asymmetrically arranaged ,the octahedral shape of the complex will distorted,since the electrons present in symmetrically filled d orbitals will repeal some ligands to reater extent while other ligands will be repelled to lesser extent.The distortion in geometry of non linear system due to jahn teller effect is called jahn teller distortion

The Jahn-Teller theorem essentially states that any nonlinear molecule system possessing electronic degeneracy will be unstable and will undergo distortion to form a system of lower symmetry as well as lower energy and thus the degeneracy will be removed. This effect describes the geometrical distortion of molecules and ions that is associated with electronically degenerate configurations. A configuration is said to be electronically degenerate if more than one sites are available for the filling of a single electron. The Jahn-

Teller effect is generally encountered in octahedral transition metal complexes. The phenomenon is much more common in hexacoordinated complexes of bivalent copper. The d^9 configuration of Cu2+ ion yields three electrons in the doubly degenerate *eg* orbitals set, leading to a doubly degenerate electronic state as well. Such complexes distort along one of the molecular four-fold axis (always labeled the *z*-axis), which has the effect of removing the orbital and electronic degeneracies and lowering the overall energy. The distortion usually occurs via the elongation the metal-ligand bonds along the *z*-axis, but sometimes also occurs as a shortening of the same bonds instead. Moreover, the Jahn-Teller theorem predicts the presence of an unstable geometry only and not the direction of the distortion. When distortion involving elongation occurs to decrease the electrostatic repulsion between the electron-pair on the ligand-attached and any extra electrons in metal orbitals with a *z*-component; and hence lowering the energy of the metal complex. Inversion center is retained after *z*-out as well as *z*-in the distortion. Symmetrical configurations possess electronic degeneracy while the unsymmetrical ones do not. Various symmetrical and unsymmetrical configurations are given below.



Elongated



Compressed

Let the case of the low-spin Co2+ octahedral complex. The corresponding electronic configuration is $t2g^6$ *eg*

1.Owing to the electronically degenerate state, the Jahn-Teller distortion is expected. Now suppose that the single electron of *eg* set is present in *dz* orbital; the ligands approaching from *z*-axis will feel more repulsionthan the ligands coming from *x* and *y*-axis. Therefore, the bonds along *z*-axis will be weaker in comparison to the bond along *x* and *y*-axis. This results in a tetragonal elongation about z-axis with two longer and four shorter bonds. This is formally called as *z*-out distortion. On the other hand, if the single electron of *eg* set is present in dx_{2-y}

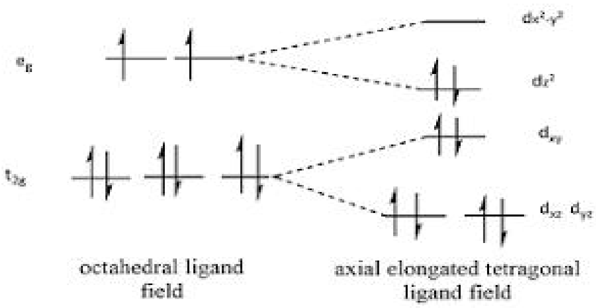
2. Orbital; the ligands approaching from *x* and *y*-axis will feel more repulsion than the ligands

coming from *z*-axis. Therefore, the bonds along *x* and *y*-axis will be weaker in comparison to the bond along *z*-axis. This results in a tetragonally flattened octahedral geometry about z-axis with two shorter and four longer bonds. This is formally called as *z*-in distortion.

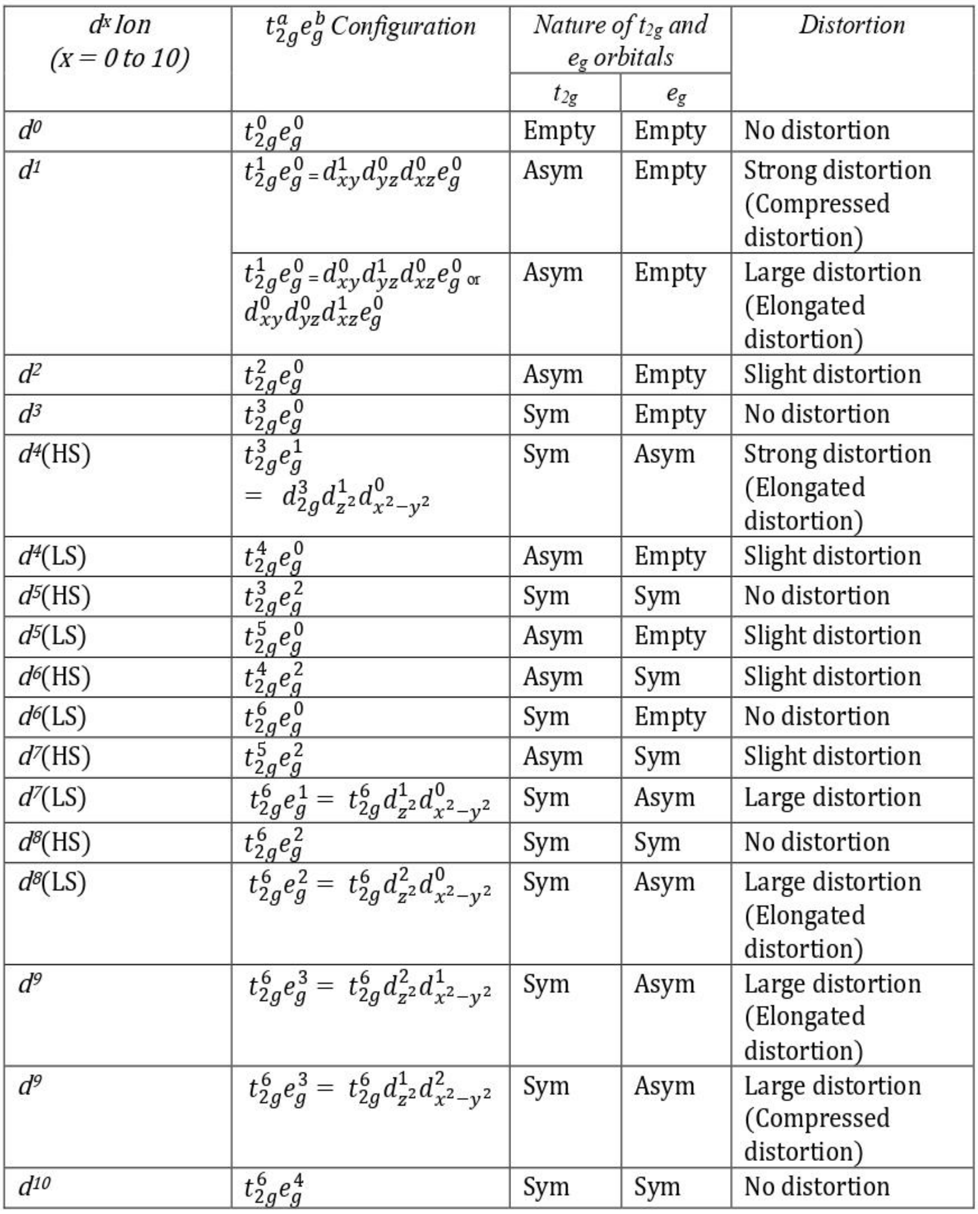
Consider the following examples

1. $[Co(CN)_6]^{4-}$: It is a low-spin complex with $t2g^{6}$ eg^{1} electronic configuration and will undergo strong Jahn-Teller distortion.
2. $[Cr(NH3)_6]^{3+}$: It is a high-spin complex with $t2g^{3}$ eg^{0} electronic configuration which is Completely symmetrical; and therefore, will not show any Jahn-Teller distortion.

   $[FeF_6]^{4-}$: It is a high-spin complex with $t2g^{4}$ eg^{2} electronic configuration and will undergoeslight Jahn-Teller distortion.



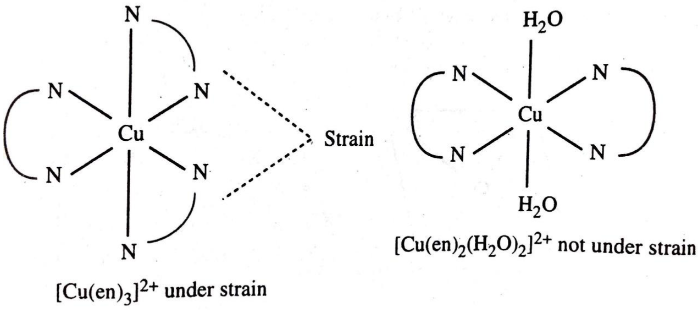
Summary of distortion in Octahedral complexes



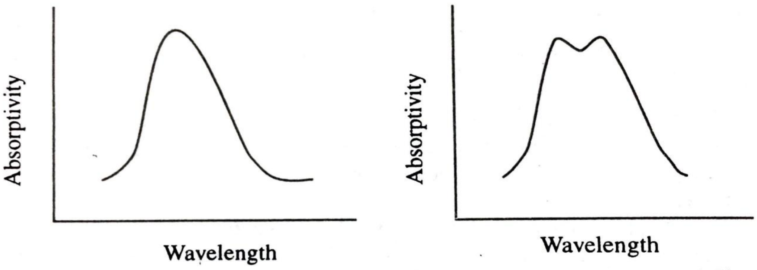
d^x Ion (x = 0 to 10)	$t_{2g}^a e_g^b$ Configuration	Nature of t_{2g} and e_g orbitals		Distortion
		t_{2g}	e_g	
d^0	$t_{2g}^0 e_g^0$	Empty	Empty	No distortion
d^1	$t_{2g}^1 e_g^0 = d_{xy}^1 d_{yz}^0 d_{xz}^0 e_g^0$	Asym	Empty	Strong distortion (Compressed distortion)
	$t_{2g}^1 e_g^0 = d_{xy}^0 d_{yz}^1 d_{xz}^0 e_g^0$ or $d_{xy}^0 d_{yz}^0 d_{xz}^1 e_g^0$	Asym	Empty	Large distortion (Elongated distortion)
d^2	$t_{2g}^2 e_g^0$	Asym	Empty	Slight distortion
d^3	$t_{2g}^3 e_g^0$	Sym	Empty	No distortion
d^4(HS)	$t_{2g}^3 e_g^1 = d_{2g}^3 d_{z^2}^1 d_{x^2-y^2}^0$	Sym	Asym	Strong distortion (Elongated distortion)
d^4(LS)	$t_{2g}^4 e_g^0$	Asym	Empty	Slight distortion
d^5(HS)	$t_{2g}^3 e_g^2$	Sym	Sym	No distortion
d^5(LS)	$t_{2g}^5 e_g^0$	Asym	Empty	Slight distortion
d^6(HS)	$t_{2g}^4 e_g^2$	Asym	Sym	Slight distortion
d^6(LS)	$t_{2g}^6 e_g^0$	Sym	Empty	No distortion
d^7(HS)	$t_{2g}^5 e_g^2$	Asym	Sym	Slight distortion
d^7(LS)	$t_{2g}^6 e_g^1 = t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^0$	Sym	Asym	Large distortion
d^8(HS)	$t_{2g}^6 e_g^2$	Sym	Sym	No distortion
d^8(LS)	$t_{2g}^6 e_g^2 = t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^0$	Sym	Asym	Large distortion (Elongated distortion)
d^9	$t_{2g}^6 e_g^3 = t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^1$	Sym	Asym	Large distortion (Elongated distortion)
d^9	$t_{2g}^6 e_g^3 = t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^2$	Sym	Asym	Large distortion (Compressed distortion)
d^{10}	$t_{2g}^6 e_g^4$	Sym	Sym	No distortion

6-coordinated complexes are found to possess distorted octahedral structures due to this effect. For example, $[Cu(H_2O)_6]^{2+}$ has a distorted octahedral structure with four near H_2O molecules in xy plane and two remote ones along the z-axis.

i. Even though $[Cu(en)_3]^{2+}$ contains three chelate rings, it is less stable than $Cu(en)_2(H_2O)_2]^{2+}$ which contains only chelate rings. This is contrary to the general trend of chelation; greater the number of chelate rings greater will be the stability. But here the opposite trend is observed. In the former case, two chelate rings make use of two elongated bonds (due to z-out) along the z-axis. These rings are under strain; hence it is less stable.



ii. The absorption spectra of complexes having this distortion are different from the spectra of complexes having no distortion; instead of getting a single Gaussian curve, a curve with a shoulder as shown in figure is obtained in the spectrum due to distortion.



(a) Gaussian curve (where there is no distortion)

(b) Gaussian curve with a shoulder (where there is distortion)

Absorption spectra of complexes: a) without J-T distortion b) with J-T distortion

iii. This distortion also affects the reactivity of complexes. For example, $[Cu(H_2O)_6]^{2+}$ (d^9 system) exchanges two of its H_2O molecules on the elongated z-axis more rapidly than its four H_2O molecules in the *xy*-plane.

Molecular Orbital Theory and Energy Level Diagrams Concept of Weak and Strong Fields

Molecular Orbital Theory:

Molecular Orbital Theory (MO Theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are *delocalised* over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators.

Postulates of Molecular Orbital Theory

- The overlapped atomic orbitals do not maintain their identity.
- The overlapped atomic orbitals rearranged themselves to produce molecular orbitals.
- The number of molecular orbitals obtained is equal to the number of overlapped atomic orbitals.
- Half of the total number of molecular orbitals is called bonding molecular orbitals (BMO). Whereas the other half is called anti-bonding molecular orbitals (ABMO).
- Axial overlapping of two atomic orbitals belonging to two atoms results in the formation of a bonding molecular orbitals known as σ-orbital, and anti-bonding molecular orbital known as σ*-orbitals.
- Parallel overlapping of two atomic orbitals belonging to two toms results in the formation of a bonding molecular orbital known as π-orbital, and an anti-bonding molecular orbitals known as π*-orbital.
- A bonding molecular orbital is always lower in energy whereas anti-bonding molecular orbital is always higher in energy than either of the atomic orbitals of the two atoms.
- A covalent bond is formed when a bonding molecular orbital is filed by electrons leaving anti-bonding molecular orbital completely or partially empty.
- No covalent bond is formed when equal number of bonding and anti-bonding orbitals electrons are available.

- Filling of molecular orbitals takes place according to Auf-bau Principle. Pauli Exclusion Principle and Hund’s Rule.
- Number of covalent bonds formed between two atoms is called bond order.

Bond Order

- Bond order is the number of chemical bonds between a pair of atoms. The bond order of a molecule can be calculated by subtracting the number of electrons in anti-bonding orbitals from the number of bonding orbitals, and the resulting number is then divided by two. A molecule is expected to be stable if it has bond order larger than zero. It is adequate to consider the valence electron to determine the bond order. Because (for principal quantum number, n>1) when MOs are derived from 1s AOs, the difference in number of electrons in bonding and anti-bonding molecular orbital is zero. So, there is no net effect on bond order if the electron is not the valence one.

Bond Order = 1/2 [(Number of electrons in bonding MO) - (Number of electrons in anti-bonding MO)]

Bond Length

Bond length is defined as the distance between the centers of two covalently bonded atoms. The length of the bond is determined by the number of bonded electrons (the bond order). The higher the bond order, the stronger the pull between the two atoms and the shorter the bond length Bond length is reported in picometers. Therefore, bond length increases in the following order: triple bond < double bond < single bond.

Bonding Molecular Orbital (σ)

The two 1s atomic orbitals overlap constructively, leading to the formation of a bonding molecular orbital. Electrons in this orbital contribute to the stability of the molecule.

Antibonding Molecular Orbital (σ)*

The two 1s atomic orbitals overlap destructively, forming an antibonding molecular orbital. Electrons in this orbital would destabilize the molecule.

σ Bonding Molecular Orbital

The overlap of the two 2p orbitals along the internuclear axis forms a σ bonding molecular orbital.

π Bonding Molecular Orbitals

The sideways overlap of the two sets of 2p orbitals results in two π bonding molecular orbitals.

σ and π Antibonding Molecular Orbitals**

There are corresponding σ* and π* antibonding molecular orbitals formed by the destructive overlap of atomic orbital

Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram For a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the center. Dashed lines show which of the atomic orbitals combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus we can see that combining the six 2*p* atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ* and two π*).

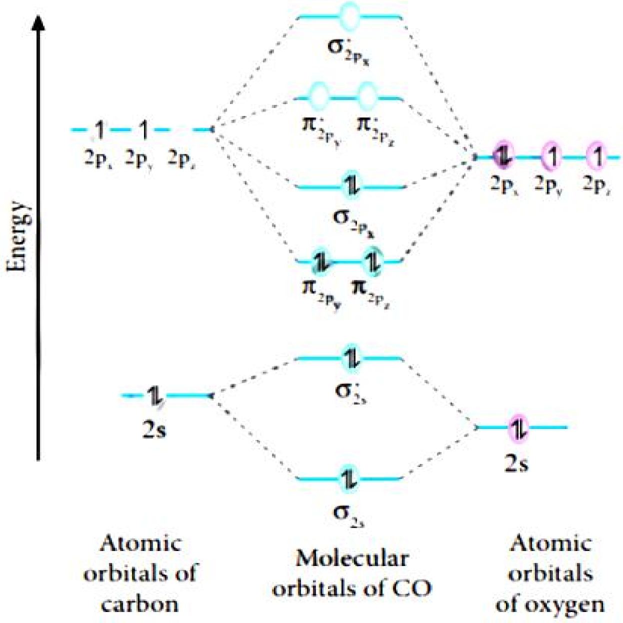
Energy Level Diagram of Strong Field Ligands:

Energy Level Diagram of CO Molecule

The carbon monoxide molecule consists of a carbon atom bonded to an oxygen atom. The molecular orbital diagram of carbon monoxide shows the distribution of electrons in the bonding and antibonding molecular orbitals. The electrons occupy the molecular orbitals in accordance with the Aufbau principle, filling the lower energy orbitals first before moving to higher energy levels.

In the case of carbon monoxide, the carbon atom has two valence electrons, while the oxygen atom has six valence electrons. The two valence electrons of carbon occupy the sigma bonding molecular orbital (σ), resulting in a strong carbon-oxygen bond. The remaining four valence electrons of oxygen occupy the π* antibonding molecular orbitals, which weaken the carbon-oxygen bond.

The molecular orbital diagram of carbon monoxide illustrates the delicate balance between the bonding and antibonding interactions. This balance contributes to the stability and reactivity of carbon monoxide, making it a versatile molecule with diverse applications in various industries.



Molecular orbital diagram of Carbon monoxide molecule (CO)

Electronic configuration of C atom: 1s2 2s2 2p2

Electronic configuration of O atom: 1s2 2s2 2p4

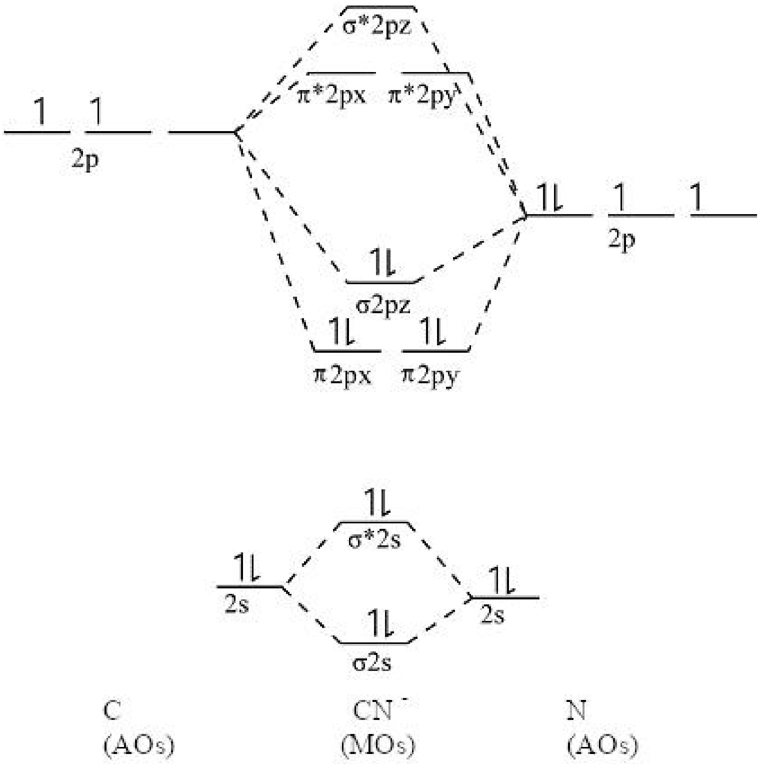
Electronic configuration of CO molecule : σ1s2, σ1s*2, σ2s2, σ2s*2, π2py2, π2pz2 σ2px2

Bond order = N b − N a /2 *N b*

=10 – 4/ 2 = 3

The molecule has no unpaired electrons hence it is diamagnetic.

Energy Level Diagram of CN− Molecule:



CN− has 14 electrons which are similar to that of nitrogen molecules.

Due to the MOT concept, Nitrogen molecules are diamagnetic.

All the electrons are paired. Bond order finds by the bonding and antibonding electrons.

All the electrons are paired, this ion should be diamagnetic.
B.O. =1/2[N_b−N_a]

= 1/2[8−2]

=3.

Electronic configuration of C atom: $1s^2\ 2s^2\ 2p^2$

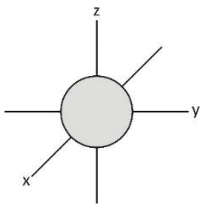
Electronic configuration of N- atom: $1s^2\ 2s^2\ 2p^4$

Electronic configuration of CN- atom: σ21s,σ∗21s,σ22s,σ∗22s,π22px=π22py,σ22pz
Due to electron arrangement its magnetic characteristic is diamagnetic.

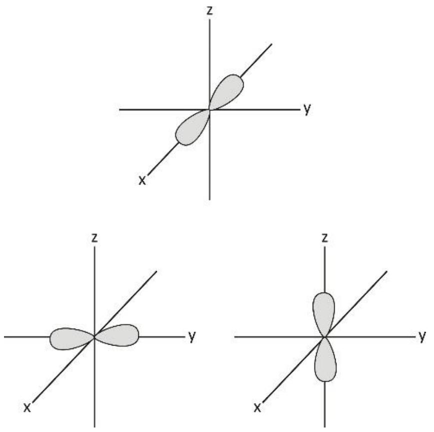
Sigma And Pi Bonding in Octahedral Complexes

Types of Atomic Orbitals that can participate in σ - Bonding :

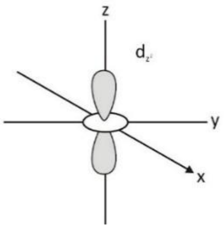
S- orbital :

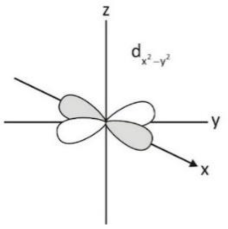


P- orbitals : (P_x, P_y, P_z)



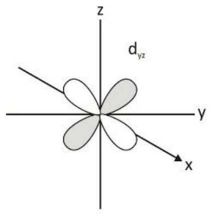
d- orbitals : $(d_z^2 ,d_x^{2-}d_y^2)$

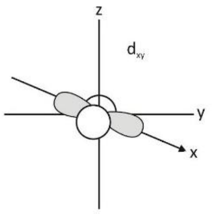


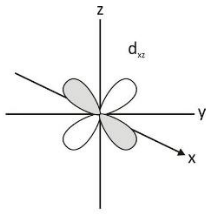


Types of Atomic Orbitals that can participate in π - Bonding :

d_{xy} ,d_{yz} ,d_{xz} :



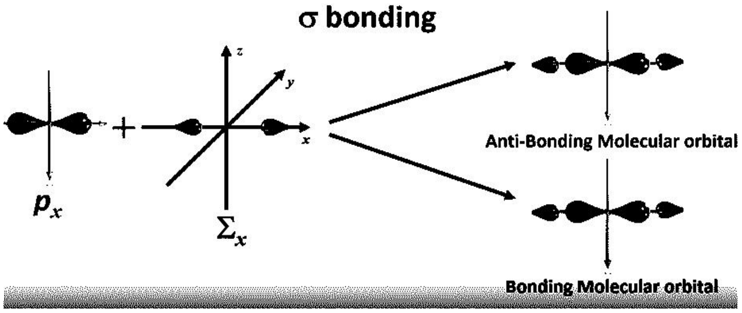




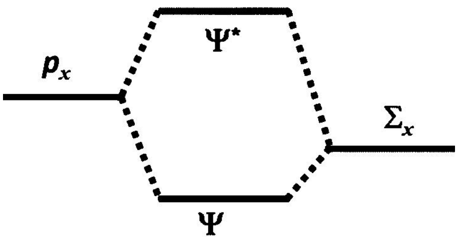
Orbitals	**Mulliken Symbols**	**LGO (Ligand Group Orbitals)**
s	a_{1g}	Σa_{1g}
d d_{x2-y2} d_z^2	e_g	Σ_{x2-y2} Σ_z^2
p p_x p_y p_z	T_{1u}	Σ_x Σ_y Σ_z

Let us try to understand how the bonding takes place.

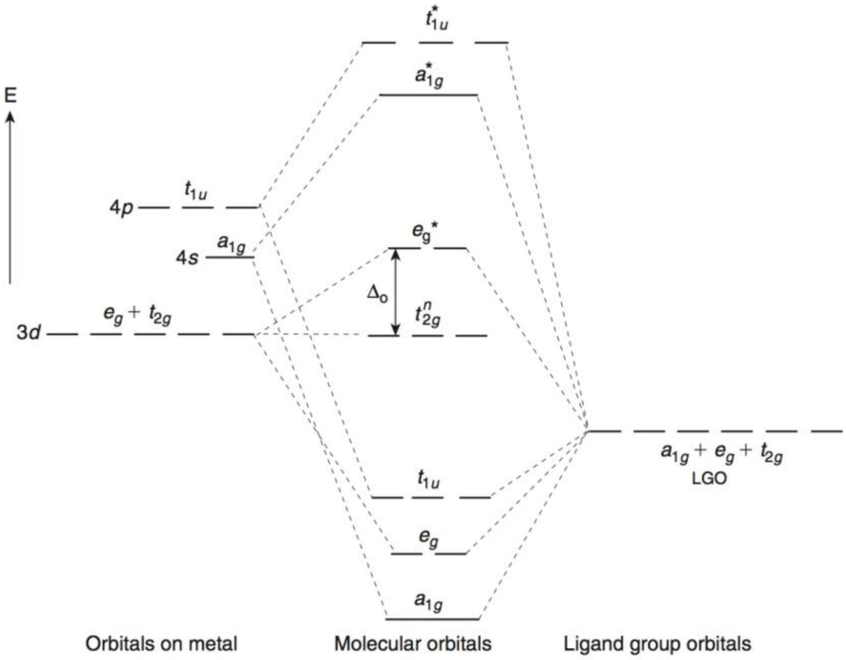
According to the postulates of MOT, 2 atomic orbitals combine to form 2 Molecular Orbitals.



Bonding molecular orbitals are in-face and thus they can overlap with each other to form the bond whereas anti-bonding Molecular orbitals are out of face so they do not overlap with each other so the possibility of bond formation is zero. Diagrammatically,



Sigma bonding in Octahedral complexes :



In metals ,for t_{2g} orbital ,there is no corresponding similar orbital for overlapping ,so it remains non-bonding at center .Orbitals which are more electro negative in nature occupies the BMO while the electro positive occupies ABMO or Non- bonding orbital .

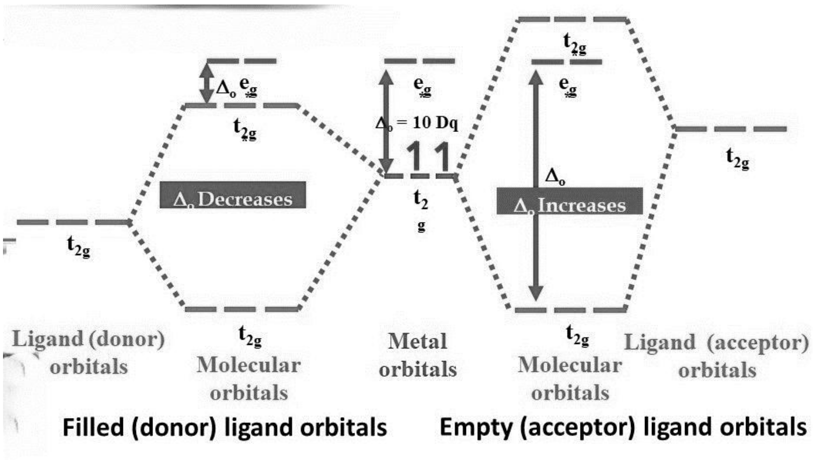
π – Bonding in octahedral complexes :

In sigma bonding ,the t_{2g} orbitals of metal do not have symmetrical orbitals to overlap .so they are involved in π – Bonding .They are d_{xy} , d_{yz} , d_{xz} .

Types of ligand orbitals that can participate in π – Bonding:

- Simple filled p π orbitals
- Simple empty d π orbitals
- Empty π molecular orbital of poly atomic ligands like CN^- , CO etc .

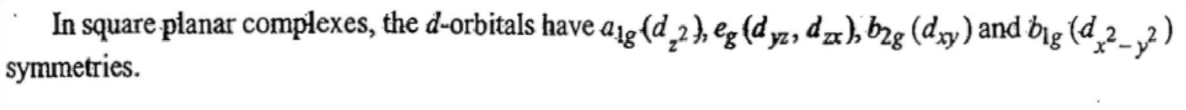
The main effect of π bonding is the metal complexes get extra stability . In octahedral complexes ,6 ligands are involved ,so total 12 π orbitals available with the ligands .



We will consider only e_{g^*} and t_{2g} . There are only 2 cases either the ligands are more electronegative or less electronegative .Only t_{2g} participate in bonding so e_{g^*} remains same .

Filled ligand orbitals	**Empty ligand orbitals**
• Ligands are more electro negative	• Ligands are more electro positive
• Metals are more electropositive	• Metals are more electronegative
• Electrons in ligands moves to BMO	• Electrons in ligands moves to ABMO
• Electrons in metals moves to ABMO	• Electrons in metals moves to BMO
• Gap between e_{g^*} and t_{2g} is decreased	• Gap between e_{g^*} and t_{2g} is increased
• Ligand to metal - π interaction	• Metal to ligand - π interaction

Sigma And Pi Bonding in Square Planar Complexes

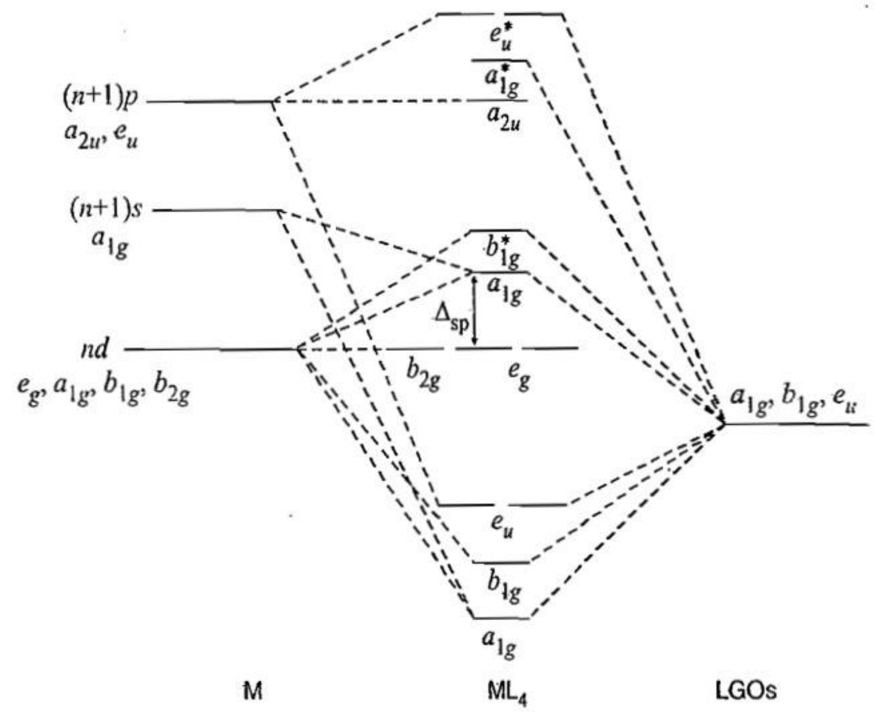


In square planar complexes, the *d*-orbitals have $a_{1g}(d_{z^2})$, $e_g(d_{yz}, d_{zx})$, $b_{2g}(d_{xy})$ and $b_{1g}(d_{x^2-y^2})$ symmetries.

The p-orbitals have a2u (Pz) and eu (Px, Py) symmetries. The four ligands lying along the x and y- axes give rise to ligand group orbitals of a1g, b1g and eu symmetries. These LGOs interact with metal orbitals of same symmetry sigma molecular orbitals as shown. The a1g

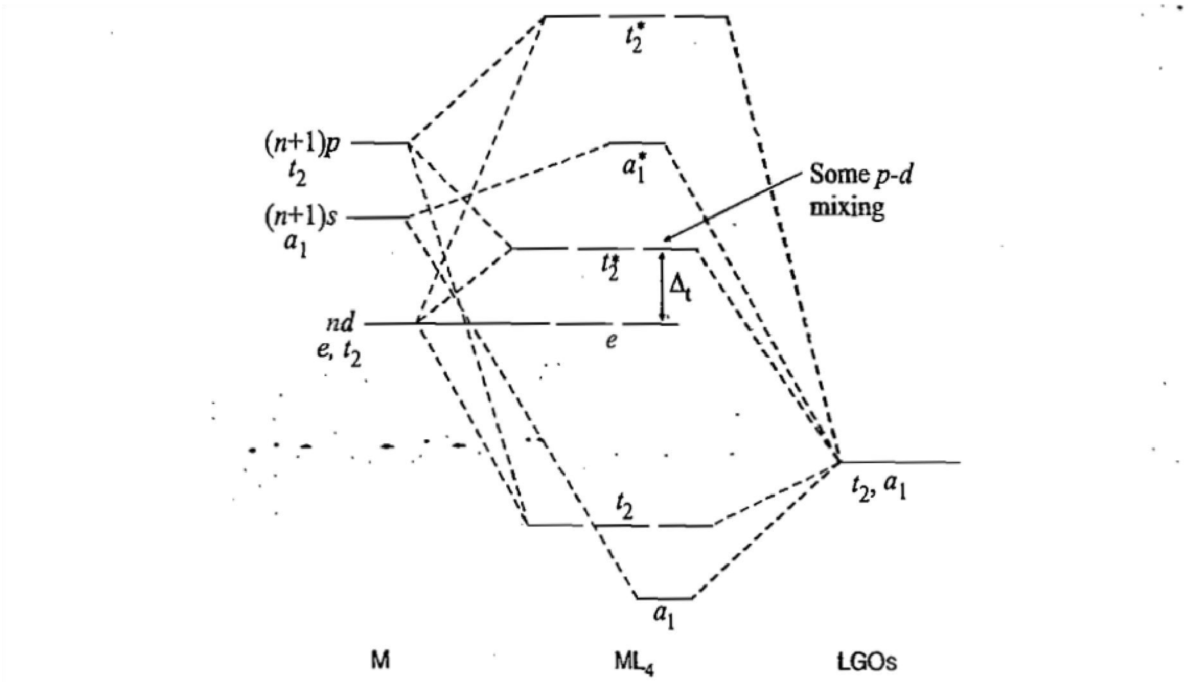
LGO interacts with both a1g metal orbitals to form one bonding ag and one slightly antibonding and one antibonding molecular orbital. The metal orbitals b2g, eg and a2u remain non-bonding because they have no symmetry similar to LGOs.

In general, the square planar complexes are formed by d^8 metal ions like Ni2+ (with strong ligands like CN^-), Pd 2+ and Pt2+ ions. There are sixteen valence electrons, eight from the four ligands and eight from the metal ion. Eight electrons from ligands occupy the bonding molecular orbitals (a1g, b1g and eu) and eight electrons from the metal ion-occupy b2g, eg and a1g (slightly antibonding) molecular orbitals and the complexes are diamagnetic. The square planar complexes are highly stable, though they contain 16 valence electrons. This is due to the reason that all the bonding MOS are filled and the antibonding MOs are empty. Adding additional electrons would destabilized the complex because the additional electrons would enter into the antibonding molecular orbitals and lower the bond order. The complexes containing electrons less than 16 are also less stable because they have lesser number of electrons in bonding molecular orbitals and lower the bond order.



Sigma And Pi Bonding in Tetrahedral Complexes

The procedure for the constitution of molecular orbital diagrams for tetrahedral and square planar cpmplexes is same as that applied for octahedral complexes. The metal atom ion in each case uses its same nine valence orbitals available for bonding but their symmetry properties are different for each geometry. For a tetrahedral ML4 complex, the metal s and p-orbitals have a1 and t2 symmetries respectively. The dxy, dyz and dzx orbitals have t2 and $dx^2 – y^2$ and dz^2 orbitals have e symmetry. It is seen that the symmetries of p-orbitals and that of dxy, dyz and dzx orbitals are identical i.e., t2 symmetry. It is due to the fact that the p-orbitals hybridized with s-orbital (sp3-hybridization) and dxy, dyz and dzx orbitals hybridized with s-orbital (sd3-hybridization) form tetrahedral geomtery. Of the four ligand group orbitals (LGOs) constructed from ligand lone pair orbitals one have a1 and three t2 symmetries. The a1 orbital LGO interacts with a1 orbital of metal to give one bonding and one antibonding MO and t2 LGOS can interact with both sets of t2 orbitals of metal (p and dxy, dyz, dzx) to give one bonding and two antibonding molecular orbitals. In contrast to the octahedral complexes, the metal e orbitals are non-bonding. The separation between the e and the next higher t2 molecular orbitals is equal to Δt as in CFT. For a complex such as $[CoCl_4]^{2-}$, there are total fifteen valence electrons of which eight electrons are produced by four ligands (two electrons per ligand) and the Co2+(d^7) ion furnishes seven electrons. Eight electrons are filled in the bonding MOS (a1 and t2), four electrons in non-bonding e orbitals and three in the slightly antibonding t2 orbitals.



Unit – II

Spectral Characteristics of Complexes

Introduction

Spectra is due to the transition of an electron from one energy level to another.

Types:

1. Absorption Spectra : It shows the particular wavelength of light absorbed (ie) particular amount of energy required to promote an electron from one energy level to higher level.
2. Emission spectra: It shows the energy emitted when the electron falls from the excited level to the lower level.

The electronic transitions are high-energy transitions. In the course of this transition, other smaller energy (vibrational and rotational transition) also takes place. But the energy difference is small in vibrational and rotational transition. Therefore difficult to resolve.

The electronic transition is governed by selection rules. The transition which obeys the selection rules are called as the allowed transition and the transition disobeys the selection rule, are called forbidden transition.

Allowed transition ⟶ quite common (high intensity)

Forbidden ⟶ transition Not common (low intensity)

Electronic transitions in complexes:

The electron (orbital motion) revolves round the nucleus. When a charge species revolves round the nucleus, a magnetic field is produced. Also, the electron spin around its own axis. So another type of magnetic field is generated.

I. Thus, even though the p-orbitals are degenerate and have the same energy, the electrons present in them interact with each other and result in the formation of ground state (lower energy) and one (or) more excited states due to electrostatic repulsion.

II. There can be interaction (or) coupling between the magnetic field produced as a result of orbital motion.

III. There can be a coupling (or) interaction between the magnetic field produced by the spin of electrons around its own axis.

If for 1-p e- , there are 6 possible ways of placing e-s in the ‘p-orbital’.

For 2p e-s, there are 15 possible ways of placing the e-s in the p orbital.

These electronic arrangement can be divided into 3 main groups of different energy called 3 energy states. They are labelled as term symbol.

Term states for *d* ions

Term symbol is an abbreviated description of the energy, angular momentum and spin multiplicity of an atom in a particular state.

Term states for dn ion: When several electrons occupy a sub shell the energy states obtained, depends upon the result of the orbital angular quantum number of each electron. The resultant of all the l-values is demonstrated by a new quantum number ‘L’ which defines the energy state for the atom

L = 0, 1, 2, 3, 4, 5, 6, 7, 8……
State = S P D F G H I K L

(The letter J is omitted since this is used for another quantum number)

Spin – multiplicity value = (2s + 1)

S Þ Spin quantum number

No of e-s present = 1 2 3 4 5 . . . .

(2s + 1) = 2 3 4 5 6 . . . .

Orbital quantum number (L) = (m1 X l)

Rules for determing the term symbols:

The e-s should be unpaired as much as possible and occupy different orbital (ground state) of low energy.

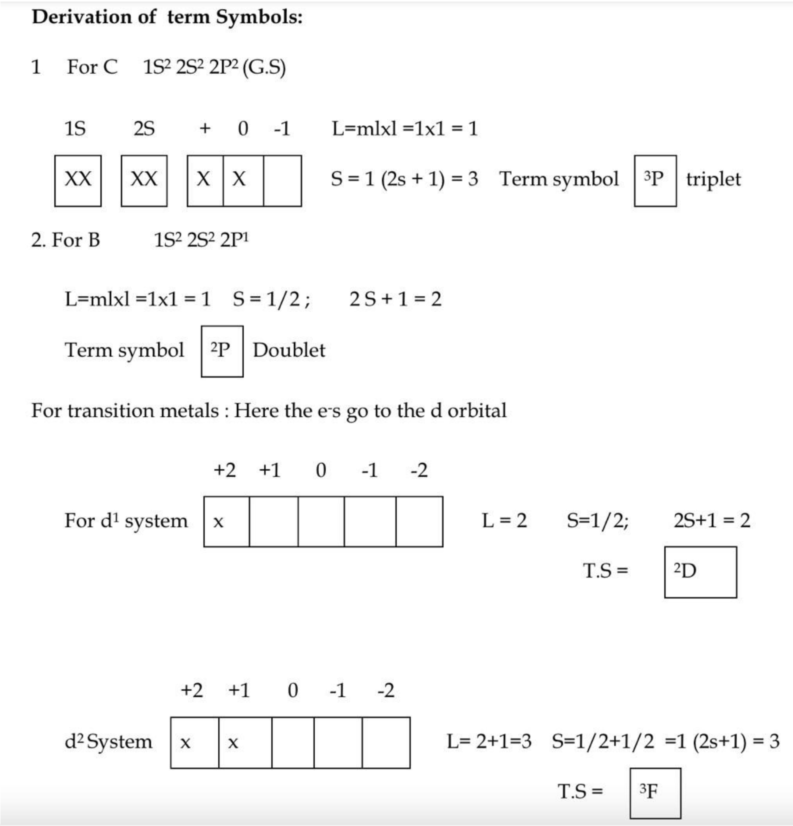
I. The spin multiplicity value must be maximum to be stable

II. The orbital angular momentum L value should be large (or) the highest (ground state).

Total angular momentum quantum number (J)

L and S values couple to give J value. Magnetic effects of L and S couple to give J value . **IV.** If sub shell is more than half filled – Smallest J value is more stable (L-S)

If the sub shell is less than half filled – Highest J value is more stable (L + S)



Derivation of term Symbols:

1 For C $1S^2\ 2S^2\ 2P^2$ (G.S)

1S	2S	+	0	-1
XX	XX	X	X	

L=mlxl =1x1 = 1

S = 1 (2s + 1) = 3 Term symbol $\boxed{^3P}$ triplet

2. For B $1S^2\ 2S^2\ 2P^1$

L=mlxl =1x1 = 1 S = 1/2 ; 2 S + 1 = 2

Term symbol $\boxed{^2P}$ Doublet

For transition metals : Here the e^-s go to the d orbital

	+2	+1	0	-1	-2
For d^1 system	x				

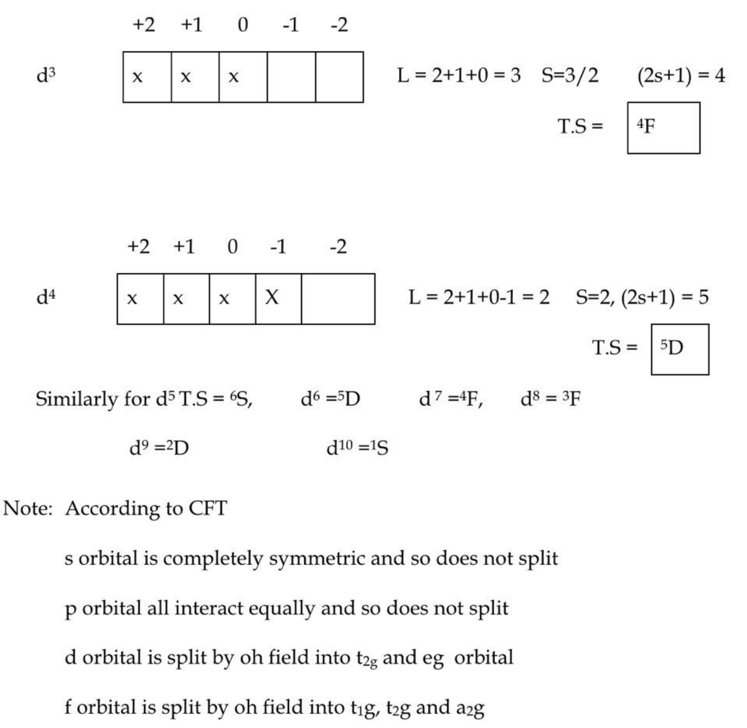
L = 2 S=1/2; 2S+1 = 2

T.S = $\boxed{^2D}$

	+2	+1	0	-1	-2
d^2 System	x	x			

L= 2+1=3 S=1/2+1/2 =1 (2s+1) = 3

T.S = $\boxed{^3F}$



	+2	+1	0	-1	-2
d^3	x	x	x		

L = 2+1+0 = 3 S=3/2 (2s+1) = 4

T.S = $\boxed{^4F}$

	+2	+1	0	-1	-2
d^4	x	x	x	X	

L = 2+1+0-1 = 2 S=2, (2s+1) = 5

T.S = $\boxed{^5D}$

Similarly for d^5 T.S = ^6S, $d^6 = {^5D}$ $d^7 = {^4F}$, $d^8 = {^3F}$

$d^9 = {^2D}$ $d^{10} = {^1S}$

Note: According to CFT

s orbital is completely symmetric and so does not split

p orbital all interact equally and so does not split

d orbital is split by oh field into t_{2g} and eg orbital

f orbital is split by oh field into t_1g, t_2g and a_2g

Characteristics of *d-d* transitions:

This actually is electron transition from t2g to eg. orbital. In this, charge distribution between excited and ground states are same. These transitions occur in visible or near U.V region. This appears to be the simple explanation for the colour in the transition metal complexes. The absorption spectra of octahedral complexes show the molar absorbance of such d-d transition are low. This is because of selection rules. The electron transition are of high energy transition. In addition much lower energy, vibrational and rotational transition always occur. The vibrational and rotational level are too close in energy, to be resolved into separate absorption bands, but they result in considerable broadening of electronic absorption bands in d-d spectra. Band widths are commonly found to be the order of 1000 – 3000 cm^{-1}.

Charge Transfer Spectra

The absorption of light is to cause an electronic transition within an atom or molecule. It is essential that the absorption results in a charge density displacement. This displacement may be localized on one atom (as it is, to first approximation, in the d-d spectra) or it may be the displacement of charge from one atom to another, so in electronic transition electrons move between orbitals that have predominantly metal d-orbital character. Thus the charge distribution is about the same in the ground state and excited state. There is another important class of transition in which the electron moves from a M.O centered mainly on the ligand to one centered mainly on the metal atom and vice versa. In these the charge distribution is different, considerably from ground state and excited state and so they are called as charge transfer transition.

Differences between d-d and charger-transfer transition

d-d transition	**Charge transfer spectra**
Here electron moves from one d- orbitals to another results in the d-d transition. It is forbidden transition against selection rule gg (forbidden)	This arises when an electron from one atom goes into another atom within the same molecule. The transition is not against any selection rule (g or u) allowed.
The Charge distribution between the ground state and excited state remains the same.	The charge distribution between the ground state and excited state different because of this we say this is as charge transfer spectra.

Intensity (e) value is normally below 100 and have weak intensity.	e value is high 10,000 [Eg] [Ti Cl_4] $^{2-}$
Mostly they occur in the visible and near uv region.	The bands are usually obtained is near uv region and often overlap with d-d transition because of this we do not get full d-d spectrum of complex.

There are two possibilities of charge transfer process in metal complexes. Electron from metal goes to ligand (ie) M ® L transition (oxidation) electron from ligand goes to metal (ie) L (or) M transition (reduction).

[I] Metal - Ligand (oxidation)

Here the electron from t2g (or) eg orbital of metal may go to the p *of ligand. The direction of transition depends on the energy of the ligand and metal orbital and also on the occupancy of orbital.

I. M - L transition will occur when the metal is in the lower oxidation state.

II. The ligand orbitals should be empty and also of lower energy.

III. More the reducing power of the metal the lower will be the energy of transition.

The energy of this type of transition probably occurs in the aqua ions of divalent metal of the first transition series (first half) because they have valency ions and reducing power. So they give deeply coloured complex with electron acceptor ligand like o – phenanthrene, pyridine (neutral) due to delocalized p electrons they are of intense colour Intense colour is absent in Ni $^{2+}$ and Co $^{3+}$ (Higher oxdn state). (Here the metal has more reducing property and more the oxidizing ligand- lower the energy of transition).

(II) Ligand = metal (reduction)

Here the electrons from p orbital of ligand may go to t2g or eg. (Note: Electron from p-p transition is intra ligand transition)

I. L - M transition will occur when the metals are in the higher oxidation states.

II. The ligand orbital should be filled and also of higher energy.

III. Higher the oxidizing power of the metal lower will be the energy of transition.

Thus charge transfer absorption in the visible spectrum is more common in complexes of Iron (III) than in those of Cr (III). This accounts for the use of iron (III) in colour tests in organic chemistry. Eg. Phenols and hydroxamic acid gives neutral $FeCl_3$ test.

Metal – Metal Charge transfer

A number of inorganic compounds contain a metal in two valence states. Eg. (i) Prussian blue K(Fe (III) { Fe(II) } (CN_6)). Here Fe (III) is high spin and Fe(II) is low spin as shown by the study of Mossbauer effect. Here the charge transfer occurs from the t2g orbitals of Fe (III) to Fe (II) via interfering CN.

Ligand – Ligand Charge transfer

A ligand such as SCN- has internal charge transfer transition usually located in the u-v region of the spectrum, corresponding transition occur in co-ordinated ligand, but can be usually identified by comparison with spectra's of the free ligand.

M- L (oxidation) Charge transfer transition

This type of transition can only be expected when ligands possess low lying empty orbitals and the metal ion has filled orbitals lying higher than the highest filled ligand orbitals. The best examples are provided by complexes containing CO, CN- or aromatic amines (pyridine, or phenanthroline) as ligands. In the case of octahedral metal carbonyls Cr(CO)6 and Mo (CO)6 pairs of intense bands at 35,800 and 44,500 cm-1 for the former and 35,000 and 43,000 cm-1 for the latter have been assigned to transition from the bonding to the anti-bonding (Ligand p *) components due to metal-ligand p bonding interaction.

For [Ni(CN)4]2- there are 3 medium to strong bands at 32,000, 35,200 and 37,600 cm-1 which have been assigned as transition from the three types of filled metal d-orbitals [dxy, and (dxz, dyz)] to the lowest energy orbitals formed from the p * orbitals of the set of CN- groups.

Selection rules for Electronic Spectra

Not all the theoretically possible transition are actually observed. The selection rule distinguish allowed and forbidden transition. Allowed transitions are common but forbidden transition less frequently occur. They are of much low intensity.

A. Laporte orbital selection rules: Transitions involving a change in subsidiary quantum number Dl = ± 1 are, Laporte allowed transition and therefore they have high absorbance.

e.g as S2 ⟶ S1 P1 (changes by +1) and moral absorption co-efficient is S = 5000 – 10000 l/μ/cm.

In contrast: d-d transitions are laporte forbidden transition because Dl=0 and therefore have a lower absorbance. But spectra of much lower absorbance are observed, because of slight relaxation in the laporte rule. This enable the transition metal complex to have bright coloured.

B. In cpxes with a centre of symmetry the only allowed transitions are those with a change of parity. i.e gerade to ungerade . u ⟶ g are allowed, but not g ⟶ g and ⟶ u u. Since all d orbitals have gerade symmetry, all d-d transitions are forbidden.

Types of Relaxation:

1. A molecule with no centre of symmetry (E.g) Td →[CoCl4] 2- , [MnBr4] 2- also unsymmetrically substituted octahedral complexes e.g. [Co(NH3) 5Cl]2+ are coloured, in such cases mixing of d and p ortritals may occur in which case transitions are no longer pure d-d in nature. Therefore transitions can take place between d-orbitals having different p-character and such transitions are called as partially-allowed transitions.

2. Mixing do not occur in octahedral complexes which have a centre of symmetry such as [Co(NH3) 6] 3+ (or) [Cu(H2O)6] 2+. Here the M-L bonds vibrate so that for a fraction of time, the d-p mixing will be possible. Thus, a very small amount of mixing occurs and low intensity spectra are observed. These transitions are said to be vibrationally allowed transitions and the effect is described as vibronic coupling. The intensity of band is roughly proportional to the extent of mixing.

3. Spin selection Rules: During the transition between energy levels, the spin of the electrons does not change but remains the same [DS = 0] Spin forbidden transitions have very weak intensity (DS ^{1}0) (can be ignored). Eg. [Mn(H2O)6] 2+. So many Mn2+ compounds are flesh coloured or colourless . Spin – allowed transitions have very high intensity.

Sl. No	**Laporte orbital**	**Spin**	**Type of spectra**	**ε= A/cl**	**Example**
1	Allowed	Allowed	Charge transfer	10,000	$[Ti\ Cl_6]^{2-}$
2.	Party allowed some d-p mixing	Allowed	d – d	500	$[Co\ Cl_4]^{2-}$
3.	Forbidden	Allowed	d – d	8 -10	$[Ti\ (H_2O)_6]^{3+}$
4.	Partly allowed some d-p mixing	Forbidden	d – d	4	$[Mn\ Br_4]^{2-}$
5.	Forbidden	Forbidden	d-d	0.02	$[Mn(H_2O)_6]^{2+}$

Orgel Correlation Diagrams

The orgel diagram is the quantum mechanically calculated energy of the term level (as ordinate) against an increasing value of field strength, the ligand field splitting parameter.

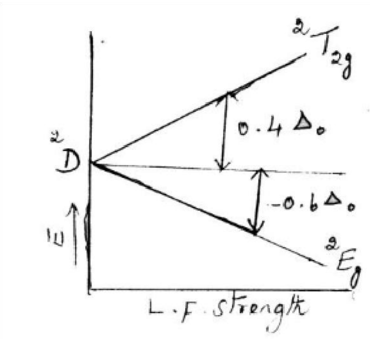
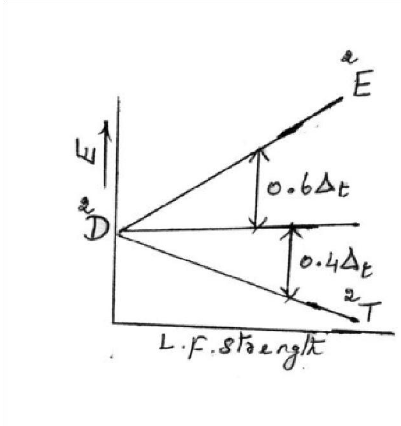
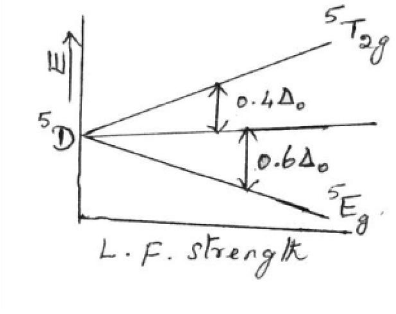
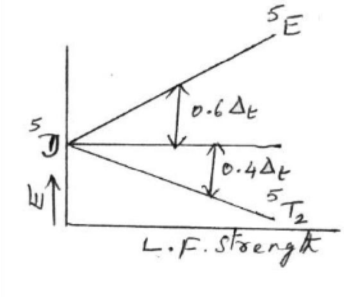
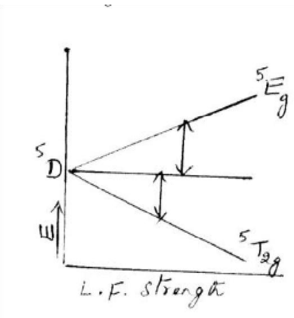
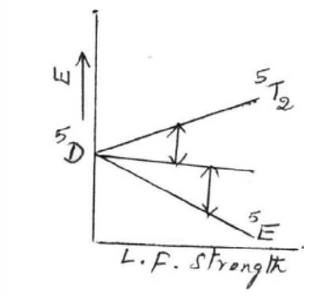
Octahedral field	**Tetrahedral field**
d1 system Ex – [Ti Cl6] $^{3-}$, [Ti(H20)6] $^{3+}$ here the ground state of the free ion is described by the term symbol 2D. The degenerate ‘d’ orbitals or levels are split into T2g and eg in the presence of octahedral field	d1 system: Here also the ground state of the free ion is described by the term symbol 2D. The degenerate d orbitals are split into doublet eg and triplet t2g in the presence of a tetrahedral field.
The lower T2g state corresponds to the single d electron occupying one of the T2g orbital and 2eg state corresponds to the electron occupying one of the eg orbitals.	The lower E corresponds to the single d electron occupying one of the eg orbital and $^{2}T_{2g}$, state corresponds to the electron occupying one of the t2g orbital.

Note: The magnitude of splitting Δo depends on the nature of the ligand and hence affects the energy of transition. As the ligand is changed, Dq varies and the colour of the complex also varies.

Note:

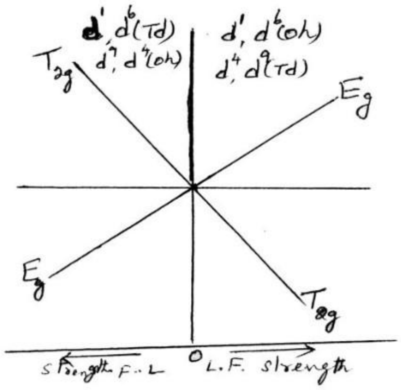
In d1 case, there is a single electron in the lower t2g level while in the d9 case there is a single hole in the upper eg level.

Thus, the transition of the d1 case is the promotion of an electron from t2g to eg level, while in d9 ion, it is simpler to consider as the transfer of a hole from eg to t2g. Thus the energy level diagram for d9 is therefore the inverse of that for a d configuration.

For d9 system (octahedral)	**For d9 system (tetrahedral)**
In the octahedral field the term symbol 2D is split as 2 Eg and 2T2g 0.6Δo below and 0.4 Δo above degenerate states 	In the tetrahedral field the term symbol 2D is split as 2 E and 2 T2 
For d4 system term symbol 5D is split into 5 Eg & 5 T2g 	For d4 system, term symbol 2D is split into 5T2 and 5E 
For d6 system Here in the octahedral field, the term symbol 5D is split as 5T2g and 5Eg 	For d6 system 5D is split as 5 E and 5 T2 

Note: d6 is inverse of that for d4 configuration. From the above energy diagrams we can come to conclusion that d1 and d9 are inverse. Similarly d4 and d6 are inverse (or) we can say that d1 is similar to d6 and d9 is similar to d4.

We can also state that d1 (Td) and d9 (oh) complexes have similar orgel diagram. So d1, d9, d4 and d6 diagrams can be combined to a single orgel diagram.



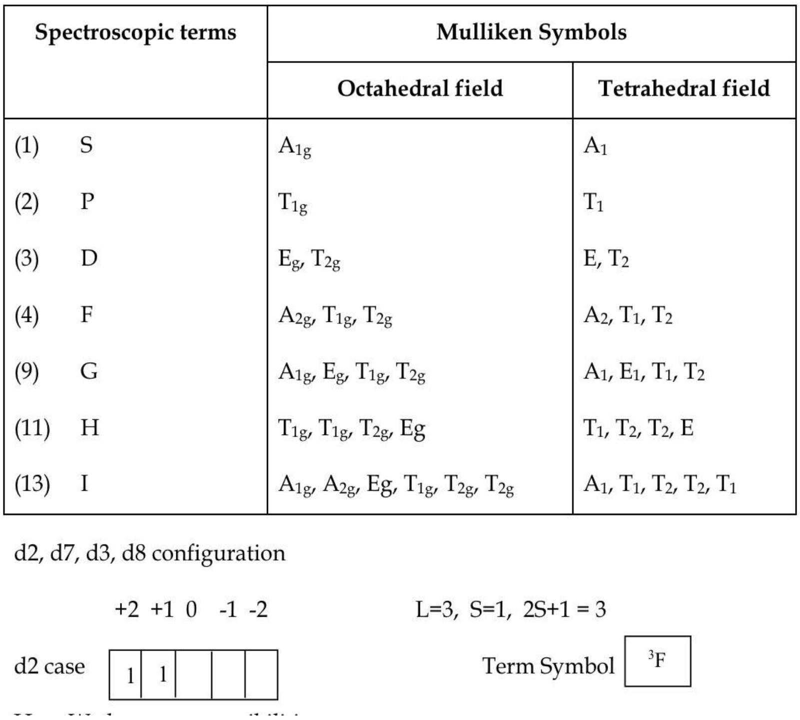
The spectra of these complexes have only one band due to the single d-d transition, that occur is assigned as E - T2.

Hole Formalism: When a subshell is more than half filled it is simpler and more convenient to work out the terms by considering the holes (ie the vacancies) rather than considering the large number of electrons actually present.

By considering the holes, the terms which arises for pairs of atom with p^n and p^{6-n} and d^n and d^{10-n} give rise to identical terms.

Electronic configuration	G.S terms	Other term
1) p^1, p^5	^2P	^1S ^1D
2) p^2, p^4	^3P	^2P ^2D
3) p^3	^4S	
4) p^6	^1S	
5) d^1, d^9	^2D	
d^2, d^8	^3F	^3P, ^1G, ^1D, ^1S
d^3, d^7	^4F	^4p, ^2H, ^2G, ^2F,^3G, ^3H, ^3F,
d^4, d^6	^5D	^3P,^1F,^1D,^1S
d^5	^6S	^4G, ^4F, ^4D, ^4P,
d^{10}	^1S	^2G, ^2F, ^2D, ^2P

Transformation of Spectroscopic symbols into mulliken symbols Splitting of d terms in an octahedral and Tetrahedral field



Spectroscopic terms	Mulliken Symbols	
	Octahedral field	Tetrahedral field
(1) S	A_{1g}	A_1
(2) P	T_{1g}	T_1
(3) D	E_g, T_{2g}	E, T_2
(4) F	A_{2g}, T_{1g}, T_{2g}	A_2, T_1, T_2
(9) G	A_{1g}, E_g, T_{1g}, T_{2g}	A_1, E_1, T_1, T_2
(11) H	T_{1g}, T_{1g}, T_{2g}, Eg	T_1, T_2, T_2, E
(13) I	A_{1g}, A_{2g}, Eg, T_{1g}, T_{2g}, T_{2g}	A_1, T_1, T_2, T_2, T_1

d2, d7, d3, d8 configuration

	+2	+1	0	-1	-2
d2 case	1	1			

L=3, S=1, 2S+1 = 3

Term Symbol ^3F

Here We have two possibilities

1) Parallel Spin
2) Anti Parallel Spin

For parallel spin (2S+1) = 3 (Triplet)

For anti parallel spin (2S+1) = 1 (Singlet)

So, the ground state 3F

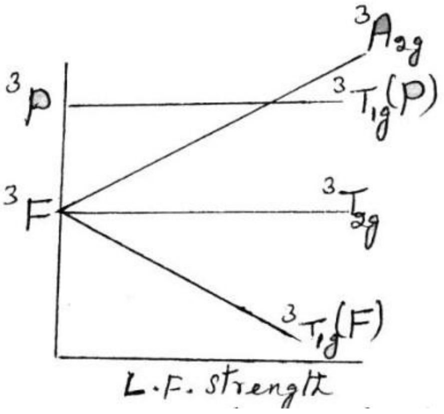
Excited State 3P, 1G, 1D, 1S

Here 1G, 1D, 1S states contain electrons with opposite spin. The transition from the ground state to 1G, 1D, 1S are spin-forbidden and will be very weak and can be ignored.

So, the only important transition is from 3F to 3P.

In the octahedral ligand field, the P state, transforms into a T1g Mulliken term and the F state splits into 3 terms, namely, A2g, T1g and T2g.

The energy level diagram of d2 complex ion. [V(H2O)6] 3+ can be shown in the figure.



Here it can be seen that 3 transitions are possible from the ground states, hence three peaks should occur in the spectrum.

Note: 1) In d1, d4, d6, d9 system only one transition occurs (because there are only 2 energy levels)

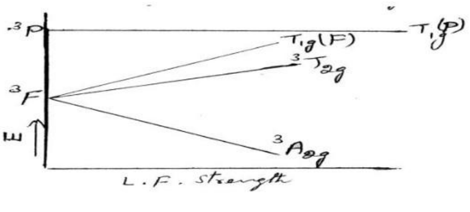
2) In d2 systems, nothing common. So energy can cross (ie) Crossing is allowed also spin allowed transition.

The first excited state 3T2g + 3T1g(p) if the second electron also excited $^3A_{2g}$

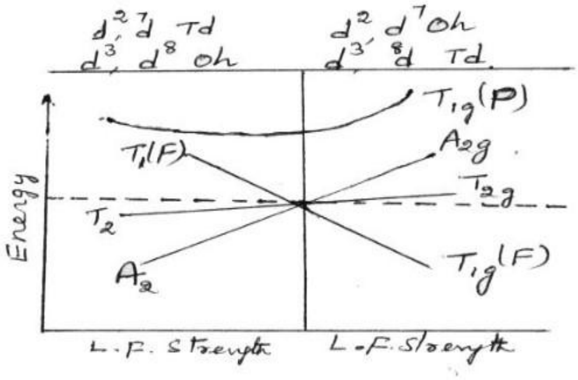
d8 System Eg [Ni(H2O)6] 2+, [Ni(NH3)6] 2+

The complex with d8 configuration in an octahedral field may be regarded as having two holes in the eg level hence promotion of an electron from the lower t2g level to the eg level is similar to transfer of a hole from eg to t2g. So this is inverse of d2 case. Using the same arrangement applied to d1 case, we can say that

d^2	$\rightarrow$	d^7	d^2	$\rightarrow$	d^7
Oh		Oh	Td		Td
d^8	$\rightarrow$	d^3	d^8	$\rightarrow$	d^3
Oh		Oh	Td	-	Td



So combined orgel diagram for 2 electron and 2 hole configuration is shown Fig.



***d^5* system Eg $[Mn(H_2O)_6]SO_4$**

In orgel diagram d5 configuration is left out because of the following reason.

i) It is spin forbidden transition. The compound is almost colourless. So weak intensity is observed in the spectra.

Orgel diagram for low spin complex

Orgel diagram can be modified to take into account low spin complex also. But generally orgel diagram treats only the weak field (or) high spin case. So in these cases the excited state is not included.

Example:

For d6 system : Ex Co3+ for the free ion 1I has higher energy compared to quintet 5D. So 1I (one of the exited state) is least important.

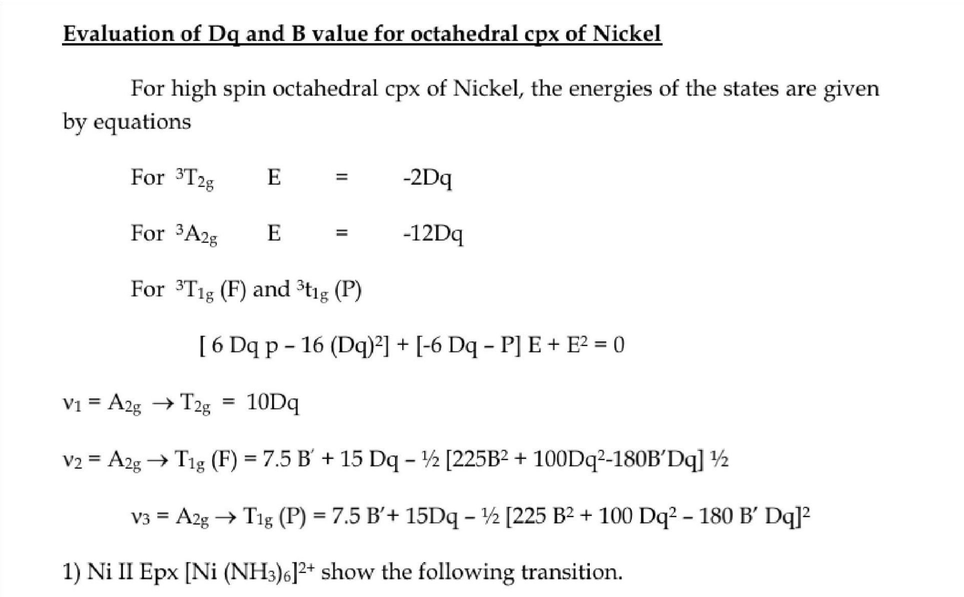
But in the presence of ligand a ligand field or crystal field the state 1I split into several terms. Out of these several terms 1A1g drops in energy as the strength of the field increases and at a certain stage (critical point) A1g cross over (get stabilised) 5T2g and becomes the ground state.

Note : After the critical point the complex would be low spin. For low spin complex theoretically 5 transitions are possible, but we observe only two transition in spectra.

For d5 system

Here ^2I ie of higher energy compared to sextet S. For the free ion ^2I is not important. But in the presence of ligand (or) crystal field the ^2I state splits into several terms. Out of these $^2T_{2g}$

drops in as the strength of the field increases and at a certain stage (critical pts) $^2T_{2g}$ cross over. So becomes ground state.



Evaluation of Dq and B value for octahedral cpx of Nickel

For high spin octahedral cpx of Nickel, the energies of the states are given by equations

For $^3T_{2g}$ E = -2Dq

For $^3A_{2g}$ E = -12Dq

For $^3T_{1g}$ (F) and $^3t_{1g}$ (P)

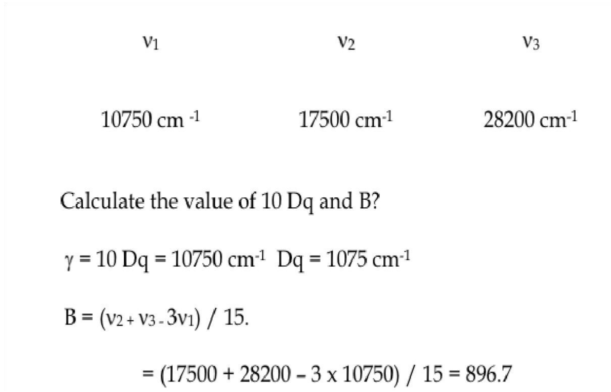
$$[\,6\ Dq\ p - 16\ (Dq)^2] + [-6\ Dq - P]\ E + E^2 = 0$$

$v_1 = A_{2g} \rightarrow T_{2g} = 10Dq$

$v_2 = A_{2g} \rightarrow T_{1g}\ (F) = 7.5\ B' + 15\ Dq - \frac{1}{2}\ [225B^2 + 100Dq^2 - 180B'Dq]\ \frac{1}{2}$

$v_3 = A_{2g} \rightarrow T_{1g}\ (P) = 7.5\ B' + 15Dq - \frac{1}{2}\ [225\ B^2 + 100\ Dq^2 - 180\ B'\ Dq]^2$

1) Ni II Epx $[Ni(NH_3)_6]^{2+}$ show the following transition.



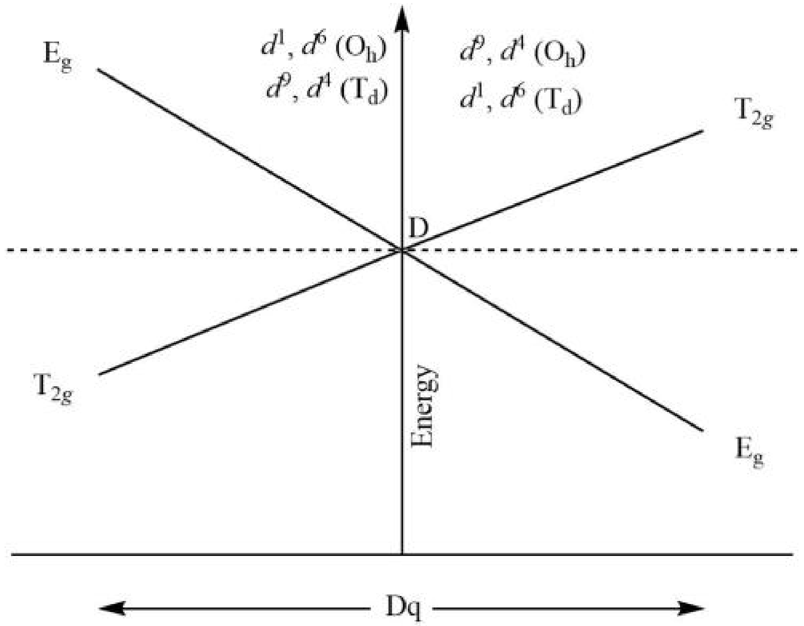
v_1	v_2	v_3
10750 cm^{-1}	17500 cm^{-1}	28200 cm^{-1}

Calculate the value of 10 Dq and B?

$\gamma = 10\ Dq = 10750\ cm^{-1}$ $Dq = 1075\ cm^{-1}$

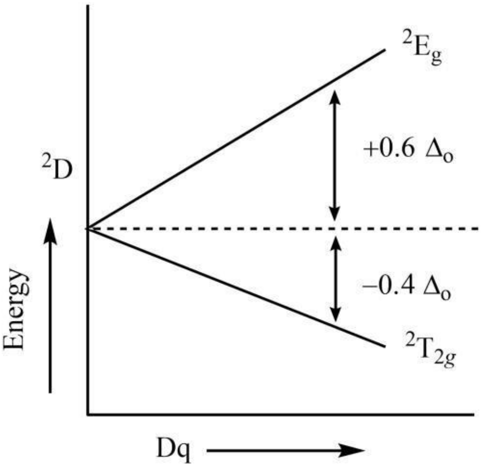
$B = (v_2 + v_3 - 3v_1)\ /\ 15.$

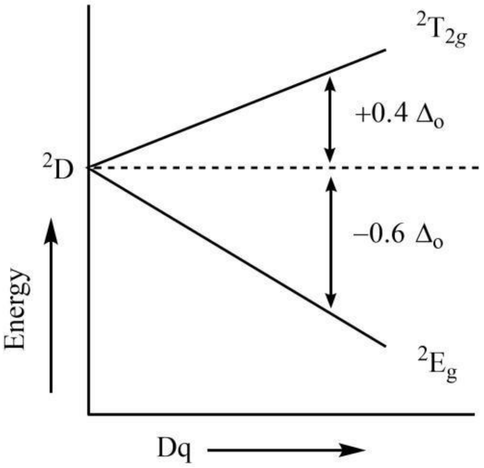
$= (17500 + 28200 - 3 \times 10750)\ /\ 15 = 896.7$

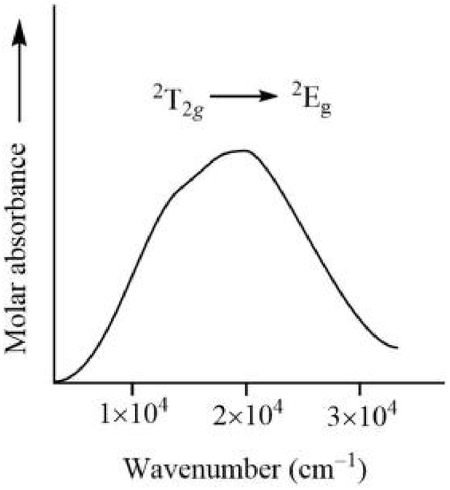


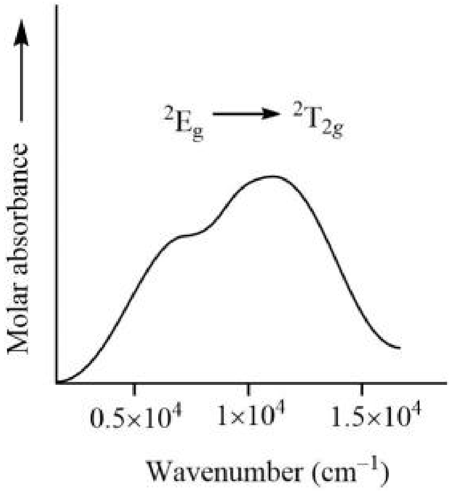
Orgel diagram for d^1, d^9, d^4, d^6 complexes in octahedral (O_h) and tetrahedral (T_d) crystal fields.

Spectra of d^1 and d^9 octahedral complexes

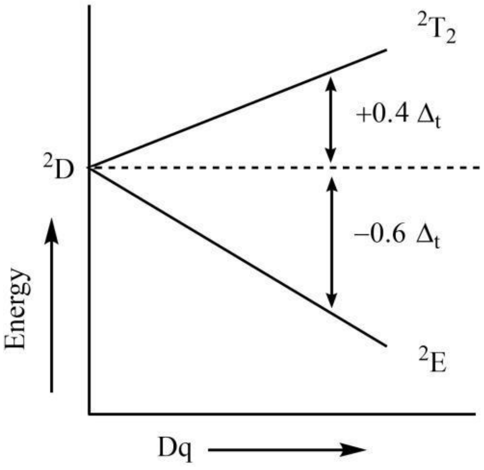


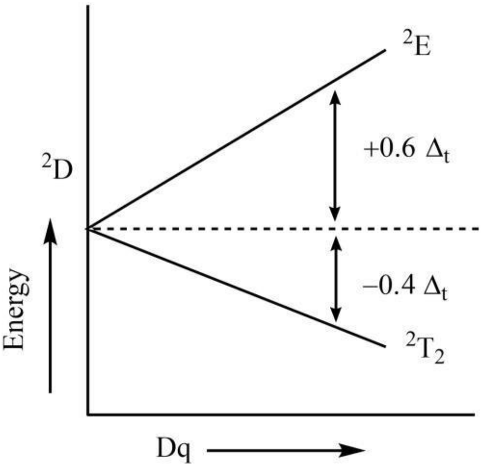


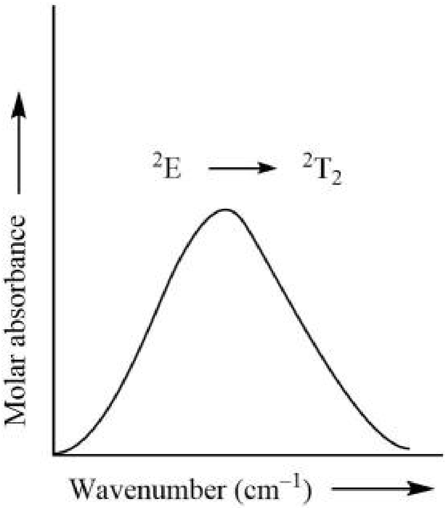


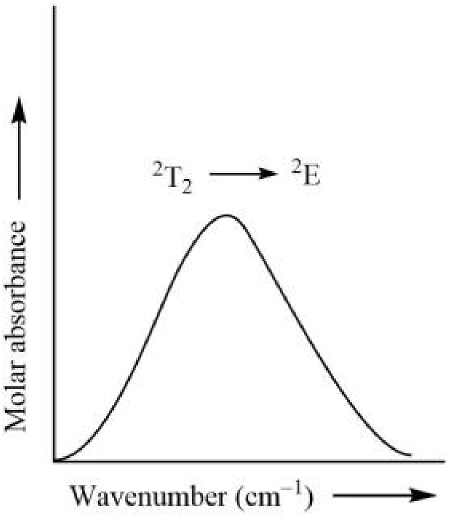


Spectra of d^1 and d^9 tetrahedral complexes

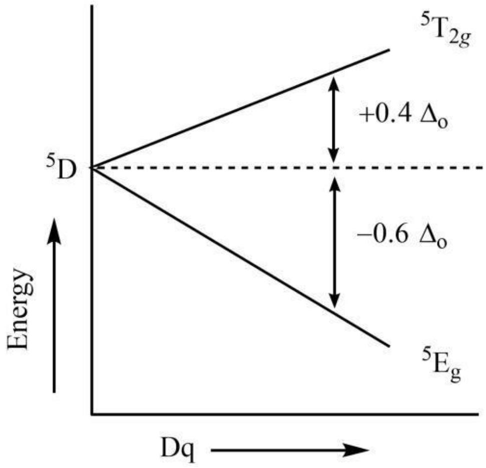


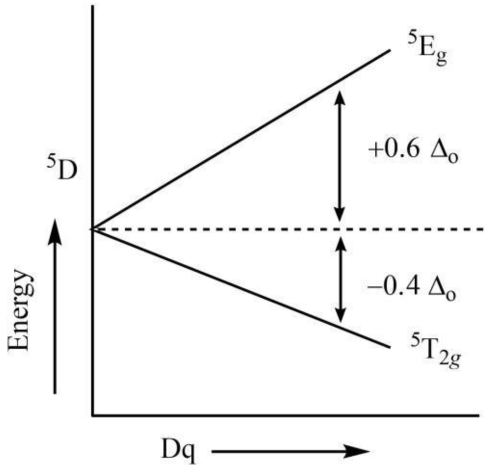


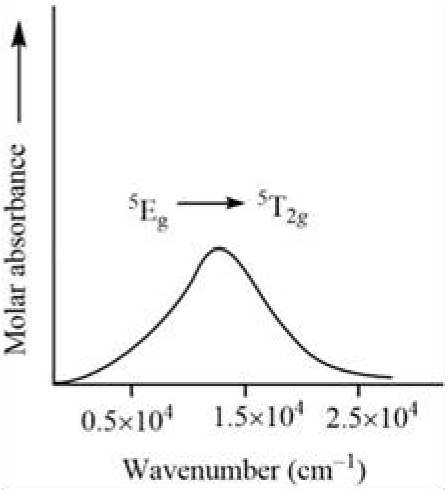


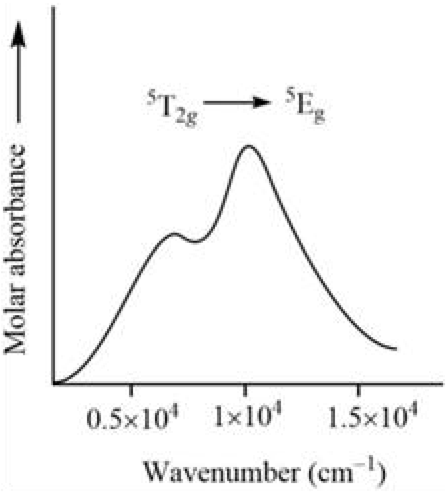


Spectra of d^4 and d^6 octahedral complexes

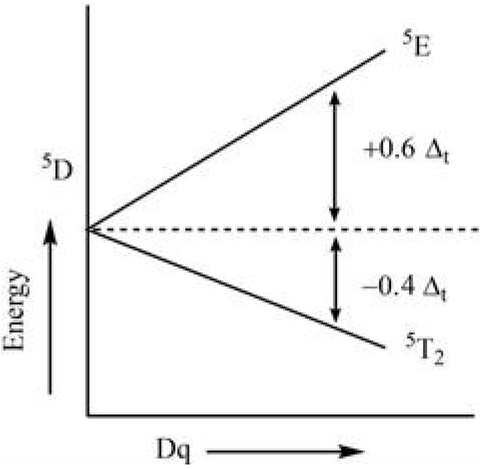


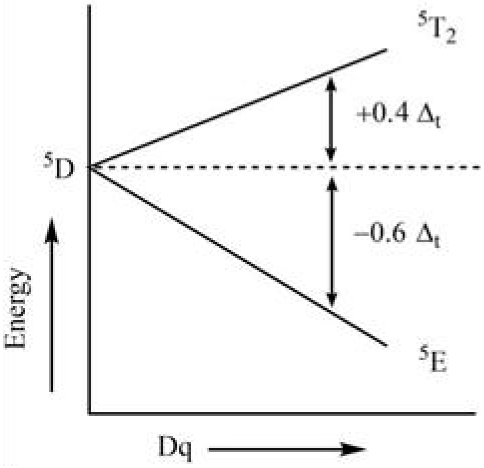


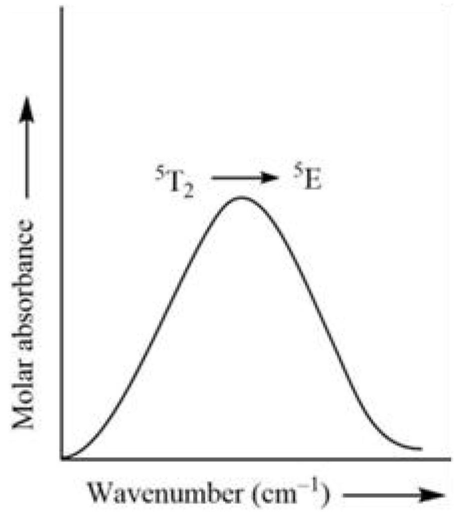


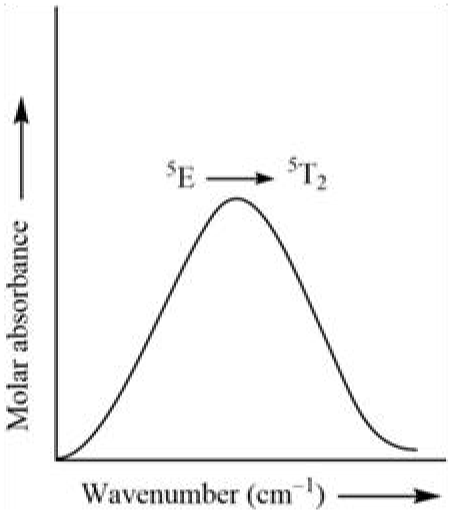


Spectra of d^4 and d^6 tetrahedral complexes

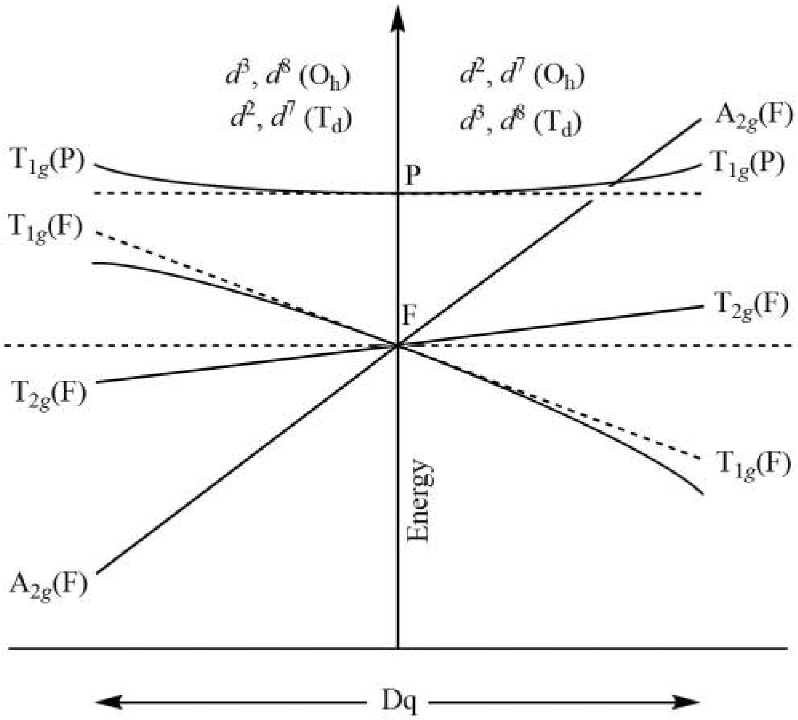




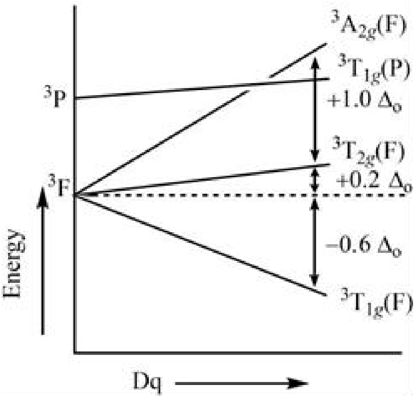


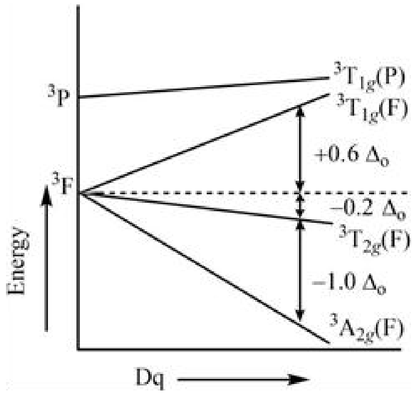


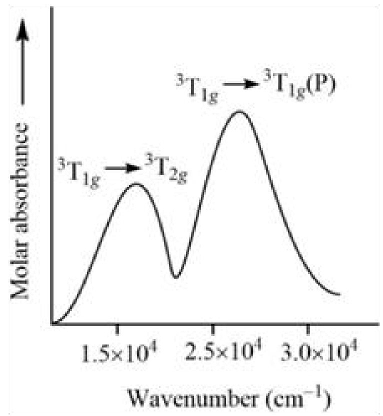
d^2, d^8, d^3, d^7 systems

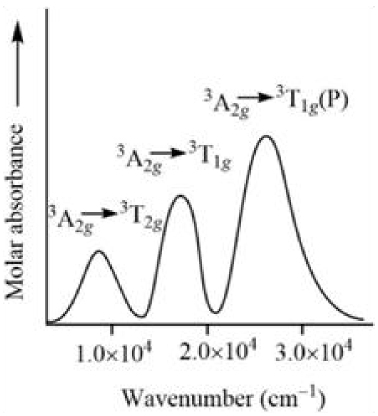


Spectra of d^2 and d^8 octahedral complexes

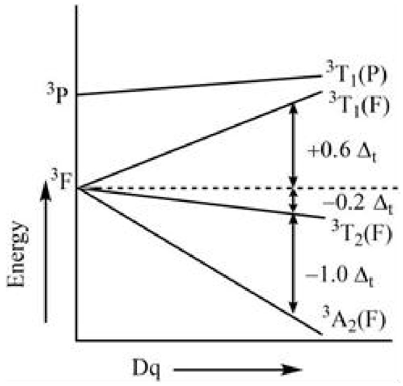


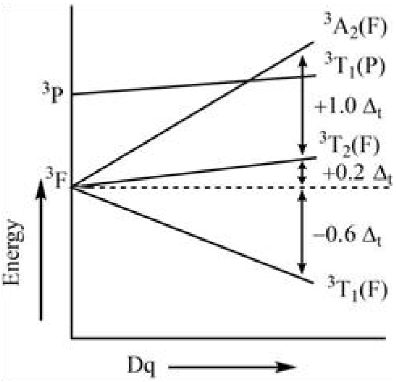


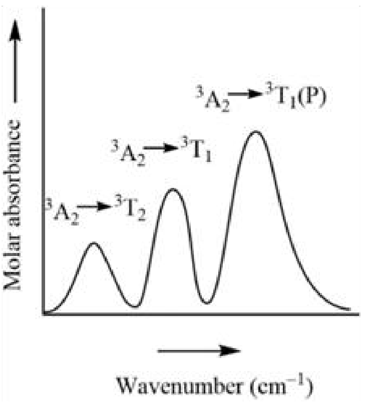


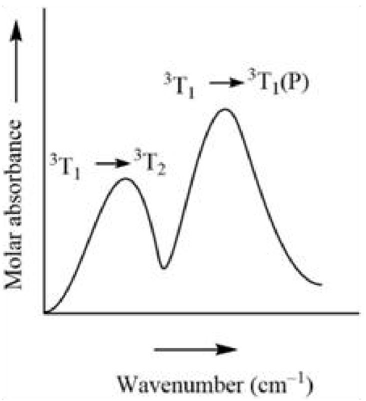


Spectra of d^2 and d^8 tetrahedral complexes

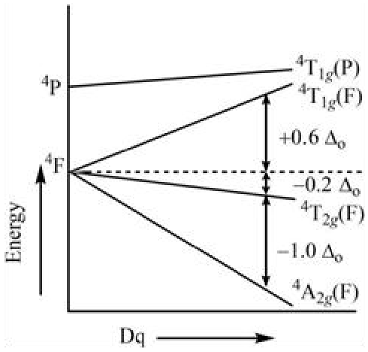


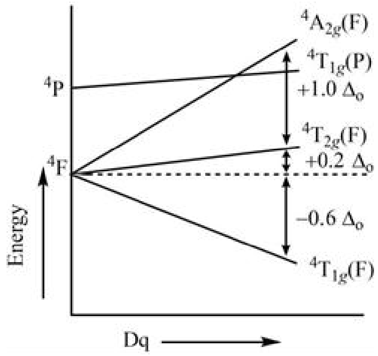


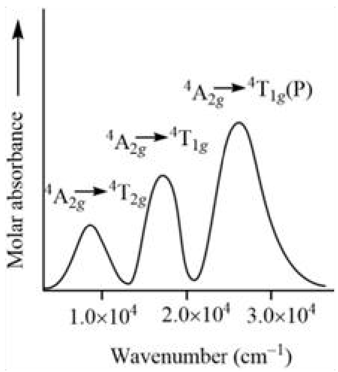


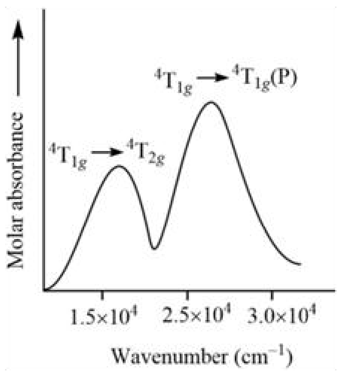


Spectra of d^3 and d^7 octahedral complexes

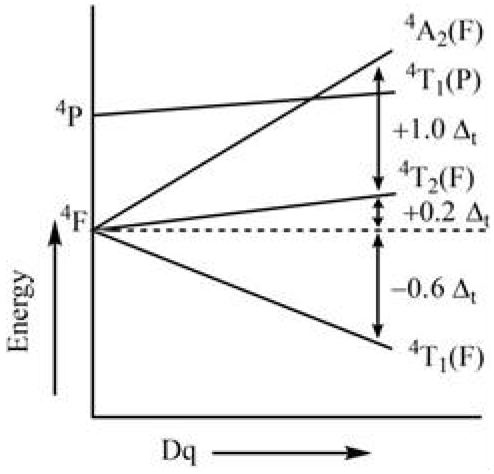


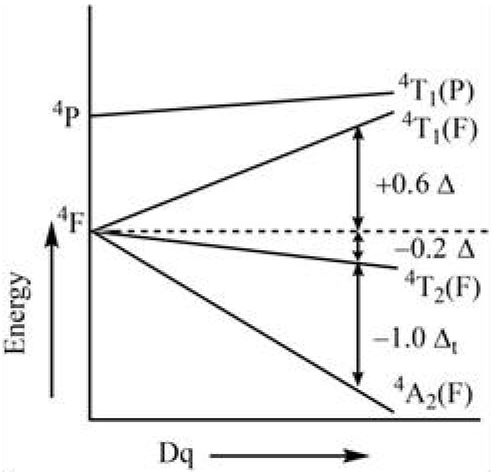


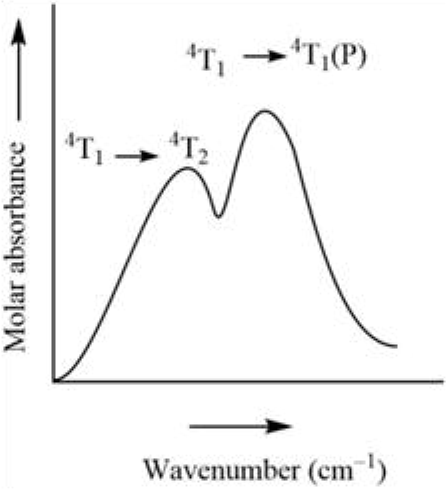


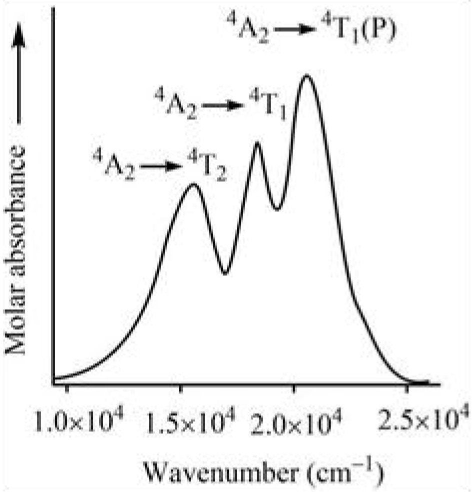


Spectra of d^3 and d^7 tetrahedral complexes

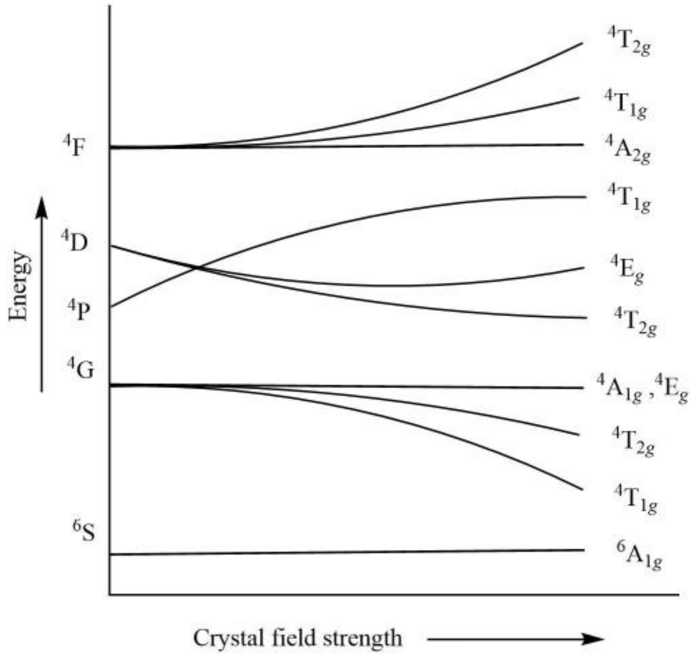








d^5 Systems



Sugano-Tanabe Energy Level Diagrams

Tanabe–Sugano diagrams are used in coordination chemistry to predict absorptions in the UV, visible and IR electromagnetic spectrum of coordination compounds. The results from a Tanabe– Sugano diagram analysis of a metal complex can also be compared to experimental spectroscopic data. They are qualitatively useful and can be used to approximate the value of 10Dq, the ligand field splitting energy. Tanabe–Sugano diagrams can be used for both high spin and low spin complexes, unlike Orgel diagrams, which apply only to high spin complexes. Tanabe–Sugano diagrams can also be used to predict the size of the ligand field necessary to cause high-spin to low-spin transitions.

In a Tanabe–Sugano diagram, the ground state is used as a constant reference, in contrast to Orgel diagrams. The energy of the ground state is taken to be zero for all field strengths, and the energies of all other terms and their components are plotted with respect to the ground term.

Parameters

The x-axis of a Tanabe–Sugano diagram is expressed in terms of the ligand field splitting parameter, Dq, or Δ, divided by the Racah parameter B. The y-axis is in terms of energy, E, also scaled by B. Three Racah parameters exist, A, B, and C, which describe various aspects of interelectronic repulsion. *A* is an average total interelectron repulsion. *B* and *C* correspond with individual d-electron repulsions. *A* is constant among d-electron configuration, and it is not necessary for calculating relative energies, hence its absence from Tanabe and Sugano's studies of complex ions. *C* is necessary only in certain cases. *B* is the most important of Racah's parameters in this case. One line corresponds to each electronic state. The bending of certain lines is due to the mixing of terms with the same symmetry. Although electronic transitions are only "allowed" if the spin multiplicity remains the same (i.e. electrons do not change from spin up to spin down or vice versa when moving from one energy level to another), energy levels for "spin-forbidden" electronic states are included in the diagrams, which are also not included in Orgel diagrams. Each state is given its symmetry label (e.g. A_{1g}, T_{2g}, etc.), but "g" and "u" subscripts are usually left off because it is understood that all the states are *gerade*. Labels for each state are usually written on the right side of the table, though for more complicated diagrams (e.g. d^6) labels may be written in other locations for clarity. Term symbols (e.g. ^3P, ^1S, etc.) for a specific d^n free ion are listed, in order of increasing energy, on the y-axis of the diagram. The relative order of energies is determined using Hund's rules. For an octahedral complex, the spherical, free ion term symbols split accordingly:

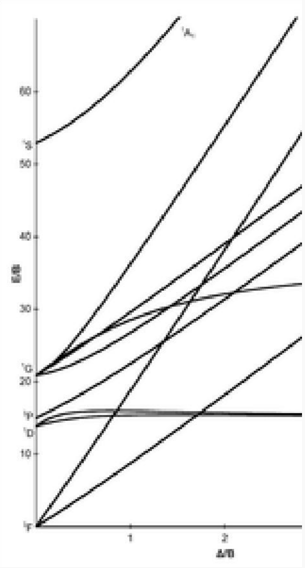
Splitting of Term Symbols from Spherical to Octahedral Symmetry

Term	**Degeneracy**	**States in an octahedral field**
S	1	A_{1g}
P	3	T_{1g}
D	5	$E_g + T_{2g}$
F	7	$A_{2g} + T_{1g} + T_{2g}$
G	9	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	11	$E_g + T_{1g} + T_{1g} + T_{2g}$
I	13	$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$

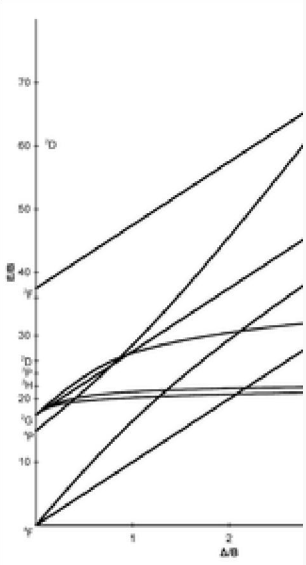
Certain Tanabe–Sugano diagrams (d^4, d^5, d^6, and d^7) also have a vertical line drawn at a specific Dq/B value, which corresponds with a discontinuity in the slopes of the excited states' energy levels. This pucker in the lines occurs when the spin pairing energy, P, is equal to the ligand field splitting energy, Dq. Complexes to the left of this line (lower Dq/B values) are high-spin, while complexes to the right (higher Dq/B values) are low-spin. There is no low-spin or high-spin designation for d^2, d^3, or d^8.

Tanabe-Sugano diagrams

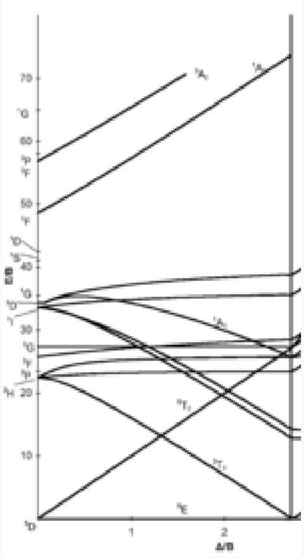
The seven Tanabe–Sugano diagrams for octahedral complexes are shown below.



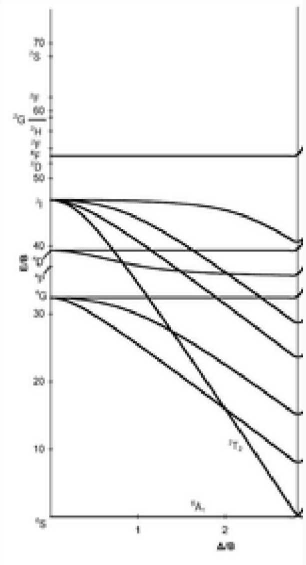
d^2 electron configuration



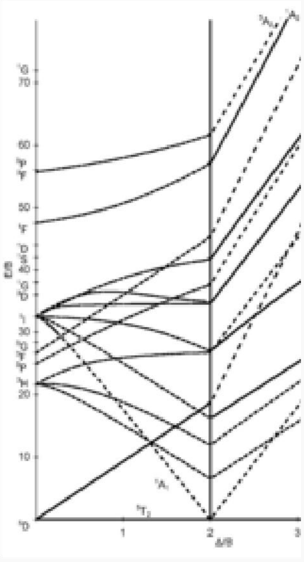
d^3 electron configuration



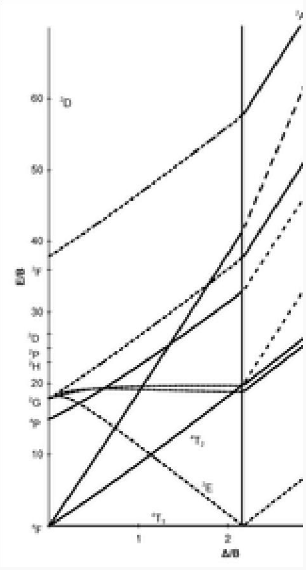
d^4 electron configuration



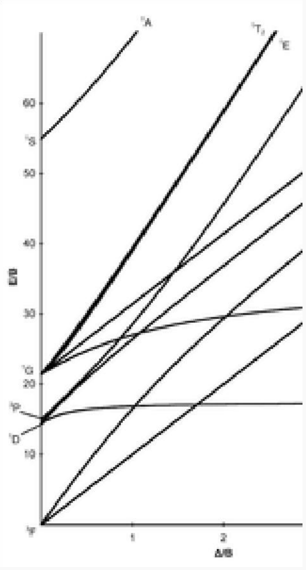
d^5 electron configuration



d^6 electron configuration



d^7 electron configuration



d^8 electron configuration

Nephelauxetic series and Racha parameter and Calculation of Inter-Electronic Repulsion Parameter.

The nephelauxetic series is a list of ligands or metal ions ordered on the basis of the strength of their nephelauxetic effect.

In the inorganic studies, the term “nephelauxetic effect” is very frequently used for transition metal complexes. This refers to a decreasing Racah parameter (B), a measure of inter-electronic repulsion, that occurs when a free transition-metal ion forms a complex with different types of ligands. The label "nephelauxetic" is for cloud-expanding in the Greek language. The presence of the nephelauxetic effect brings out the drawbacks of crystal field theory, as this suggests a somewhat covalent character in the metal-ligand bonding.

The declining value of the Racah parameter hints that in a metal complex, there is less repulsion between the two electrons in a given doubly occupied metal d-orbital than what is in the free ion counterpart, M”+; which consecutively implies that the orbital size is larger after complexation. Two reasons for electron- cloud-expansion effect may be given; one is that the effective positive charge on the metal is reduced by any negative charge on the ligands, the d-orbitals can expand a slight manner; the second is the considers the overlapping with ligand orbitals and creation of covalent bonds increases the size of the orbital.

The reduction of B from its free ion value is normally reported in terms of the nephelauxetic parameter, ß, as:

$$\text{ß} = \xrightarrow[\text{B (Free ion)}]{\text{B' Complex)}}$$

Moreover, it is also observed experimentally that the magnitude of the nephelauxetic parameter always follows a certain order with respect to the nature of the ligands attached. However, there are many ligands which do not form complexes with a particular metal ion and the vice-versa is also true. It clearly means that the value of the Racah parameter for these complexes cannot be calculated experimentally. Therefore, an empirical method must be used to find out their B values. In this method, two empirical parameters have been suggested for metal ions and ligands.

Unit - III

Stability and Magnetic Property of the Complexes

Stability of Complexes

Stability of a complex compound is assigned to be its existence in aqueous solution with respect to its bond dissociation energy, Gibbs free energy, standard electrode potential or pH of the solution and rate constant or activation energy for substitution reactions. On account of these parameters stability of complexes is of two types.

1. Thermodynamic stability
2. Kinetic stability

Factors Affecting Stability of Complexes

The factors which determine the stability of complexes are:

(1) Nature of the Central Metal Ion

(2) Nature of the ligand

(3) The Chelate Effect

(4) Macrocyclic Effect

(5) Resonance Effect

(6) Steric Effect or Steric Hindrance

(1) Nature of the central Metal ion

Variations in the stabilities (ie., stability constants) for a series of complexes of metals ions with a common set of ligands.

(a) Charge on Metal Cation: In general, a metal cation in higher oxidation state form more stable complexes than that of in lower oxidation states with a given ligand like X or NH_3 or H_2O. However there are a few exceptions with ligands such as CO, PMe3, 0-phenanthroline, bipyridyl, CN^- which form more stable complexes with metals in lower oxidation states. These ligands have vacant л* molecular orbitals for accommodation of lone pair of electrons donated by metal atom or cation and hence for π-back bonding. The electron rich CN is not only a poor л-acceptor but is also a good σ-donor and, therefore, forms complexes with metal atoms in higher oxidation state.

(b) Size of Central Metal Cation: For a given ligand and metals of same oxidation states, stability of the complexes increases with decrease in size of metal cations. For M^2+ ions, the general trend in stability for complexes is :

$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

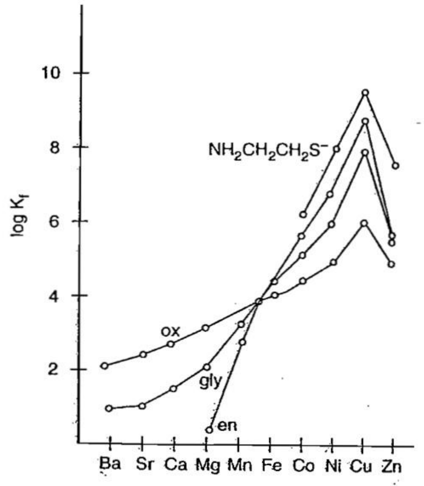
This trend in stability is known as Irving-Williams series.

This order of stability is consistent with charge to radius ratio concept because the radii decrease from Ba^{2+} to Cu^{2+} and then increases to Zn^{2+}. The order of size of depositive ions is:

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+} < Zn^{2+}$$

Since size of Zn^{2+} is larger than that of Cu^{2+} ion, therefore stability of Zn^{2+} complex is lower than that of Cu^{2+} ion. A plot of log K of complexes of M^{2+} ions with oxalate ions is shown. The log K_f values of Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+} (HS complex) and Zn^{2+} complexes lies on a line because there is no additional CFSE (ie., CFSE = 0) is larger than that of Cu ion, therefore, stability of Zn 2+ complex is lower than

Though Cu(II) complexes have an additional eg antibonding electron, they are more stable than Ni(II) complexes. This is due to the Jahn-Teller distortion. During the distortion two electrons are lowered in energy ($d^2{}_{Z2}$) while only one electron d_{x2-y2} orbital is raised by an equal amount in energy as compared to octahedral field. It results in strong bonding of four ligands in the xy-plane of tetragonally distorted Cu(II) complex and increases the value of formation constant. The axial positions are weakly bound which is responsible for higher lability of complex.



Variation of formation constants for M^{2+} ions of Irving Williams series

The value of stability constant for octahedral complexes of Mn^{2+} to Cu^{2+} ions increases more rapidly because these ions are additionally stabilized by CFSEs in octahedral field. The stability of octahedral complexes of Zn^{2+} is lower than that of Cu 2+ ion because its CFSE is zero and it lies on the line representing the stabilities of Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+} ions where CFSE is also zero.

c) Class 'a' and Class 'b' Metals:

Ahrland-etal in 1958 have classified the metals into three categories on the basis of their electron acceptor properties : (i) Class 'a' metal

(ii) Class 'b' metals

(ii) Borderline metals

Class ‘a' metals: Class a metal ions are characterized by high electropositive character (i.e, low electronegativites), small size, high oxidation states (+3 or higher) and no easily distorted outer electrons. These metal ions form their most stable complexes with ligands favoring electrostatic bonding. Class a metals form their most stable complexes with the first elements of group 15, 16 and 17 (e.g., N,O and F).

Class *a* metal ions include smaller ions from alkali metals, alkaline earth metals, lighter transition metals in high oxidation states (+3 or higher). Class a metals are also called as hard acids or hard metals.

Class *a* metals (or hard metals) are H+ , Li+, Na+, K+, Be^{2}+, Mg^{2+}, Ca^{2}+, Sr^{2}+, Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, In^{4+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, La^{3+} , Ce^{3+} , Gd^{3+}, Zr^{4+}, Hf^{4+}, Th^{4+},U^{4+}, Pu^{4+}, etc.

The order of stabilities of complexes of class 'a' metals with the ligands having the following donor atoms is as follows:

$F^{-} > Cl^{-} > Br^{-} > I^{-}$

O >>> S > Se > Te

N >> P > As > Sb

(i) Class 'b' metals: Class '*b*' metals are less electropositive, have relatively full d-orbitals and form their most stable complexes with ligands which, in addition to possess lone pairs of electrons, have empty π-orbitals available to accommodate electron pair from the d-orbitals of the metal. Class 'b' metals form stable complexes with ligands which have donor atoms from period 3 or subsequent periods. The metal ligand bond in these complexes is covalent. The order of stability is the reverse of class '*a*' metals.

The increase in availability of empty d-orbitals in heavier elements favors an increase in stability of the complexes. Class b metals are also called as soft acids or soft metals.

The order of stabilities of complexes with ligands having the following donor atoms is as follows: $F^- < Cl^- < Br^- < I^-$

$O << S < Se < Te$

$N << P < As < Sb$

Furthermore, class 'b' metals form stable complexes with CO, o-phenanthroline, olefins because these have vacant π-orbitals of low lying energy.

Class 'b' metals are:

Cu^+, Ag^+, Au^+, TI^+, Cd^+, Hg_2^{2+}, Hg^{2+}, Pd^{2+}, Pt^{2+}, Pt^{4+}, $T1^{3+}$, etc.

(ii) Borderline Metals: Borderline metals include dipositive metal ions of 3d-series which are Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}. For a given ligand order of stability of complexes is : $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ (Irving-Williams series)

According to Pearson hard metals or acids prefer to bind to hard bases or hard ligand and soft acids or metals prefer to bind to soft bases or ligand.

(2) Nature of Ligands

(i) Basic Character of Ligands: In general, more is the basic character of ligands, more easily it can donate its lone pair of electrons to the central metal ion and hence greater is the stability of the complex formed. For example, for a given dipositive (M^{2+}) 3d series transition metal ion, order of stability of complex with NH3, H_2O and F^- is:

$NH_3 > H_2O > F^-$ is :

(ii) Covalent Character: Higher the covalent character, higher will be the stability of the complex. For example, order of stability and covalent character of complexes of Ag* with halogen is:

$AgI_2^- > AgBr_2^- > AgCl_2^- > AgF_2^-$

-Decreasing order of covalent character →

- Decreasing order of stability of complex →

(iii) π- Bonding Capacity of Ligands: The ligands like CO, CN^-, alkenes, phenanthroline, pipyridyl, R_3P, R_2S, etc have vacant π- or d-orbital to form π - bond and hence form stable complexes with metals.

(iv) Dipole Moment of Ligands: For neutral ligands, higher the magnitude of dipole moment,

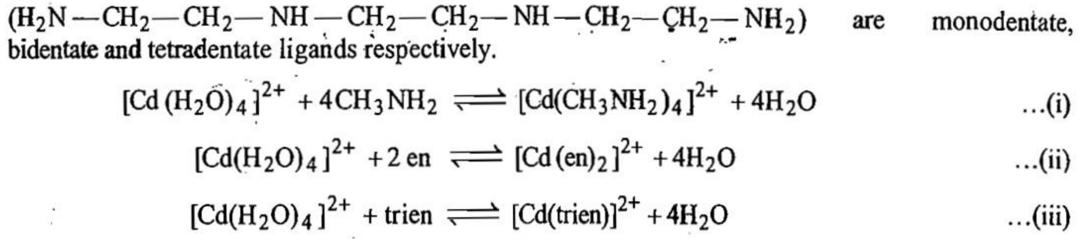
higher will be the stability of the complex. For example, the order of stability of complexes of ligands having N as donor atom is :

ammonia > ethylamine > diethylamine > triethylamine

3) The Chelate Effect

The polydentate ligands (with more than one donor atoms) have geometries such that they can form more than one coordinate bond to the same metal cation, such ligands are called chelating ligands. These ligands, generally are non-linear. The complex formed by the coordination of a polydentate ligand to a metal cation is called a chelate complex or a chelate. Chelating ligands form more stable complexes than the analogous monodentate ligands (containing the same donor atom). It means that chelated complexes are more stable than their non-chelated analogs. This effect is called as chelate effect.

Let us consider the formation of complexes from hydrated cadmium ion, $[Cd(H2O)_4]^{2+}$ with ethylamine (CH3NH2), ethylenediamine (en) and triethylenetetraamine (trien) ligands. Where ethylamine (CH3NH2), ethylenediamine (H2N-CH2-CH2-NH2) and triethylenetetramine



$(H_2N—CH_2—CH_2—NH—CH_2—CH_2—NH—CH_2—CH_2—NH_2)$ are monodentate, bidentate and tetradentate ligands respectively.

$$[Cd(H_2O)_4]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+} + 4H_2O \quad ...(i)$$

$$[Cd(H_2O)_4]^{2+} + 2\,en \rightleftharpoons [Cd(en)_2]^{2+} + 4H_2O \quad ...(ii)$$

$$[Cd(H_2O)_4]^{2+} + trien \rightleftharpoons [Cd(trien)]^{2+} + 4H_2O \quad ...(iii)$$

[Cd CH3NH2)4]^2+ is a non-chelated complex ion whereas [Cd(en)2]2+ and [Cd (trien)]^2+ are chelated complex ions. Thus, [Cd(CH3NH2)4]^2+ is less stable than [Cd (en) 2]^2+ and [Cd (trien)]$^{2+}$. It is also observed that [Cd (trien)] 2+ is more stable than [Cd (en) 2] 2+ chelate ion. Therefore, order of stability of these complex ions is:

[Cd (CH3NH2)4]2+ < [Cd (en)2]2+ < [Cd (trien)]$^{2+}$

The above order of stability of complexes can be explained in two ways:

1. **In reaction**: (i) a non-chelated complex ion [Cd (CH3NH2)4]$^{2+}$ is formed and there is no net change in the number of molecules and entropy of reaction. On the other hand, in reaction (ii) and (iii) there is an increase in number of molecules and hence there is an increase in entropy of reaction. Since increase in number of molecules in reaction (iii) is greater than that of reaction (ii) Therefore, the increase in entropy is greater in reaction (iii) than reaction (ii). Since bonding in all the above three reactions is same, (i.e., Cd^{2+} —N bond) thus, ΔH° in all the three reactions is same and negative in sign.

Thermodynamically, the stability of a complex is expressed in terms of ΔG°. For a stable complex ΔG° is negative and large.

$\Delta G = \Delta H° - T\Delta S°$

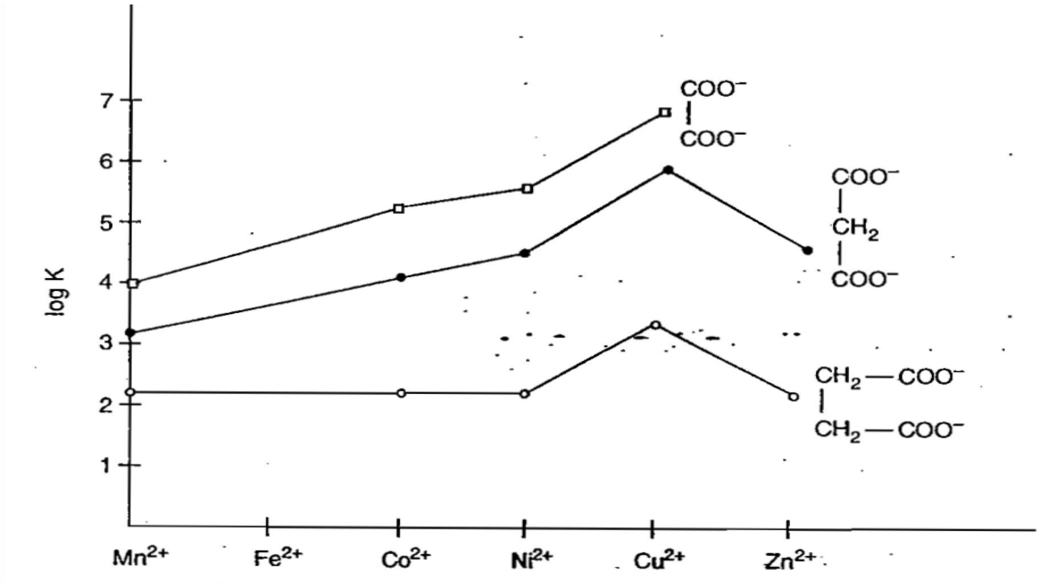
Since ΔH° in all the above three reactions is same and entropy increases from reaction (i) to (ii) to (iii) and thus, free energy change will be negative in the three reactions and increases from reaction (i) to (ii) to (iii).

A large negative value of AG° indicates the large value of stability constant (K) because Δ G°=-RT In K Thus, order of stability of the three complexes is :

[Cd(CH3NH2)4]2+ < [Cd(en)2]$^{2+}$ < [Cd(trien)]$^{2+}$

2. **CH3NH2**, en and trien ligands are competing for the formation of complexes with Cd^{2+} ion in aqueous solution, the probability of either of them coordinating to the first site may be taken as equal. Once one end of en or trien is attached to Cd 2+; ion, it is seen that the second amine group of en and trien is now greater in vicinity of Cd 2+ ion than the second CH3NH2 ligand which is free to move randomly in the solution. Thus, probability of second amine group of en or trien to attach to Cd 2+ ion is greater than that of monodentate ligand CH 3 NH2. This indicates that formation constant is larger for the formation of chelates. Further, the third and fourth donor atoms (amine groups) of trien are now greater in vicinity whereas the second en and the monodentate ligand CH3NH2 are moved freely and randomly in the solution.

Thus, probability of third and fourth amine groups of trien to attach to Cd 2+ ion is greater than that of en and CH3NH2 ligands. This indicates that stability of complex increases with the denticity of the ligand (denticity of a ligand is the number of donor atoms). In other words, we can say that the chelates in which one ligand form two or more rings are more stable than the complex in which one ligand form only one ring or no ring. The dependence of stability of chelates on the size of chelate ring is shown in Figure.



Dependence of complex stability on the size of the chelate ring

In general, the chelates having five membered rings (including the metal) are more stable than six membered rings which are in turn more stable than the seven membered rings. Thus, the chelate effect weakens as the ring size increases. The chelate effect is usually most pronounced for 5- and 6- membered rings. Smaller rings generally involve excessive strain and become less stable. When the chains and rings become much larger, the enhancement of local concentration (i.e., vicinity of seco donor atom of bidentate ligand) decreases and the resulting complex becomes less stable.

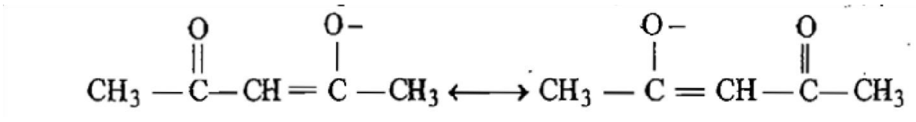
Furthermore, for the chelates formed by different bidentate ligands of same size with the same met: the stability will be in the order, for example, oxalate <glycinate < ethylenediamine.

(4) Macrocyclic Effect

Macrocyclic ligands are large ring size compounds even without a metal atom present and the ligands have several donor atoms-inside their rings to form coordinate bonds with a metal ion Chlorophyll, heme and vitamin B12 all contain tetradentate macrocyclic ligands. As stated earlier the chelating ligands form more stable complexes than analogous monodentate ligands and the macrocyclic ligands of appropriate size form more stable complexes than chelating ligands. There is a competition between a non-cyclic ligand and a macrocyclic ligand (a cyclic multi dentate ligand) having the same type of donor atoms and the complex formed by macrocyclic ligand will be more stable. This effect is called as macrocyclic effect. Chlorophyll, heme and vitamin B12 all contain tetradentate (four N-donor atoms) macrocyclic ligands.

(5) Resonance Effect

Resonance enhances the stability of complexes. For example, acetylacetonate anion ligand show resonance and form stable chelated complex.



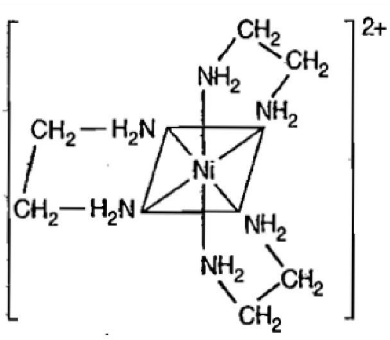
$$CH_3-\overset{\overset{O}{\|}}{C}-CH=\overset{\overset{O^-}{|}}{C}-CH_3 \longleftrightarrow CH_3-\overset{\overset{O^-}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-CH_3$$

As a result of resonance the M-O bonds are equal in length and strength.

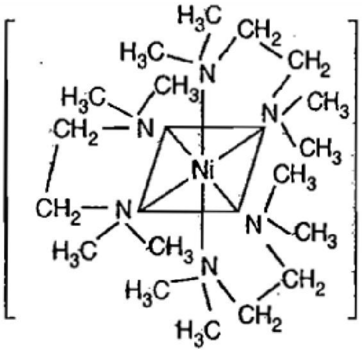
(6) Steric Effect or Steric Hindrance

If a bulky group is either attached to donor atom or to the atom adjacent to donor atom, the metal-ligand bond becomes weak and the stability of the complex decreases. This effect is called steric effect. For examples:

(i) Ethylene diamine (H2N —CH2 —CH2 -NH2) and N— tetramethyl ethylenediamine (CH3)2 NCH2-CH2-N (CH3)2 both are bidentate ligands and form chelates with Ni2+ ion as shown.



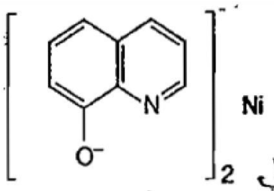
(I)



(II)

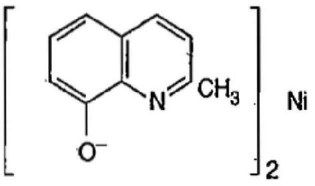
The complex (II) is less stable than (1) because in complex (II) the methyl groups attached to donor atoms create steric hindrance and decrease the stability of complex.

(ii) 8-hydroxyquinoline and 2-methyl-8 – hydroxy quinoline both are bidentate ligands and form chelated complexes with Ni2+ ion as shown.



(I)

More stable



(II)

The complex (II) is less stable than complex (I) because in complex (II) a bulky group is attached to an atom adjacent to donor atom which causes a steric hindrance and lowers the stability of the complex.

The chelates containing chelating ligands with delocalized electronic structures are also stabilized by electronic effect in addition to entropy effect. The examples of such type of ligands are diimine ligands such as bipyridine and o-phenanthroline. These ligands stabilize the complexes because of their ability to act as σdonors as well as π-acceptors. These ligands form π-bonds by overlapping their empty ring π * orbitals with filled metal d orbitals. An important example of such type of complexes is [Ru(bpy)3]2+

Thermodynamic Aspects of Complex Formation

Thermodynamic stability of a complex refers to the tendency to exist under equilibrium condition.

In other words,Thermodynamic stability of a complex is the measure of tendency of a metal ion to form a particular complex ion. Thermodynamic stability is directly related to metal – ligand bond energies. Thermodynamic stability of a complex is given by formation constant (also called the stability constant which is the equilibrium constant for the complex ion formation).

In general complex are not prepared from their components in gaseous phrase but these are prepared in aqueous solution.In aqueous solution a metal cation gets hydrated to give,[M(H2O)X]^n+ complex ion.

When a ligand replaces water molecule from aqua complex ion,a new complex ion is formed and an equilibrium is established as shown below;

$$[M(H_2O)_x]^{n+} + L \overset{K_f}{\rightleftharpoons} [M(H_2O)_{x-1}L]^{n+} + H_2O$$

Where;

X is the number of water molecule

n is the oxidation number of the metal cation

L is the neutral and monodentate ligand

For simplicity, the above reaction can be written in generalized form as given below;

$$M+L \overset{K_f}{\rightleftharpoons} ML$$

The equilibrium constant of the reaction is given by;

Kf=[ML]\[M] [L]

Concentration of H_2O is constant in dilute solution of the metal complex and it is incorporated into kf. The water molecule which enters the bulk solution does not affect the equilibrium constant.

High the value of kf more will be the stability of complex formed.A high value of equilibrium constant (kf>1.0) indicates that at equilibrium activity of complex ML is larger than the product of activities of M and L.

Thus, larger value of kf indicates that ligand L binds to the metal ion more strongly than H_2O and hence L is stronger ligand H_2O.

(kf <1.0) the ligand L is weaker than H_2O.Thus stability constant is used as a measure of thermodynamic stability of complex.

The formation constant(kf) is related to the standard Gibbs free energy change and standard electrode potential according to following relation;

$\Delta G° = -RT\ln K_f$

$\Delta G° = -nFE°$

$RT\ln K_f = nFE°$

Since ΔG° is a thermodynamic property thus formation constant is the measure of thermodynamic stability.

The equations indicates that the thermodynamic stability of a complex can be measured in terms of formation constant, ΔG° and standard electrode potential. A high negative value of ΔG° indicates that the position of equilibrium favours the product. Therefore, high negative value of ΔG° indicates that the complex formed will be more stable.

Stepwise And Overall Formation Constants

Stepwise formation constants are the equilibrium constants for each individual process of complex ion formation, while overall formation constants are the cumulative equilibrium constants for the complete process of complex ion formation.

The formation of a complex between a metal ion and a bunch of ligands is in fact usually a substitution reaction. However, ignoring the aqua ions, the formation of the complex can be written as:

$$M + nL \rightleftharpoons ML_n$$

Where M represents the metal center, L is the ligand type involved, n represents the number of ligands. The expression for β (overall stability constants) for the above equilibria can simply be written as:

$$\beta_n = \frac{[ML_n]}{[M][L]^n}$$

When a free metal ion (M^+) in aqueous medium that metal ion is surrounded by water molecules(solvent molecules), the coordinated water molecules are replaced by strong ligand molecule.Formation of ML6 metal complex treated with ligand

$$[MS6]+ L \rightleftharpoons [ML6]+6S$$

$$\text{Overall reaction } (\beta) = [ML6][S]^6 / [MS6][L]^6$$

Solvent is present in large excess so it can be ignored therefore

$$\text{Overall reaction } (\beta) = [ML6] / [MS6][L]^6$$

If the six ligands are added to the metal ions one by one the formation of metal complex [ML6] can be supposed to takes place in different six steps

$[MS_6] + L \rightleftharpoons [MS_5L] + S$ $\quad K_1=[MS_5L]\backslash[MS_6][L]$

$[MS_5L] + L \rightleftharpoons [MS_4L_2] + S$ $\quad K_2=[MS_4L_2]\backslash[MS_5L][L]$

$[MS_4L_2] + L \rightleftharpoons [MS_3L_3] + S$ $\quad K_3=[MS_3L_3]\backslash[MS_4L_2][L]$

$[MS_3L_3] + L \rightleftharpoons [MS_2L_4] + S$ $\quad K_4=[MS_2L_4]\backslash[MS_3L_3][L]$

$[MS_2L_4] + L \rightleftharpoons [MSL_5] + S$ $\quad K_5=[MSL_5]\backslash[MS_2L_4][L]$

$[MSL_5] + L \rightleftharpoons [ML_6] + S$ $\quad K_6=[ML_6]\backslash[MSL_5][L]$

Where K_1, K_2, K_3......K_n are the equilibrium constants for different steps and the

$$\beta\text{overall} = K1*K2*K3*K4*K5*K6$$

$$=[MS_5L] / [MS_6][L] * [MS_4L_2] / [MS_5L][L] * [MS_3L_3] / [MS_4L_2][L] * [MS_2L_4] / [MS_3L_3][L] *[MSL_5] / [MS_2L_4][L] *[ML_6] / [MSL_5][L]$$

$$\beta_{\text{overall}} =[ML6] / [MS6][L]^6$$

Taking log ,

$$\log\beta_n = \log(k1) +\log(k2)+ \log(k3)+\log (k4)+\log(k5)+\log(k6)....\log(kn)$$

The above equation indicate that the overall formation constant(β) is equal to the product of the stepwise formation constant k1,k2,k3……kn.

Example :1

$[Cu(H_2O)_4]^{2+} + NH_3 \rightleftharpoons [Cu(H_2O)_3(NH_3)]^{2+} + H_2O \quad K1 = 1.66*10^4$

$[Cu(H_2O)_3(NH_3)]^{2+} + NH_3 \rightleftharpoons [Cu(H_2O)_2(NH_3)_2]^{2+} + H_2O \quad K2 = 3.10*10^3$

$[Cu(H_2O)_2(NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Cu(H_2O)(NH_3)_3]^{2+} + H_2O \quad K3 = 8.31*10^2$

$[Cu(H_2O)(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + H_2O \quad K4 = 1.51*10^2$

$\beta_4 = 1.66*10^4 * 3.10*10^3 * 8.31*10^2 * 1.51*10^2 = 64.57*10^{11}$

Example :2

$[Cd(H_2O)_4]^{2+} + CN^- \rightleftharpoons [Cd(H_2O)_3(CN)]^+ + H_2O \quad K1 = 10^{5.48}$

$[Cd(H_2O)_3(CN)]^+ + CN^- \rightleftharpoons [Cd(H_2O)_2(CN)_2] + H_2O \quad K2 = 10^{5.12}$

$[Cd(H_2O)_2(CN)_2] + CN^- \rightleftharpoons [Cd(H_2O)(CN)_3]^- + H_2O \quad K3 = 10^{4.63}$

$[Cd(H_2O)(CN)_3]^- + CN^- \rightleftharpoons [Cd(CN)_4]^{2-} + H_2O \quad K4 = 10^{3.65}$

$\beta_4 = 10^{5.48} * 10^{5.12} * 10^{4.63} * 10^{3.65} = 10^{18.88}$

where,

K1,K2,K3,K4 =Stepwise formation constant

β_4 = Overall formation constant

Thus typically as ligand is added to the solution of the metal ion , ML is first formed more rapidly than any other complex in the series. As the ligand concentration is increased , the ML2 concentration rises rapidly whereby the ML concentation drops. In the succesive stages the ML3 become dominat ,ML and ML2 become less important. In this way the highest coordination complex MLn is formed to the nearly complete exclusion of all others at very high ligand concentrations.

Stability Correlations

Stability correlation is a fundamental concept in coordination chemistry that helps predict and explain the relative stability of different coordination compounds. It involves understanding the various factors that influence the stability of coordination compounds.

Thermodynamic factors like 1. Ligand field strength: The ability of a ligand to split the d-orbitals of the metal ion, leading to greater stability.

2.Metal ion charge and size: Higher charge and smaller size increase stability due to stronger electrostatic attraction.

3.Coordinattion Number: Higher coordination numbers often lead to greater stability.

4.Chelate Effect: Chelating ligands form more stable complexes due to the “chelate ring” effect.

5. Macrocyclic Effect: Macrocyclic ligands form more stable complexes due to the “macrocyclic ring” effect.

1. IRVING-WILLIAMS SERIES

Log K values of HS octahedral oxalato complexes of bivalent metal ions viz

$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < | Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > | Zn^{2+}$

The above order of log K values (or stability constants) is called Irving Willian series of stability constants.

From this order of log K values the following points may be noted:

(i) log K values for the 1:1 oxalate and 1:1 glycinato complexes of Ba^{2+}, Sr^{2+}, Ca^{2+} and Mg^{2+} ions increase regularly from Ba^{2+} to Mg^{2+} This increasing order is because of the decreasing of ionic radii of these ions from Ba^{2+} to Mg^{2+} as shown below. log K values for the complexes are also given.

M^{2+} ions:	Ba^{2+}	Sr^{2+}	Ca^{2+}	Mg^{2+}
Ionic radii of M^{2+} ions(A):	1.29	1.00	0.99	0.65
	________	Decreasing	________	
Log K values for 1:1 oxalato Complexes:	2.31	2.54	3.00	3.43
	________	Increasing	________	
Log K values for 1:1 glycinato Complexes:	0.77	0.91	1.43	3.44
	________	Increasing	________	

(ii) log K values increase from Mn^{2+} to Cu^{2+}. The increase from Mn^{2+} to Ni^{2+} is because the CFSE values (in Dq) increase from Mn^{2+} to Ni^{2+} as shown below:

M^{2+} ions:	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}
d^x configuration of M2+ ions:	d5	d6	d7	d8
$t^{a}_{2g} e^{b}_{g}$ configuration of d^x ion in HS octahedral complexes:	$t^{3}_{2g} e^{2}_{g}$	$t^{4}_{2g} e^{2}_{g}$	$t^{5}_{2g} e^{2}_{g}$	$t^{6}_{2g} e^{2}_{g}$
CFSE values (Dq):	0	-4	-8	-12

_____________ *Increasing* _____________

(iii) CFSE values of Cu^{2+} ion is equal to – 6 Dq. Although this values is lower than that for Ni^{2+} ion(=-12Dq) yet complexes of Cu^{2+} ion have higher K values Higher K values for the complexes of Cu^{2+}ion are due to the stabilisation of this ion due to Jahn-Teller effect.Cu^{2+} ion has a tendency to form distorted octahedral complexes

(iv)Since CFSE value of Zn^{2+} ion is zero, complexes of this ion have the lowest K values, i. e. complexes of Zn^{2+} ion are least stable.

Statistical factor

The values of stepwise equilibrium constants for the formation of a particular metal-complex decrease successively in most of the cases i.e. $K_1 > K_2 > K_3 > K_4 > K_5 >\ldots> K_n$. This regular decrease in the values of stepwise formation constants may be attributed to the decrease in the number of coordinated H_2O ligands that are available for the replacement by the attacking ligands. Besides, the continuous decline in the values of successive stepwise stability constant values may also be attributed to the decreasing ability of metal ions with a progressive intake of ligands, Coulombic factors and steric hindrance. Consider the following ligand displacement reaction:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(H_2O)_2(NH_3)_4]^{2+} + 4H_2O$$

$$\beta_4 = \frac{[[Cu(H_2O)_2(NH_3)_4]^{2+}][H_2O]^4}{[[Cu(H_2O)_6]^{2+}][NH_3]^4}$$

The overall process can be supposed to take place through the following steps:

$$[\mathrm{Cu(H_2O)_6}]^{2+} + \mathrm{NH_3} \overset{K_1}{\rightleftharpoons} [\mathrm{Cu(H_2O)_5(NH_3)}]^{2+} + \mathrm{H_2O}$$

$$K_1 = \frac{[[\mathrm{Cu(H_2O)_5(NH_3)}]^{2+}][\mathrm{H_2O}]}{[[\mathrm{Cu(H_2O)_6}]^{2+}][\mathrm{NH_3}]}$$

$$[\mathrm{Cu(H_2O)_5(NH_3)}]^{2+} + \mathrm{NH_3} \overset{K_2}{\rightleftharpoons} [\mathrm{Cu(H_2O)_4(NH_3)_2}]^{2+} + \mathrm{H_2O}$$

$$K_2 = \frac{[[\mathrm{Cu(H_2O)_4(NH_3)_2}]^{2+}][\mathrm{H_2O}]}{[[\mathrm{Cu(H_2O)_5(NH_3)}]^{2+}][\mathrm{NH_3}]}$$

$$[\mathrm{Cu(H_2O)_4(NH_3)_2}]^{2+} + \mathrm{NH_3} \overset{K_3}{\rightleftharpoons} [\mathrm{Cu(H_2O)_3(NH_3)_3}]^{2+} + \mathrm{H_2O}$$

$$K_3 = \frac{[[\mathrm{Cu(H_2O)_3(NH_3)_3}]^{2+}][\mathrm{H_2O}]}{[[\mathrm{Cu(H_2O)_4(NH_3)_2}]^{2+}][\mathrm{NH_3}]}$$

$$[\mathrm{Cu(H_2O)_3(NH_3)_3}]^{2+} + \mathrm{NH_3} \overset{K_4}{\rightleftharpoons} [\mathrm{Cu(H_2O)_2(NH_3)_4}]^{2+} + \mathrm{H_2O}$$

$$K_4 = \frac{[[Cu(H_2O)_2(NH_3)_4 l^{2+}][H_2O]}{[[Cu(H_2O)_3(NH_3)_3]^{2+}][NH_3]}$$

It has been observed that log K values for K_1, K_2, K_3 and K_4 4.3, 3.6, 3.0 and 2.3, respectively. This regular decrease in stepwise stability constants can be attributed to the decreasing site availability for the attack of the incoming ligand.

In the first step, NH_3 can attack all the six-coordination site while in the number of coordination sites available for the attack is reduced to three. Hence, stepwise constant, as well as the ease of formation of the complexes, also decrease as we move from to the last step of ligand displacement.

Now although the decreasing trend in stepwise constants is pretty much common in most of the complex formation process, still some exceptions so exist in which it is found that $K_{n+1} > K_n$. This weird behaviour in stepwise equilibrium constants may be explained in terms of some unusual structural deviations and variation in the electronic structure of the metal canter. The deviations in electronic configurations cause the change in crystal field stabilization energy (CFSE), and therefore, also affect the overall stability of the metal complex i. e, complex with a large magnitude of CFSE will be more stable and consequently, will have higher value of the stepwise formation constants. Consider the following ligand displacement reaction:

$$[Cd(H_2O)_6]^{2+} + 4Br^- \rightleftharpoons [CdBr_4]^{2-} + 6H_2O$$

$$\beta_4 = \frac{[[CdBr_4]^{2-}][H_2O]^6}{[[Cd(H_2O)_6]^{2+}][Br^-]^4}$$

The overall process can be supposed to take place through the following steps:

$$\begin{aligned}
&[Cd(H_2O)_6]^{2+} + Br^- \xrightleftharpoons{K_1} [Cd(H_2O)_5Br]^+ + H_2O\\
&[Cd(H_2O)_5Br]^+ + Br^- \xrightleftharpoons{K_2} [Cd(H_2O)_4Br_2] + H_2O\\
&[Cd(H_2O)_4Br_2] + Br^- \xrightleftharpoons{K_3} [Cd(H_2O)_3Br_3]^- + H_2O\\
&[Cd(H_2O)_3Br_3]^- + Br^- \xrightleftharpoons{K_4} [CdBr_4]^{2-} + 3H_2O
\end{aligned}$$

It has been observed that log K values follow the order $K_1 > K_2 > K_3 < K_4$, instead of $\Delta\Delta K_1 > K_2 > K_3 > K_4$. This unusually high value of K_4 is because the last step is actually pretty much favoured by the release of three aquo ligands and some simultaneous structure and electronic changes.

Similarly, consider the formation of $[Fe\ (bpy)_3]^{2+}$ complex:

$$[Fe(H_2O)_6]^{2+} + bpy \overset{K_1}{\rightleftharpoons} [Fe(H_2O)_4(bpy)]^{2+} + 2H_2O$$

$$[Fe(H_2O)_4(bpy)]^{2+} + bpy \overset{K_2}{\rightleftharpoons} [Fe(H_2O)_2(bpy)_2]^{2+} + 2H_2O$$

$$[Fe(H_2O)_2(bpy)_2]^{2+} + bpy \overset{K_3}{\rightleftharpoons} [Fe(bpy)_3]^{2+} + 2H_2O$$

It has been observed that log K values follow the order $K_1 > K2 < K_3$, instead of $K_1 > K_2 > K_3$.

This unusually high value of K_3 is because the complexes formed during first two steps are high spin due to weak H_2O ligands with a CFSE of -0.4_0 ($t_{2g}^4e_g^2$), while the last complex $[Fe(bpy)_3]^{2+}$ is low spin with a CFSE value of $-2.4\Delta_0$ ($t_{2g}^6e_g^0$). Hence, large crystal field stabilization in the last step makes K_3 even greater than K_2.

Chelate Effect

The chelate effect or chelation may simply be defined as an equilibrium reaction between the Complexing agent and a metal ion, characterized by the formation of two or more bonds between metal and The complexing agent, resulting in the formation of a ring structure including the metal ion.

It can also simply be defined by, bidendate and multidendte ligands readily substitute ore exchange in a place of monodendate ligands creating a more stable complex. It is characterized by the formation of two or more bonds between metal and ligands.

Example: $[Cd\ (H_2O)_4] + 2en \rightleftharpoons [Cd(en)_2]^{+2} + 4H_2O$

Figure 1. Popular chelating ligands; (a) ethylenediamine and (b) glycinato

Thermodynamic Explanation of Chelation

The principal driving force for the chelation phenomena is the stability gain arising from the increasing entropy during the complexation. The free energy change for a general reaction is given by:

$$\Delta G° = \Delta H° - T\Delta S° \text{ or } \Delta G° = -RT \ln K$$

Now, as the enthalpy change between non-chelate and chelates is almost negligible because of the similar Metal–ligand donor type, the free energy change is primarily governed by the value of ΔS°. Furthermore, it Follows from the above equation that ΔG° will become more negative with a more positive value of ΔS°, which In turn would increase the value of stability constant K. Hence, the stability of metal complexes increases with chelation as it occurs through an increment in the entropy of the system.

$$[Cd(H_2O)_4] + 4CH_3NH_3 \rightleftharpoons [Cd(CH_3NH_3)_4]^{2+} + 4H_2O$$

$1 + 4 = 5$ $\qquad\qquad\qquad$ $1 + 4 = 5$

$$[Cd(H_2O)_4] + 2en \rightleftharpoons [Cd(en)_2]^{2+} + 4H_2O$$

$1 + 2 = 3$ $\qquad\qquad\qquad$ $1 + 4 = 5$

Thus, chelation is a thermodynamically favorable process as the number of species in the product are higher than that of what it was in the starting materials leading to enhanced randomness.

$$[Cd(H_2O)_4] + \text{trien} \rightleftharpoons [Cd(\text{trien})]^{2+} + 4H_2O$$

$$1 + 1 = 2 \qquad\qquad 1 + 4 = 5$$

It is obvious that entropy increase in case of trien is higher than ethylenediamine ligand making the trien chelate complex as more stable. The stability of chelate complexes increase with the denticity of the chelating agent.

Explanation 1: Entropy

The no. of moles of the product is increased from the reactants so entropy is increased and this is because of increased in free molecules.

Therefore, ΔS is positive.

Explanation 2: Enthalpy

Consider if there is six coordinate bonds are broken and six coordinate bonds are formed then there is very small change in enthalpy it is negligible, it is not actually zero but it is very small

Therefore, ΔH is negligible.

Explanation 3: Gibbs free energy

It is like already mentioned above, ΔG tends to below zero which is negative. Due to small ΔH value and TΔS is always a positive value for this type of ligand exchange reactions.

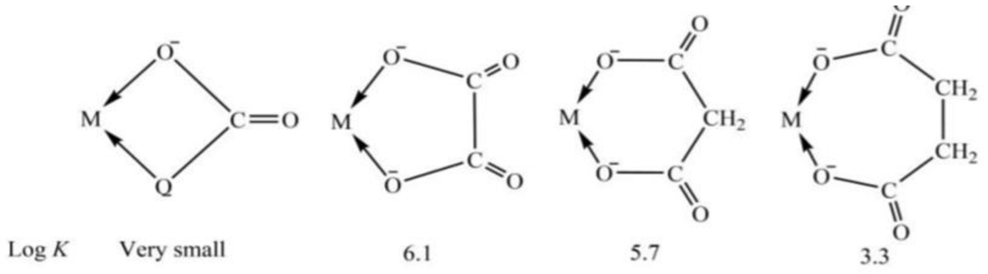
Therefore, the exchange always happens readily as it is positive at any temperature.

And ΔG is negative.

Factors Affecting the Stability of Chelate Complexes

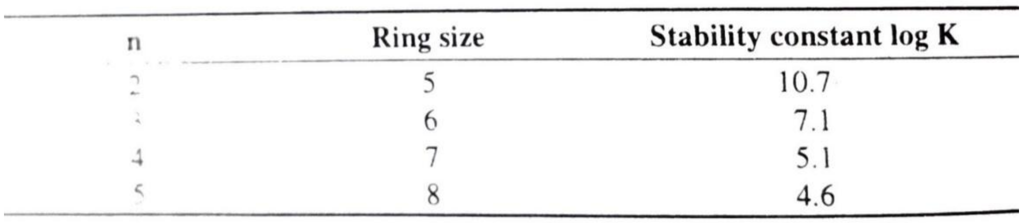
1.The size of the chelate ring:

Five or six membered chelate rings are more stable than the four, seven, eight Or higher membered chelate rings due to less steric strain. When there is no double bond in chelate ring, generally a 5- membered ring will be more stable. When there double bonds, a 6-membered ring is the stable.



Ring size 4 5 6 7

Table 1 Variation of stability constants with the ring size of chelates



n	Ring size	Stability constant log K
2	5	10.7
3	6	7.1
4	7	5.1
5	8	4.6

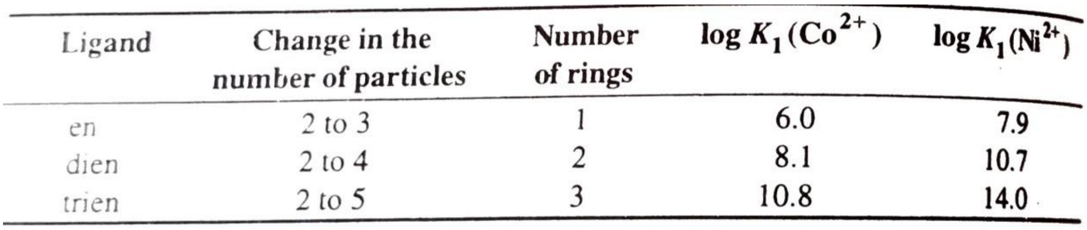
2.Number of Chelate Rings

Another factor of importance in chelation is the number of Chelate Rings. Greater the number of chelate rings, greater will be the stability of complex. This greater stability of complexes having more number of chelate rings is attributed to the greater increase in the positive entropy of the system. For example, in $[Co(en)(H_2O)_4]^{2+}$, there is one chelate ring.

Table 2.Effect of the number of chelate rings on the complex stability

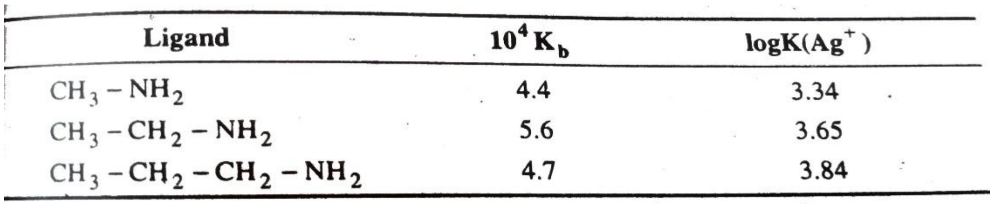
3.Basicity of the ligands

Basicity is a measure of electron pair donation. Greater the basicity of the ligand. Greater will be the tendency to donate electron pairs. This means that the more basic ligands will form more complexes.



Ligand	Change in the number of particles	Number of rings	$\log K_1(Co^{2+})$	$\log K_1(Ni^{2+})$
en	2 to 3	1	6.0	7.9
dien	2 to 4	2	8.1	10.7
trien	2 to 5	3	10.8	14.0

Similar linear relationships between base strength and coordinating ability of ligands are obtained for secondary and tertiary amines. In certain cases, the lower stability of the complexes of secondary and tertiary amines is attributed to steric hindrance between the ligands.



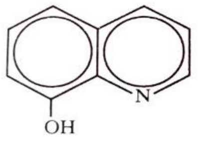
Ligand	$10^4 K_b$	$\log K(Ag^+)$
CH_3-NH_2	4.4	3.34
$CH_3-CH_2-NH_2$	5.6	3.65
$CH_3-CH_2-CH_2-NH_2$	4.7	3.84

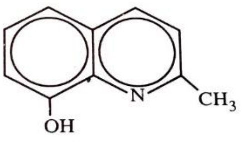
Table 3. Effect of ligans basicity on the stability of some Ag+ complexes

4.Steric Effect

One more factor of significance in chelation is the steric factor. This is associated with the presence of a bulky group either attached to the donor atom or near enough to it to cause mutual repulsion between the ligands which results in the weakening of the metal to ligand bonds.

The metal complexe of 2- methyl-8-hydroxyquinoline is less stable than those of either 8-hydroxyquinoline and 4-methyl derivative.


(a) 8-hydroxyquinoline (oxine)


(b) 2-methyl derivative

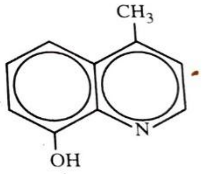
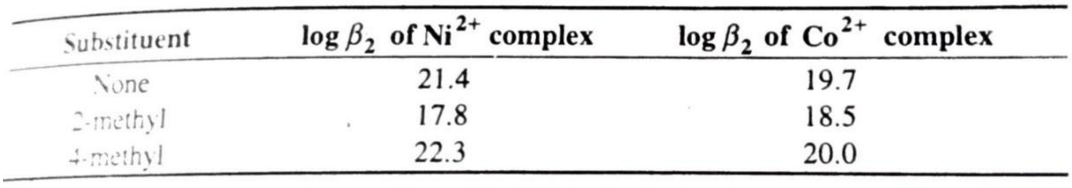

(c) 4-methyl derivative

Table 4. Steric effect on stability contants of Ni(II) and Co(II)-oxine complexes



Substituent	$\log \beta_2$ of Ni^{2+} complex	$\log \beta_2$ of Co^{2+} complex
None	21.4	19.7
2-methyl	17.8	18.5
4-methyl	22.3	20.0

Among the three ligands considered in Table 4 the 2-methyl derivative is the most basic one and hence it is expected to form the most stable complex (greater hasicity means greater complex stability). But actually, it forms the least stable complex. The least stability of this complex is attributed to the greater difficulty of chelation caused by the steric hindrance of the methyl group at position 2. Here, the bulky methyl group is near enough to the donor atom to cause mutual repulsion between the ligands. The 4-methyl derivative is more basic than oxine itself. Since the bulky methyl group in this ligand is too far away from the donor nitrogen to sterically affect the process of complex formation, it forms the most stable complex.

Determination of Stability Constant and Composition of The Complexes: Formation Curves and Bjerrum's Half Method (or) Potentiometric Method

When the ligand is a weak acid or weak base, competition between hydrogen ion and metal ion for the ligand can be used for the determination of the stability constant.

$$L + H^{+} \xleftrightarrow{K_a} [HL^{+}]$$

$$L + M^{+} \xleftrightarrow{K_f} [ML^{+}]$$

$$K_a = \frac{[HL^{+}]}{[H^{+}][L]} \qquad (1)$$

$$K_f = \frac{[ML^{+}]}{[M^{+}][L]} \qquad (2)$$

K_a and K_f are the acid association and formation constant or stability constant of a ligand respectively.

Now C_H, C_L, C_M are the initial concentration of hydrogen ion, ligand, metal ion respectively.

$$C_H = [H^{+}] + [HL^{+}] \qquad (3)$$

$$C_L = [L] + [HL^{+}] + [ML^{+}] \qquad (4)$$

$$C_M = [M^{+}] + [ML^{+}] \qquad (5)$$

From equation (1)

$$[L] = \frac{[HL^{+}]}{[H^{+}][Ka]} \qquad (6)$$

From equation (2)

$$[HL^{+}] = C_H \_ [H^{+}] \qquad (7)$$

Substitute equation (7) in (6)

$$[L] = \frac{[C_H - H^{+}]}{[H^{+}]Ka} \qquad (8)$$

From equation (4)

$$[ML^{+}] = C_L \_ [L] \_ [HL^{+}]$$

Substitute equation (7) in equation (8)

$$[ML^{+}] = C_L - \frac{[C_H - H^{+}]}{[H^{+}]Ka} - C_H + [H^{+}] \qquad (9)$$

From equation (5)

$$[M^{+}] = C_M \_ [ML^{+}]$$

$$[M^{+}] = C_M - C_L + \frac{[C_H - H^{+}]}{[H^{+}]Ka} + C_H - [H^{+}] \qquad (10$$

Thus, on substitute the value of [ML^{+}], [M^{+}] and [L] from the above equation (8), (9), (10) in equation

$$K_f = [ML^{+}] / [M^{+}] [L]$$

the value of K_f can be evaluated. For the determination of [ML^{+}], [M^{+}] and [L], the value of K_a, C_H, C_L, C_M and [H^{+}] must be known. The last quantity [H^{+}] is generally determined potentiometrically using a pH meter.

In order to get precise results, the ligand must be a medium weak base or weak acid and the formation constant K_f should be within a factor of 10^{8} of the value of the acid association constant of the ligand, K_a.

Spectrophotometric Method

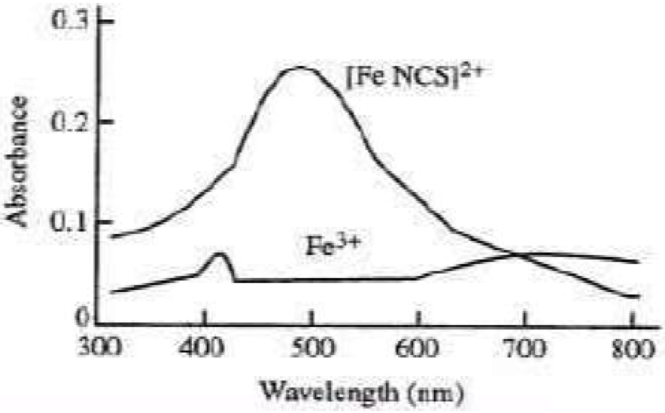
This method of determining the stability constant of a complex can be considered with the example,

$$Fe^{3+}{}_{(aq)} + NCS^{-} \rightleftharpoons \left[Fe(NCS)\right]^{2+}$$

The stability constant for this complex is given by

$$K = \frac{[[Fe(NCS)]^{2+}]}{[Fe^{3+}][NCS^{-}]}$$

Where the concentration terms represent the actual equilibrium concentrations. Ferric ion and thiocyanate ion individually are almost colorless in aqueous solution, however, the complex $[[Fe(NCS)]^{2+}]$ is bright red. Its λ_{max} is 450 nm.



Therefore, the concentration of this colored complex can be estimated by measuring its absorbance in the visible region using a spectrophotometer. The absorbance A is directly proportional to the concentration of absorbing species as per the Bear Law:

$$A = \varepsilon c l$$

ϵ = molar extinction coefficient

c = concentration of absorbing species

l = path length of the absorbing solution

The value of ε for K= $[[\mathrm{Fe(NCS]}^{2+}]$ can be determined first by measuring the absorbance of a solution of the complex of known concentration (such a solution can be prepared by mixing a known amount of Fe^{3+} with a large excess of NCS^{-}, so that all the Fe^{3+} is converted to the complex).

For determining K, a solution of Fe^{3+} of known concentration $[Fe^{3+}]_0$ is mixed with a solution of NCS^{-} of known concentration $[NCS^{-1}]_0$. The mixture is which the complex $[[\mathrm{Fe(NCS)]}^{2+}]$ has been formed is equilibrated. Its absorbance (A) at 450 nm is measured. Then K is evaluated as indicated below:

$$A = \epsilon\, l\, [[\mathrm{Fe(NCS]}^{2+}]$$

Therefore, equilibrium concentration of complex,

$$[Fe^{3+}]_0 \quad = \quad [Fe^{3+}] \quad + \quad [[\mathrm{Fe(NCS)]}^{2+}]$$

Uncomplexed Fe^{3+} complexed Fe^{3+}

Equilibrium concentration of Fe^{3+}

$$[Fe^{3+}] = [Fe^{3+}]_0 - [[Fe(NCS)]^{2+}]$$

$$[NCS^-]_0 = [NCS^-] + [[Fe(NCS]^{2+}]$$

Uncomplexed NCS^- + Complexed NCS^-

Equilibrium concentration of $[NCS^-]$

$$[NCS^-] = [NCS^-]_0 - [[Fe(NCS]^{2+}]$$

Therefore,

$$K = \frac{[[Fe(NCS)]^{2+}]}{[Fe^{3+}][NCS\text{-}]}$$

The experiment is then repeated with three or more different initial Fe^{3+} and NCS^- concentrations to check the constancy of K.

This method does not disturb the equilibrium during absorbance measurement and hence it is a reliable method of evaluating k value.

Ion Exchange Method

Ion exchange resin is an insoluble solid, organic polymer containing positive (Cationic exchange resins), negative (Anionic exchange resins). These ions can be exchanged for some other ions of similar charge.

If a cationic resin is in contact with solution of Na+ and Ca2+ ions an equilibrium constant for such system can be given by

$$K_r = \frac{[Na^+]^2_{soln}\,[Ca^{2+}]_{resin}}{[Na^+]^2_{resin}\,[Ca^{2+}]_{soln}} \quad \text{---- (1)}$$

If concentration of Na^+ is increased compared to Ca^{2+} concentration, then Na^+ concentration in two phases remains nearly constant and the following expression is given by,

$$K^1_r = \frac{[Ca^{2+}]_{resin}}{[Ca^{2+}]_{soln}} \quad \text{---- (2)}$$

When a ligand such as Citrate ion is added, calcium citrate is formed,

$Ca^{2+} + Citrate^{3-}$ = [Ca $Citrate^{-}$]

The formation constant, K for citrate formation is given by,

$$K = \frac{[Calcium\ citrate-]}{[Ca^{2+}][Citrate^{3-}]} \qquad \text{---- (3)}$$

When citrate ion is added, the concentration of free Ca^{2+} decreases; because of formation of Calcium citrate. This amount of Ca^{2+} in resin decreases. Then Distribution quotient (D) can be given by,

$$D = \frac{[Ca^{2+}]_{resin}}{[Ca^{2+}]_{soln} + [citrate-]_{soln}}$$

$$1/D = \frac{[Ca^{2+}]_{soln} + [citrate-]_{soln}}{[Ca^{2+}]_{resin}}$$

Substituting $[Ca^{2+}]_{soln}$ from (2)

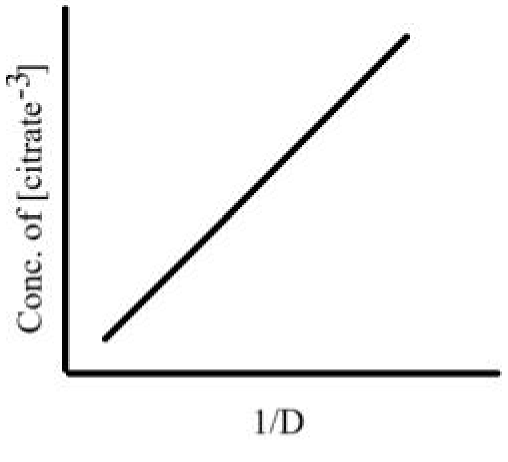
$$= \frac{[Ca^{2+}]_{soln} + [citrate-]_{soln}}{K_r^1 [Ca^{2+}]_{soln}}$$

$$= \frac{1}{K_r^1} + \frac{[citrate-]_{soln}}{K_r^1 [Ca^{2+}]_{soln}}$$

Substituting values of $[citrate]_{soln}^{-}$ from (3)

$$1/D = \frac{1}{K_r^1} + \frac{k[citrate^{3-}]}{K_r^1}$$

D can be measured at various citrate ion concentration thus it forms y=mx+c



Slope = K / K^1_r

Intercept = $1/K^1r$

K is calculated by,

K = slope/intercept = $K / K^1_r \times K^1r = K$

This method of determining stability constant is very fast and easy. If a metal ion is radioactive then the concentration of metal ion in resin phase and solution phase is conveniently determined by measuring its radioactivity.

ADVANTAGES

- ✓ Simple and rapid method
- ✓ High accuracy and Precision
- ✓ It can be used for wide range of metal ions and ligands.

LIMITATIONS

- ✓ Requires careful selection of resin and conditions.
- ✓ May be affected by factors like PH, temperature, Ionic strength.

Polorographic Method

The electrochemical method to analyse the current flow in electrolysis in a electrode when the voltage is applied.

Principle;

When voltage is applied are electrode polarasible and another non polarasible, one of these voltages is polarisable (dropping mercury electrodes) and the other non-polarisable, recording the current flowing between the two electrodes. half wave potential(electrode surface oxidation and reduction same) diffusion current to determine concentration of substance.

Polarographic method

Metal is reduced into metal ion to more complexed . complexed metal ion is negative compared to the simple metal ion, metal complex state is less easily reduced then free metal. To determine the formation of constant of complex.

$Pb^{2+} + 2e^{-} = pb$

Using Nernst equation,

$E=E^0-RT/NF \ln Q$

$E=E^0-0.0591/N \ln Q$

Pb is applied in Nernst equation of reduction

$E=E^0_{(Pb)} - 0.0591/n \log [pb/pb^{2+}]$ ……………… eq(1)

Complex is formed by ligand

$Pb^{2+}+xL = PbLx$

$K=[PbLx]/[Pb^{2+}][L]^X$

Rearranging

$Pb^{2+} =[PbLx]/k[L]^x$ ………………….eq(2)

(1) and (2) (substituting the value of [Pb) from (2) in (1))

$E=E^0_{Pb} -0.0591/n \log [Pb]/[PbLx] -0.059/n \log k -0.059\, x/n \log[L]$

Assuming the complex is reversibly reduced the value for [Pb] and [PbLx] can be obtained,

$E=\{E^0_{(Pb)} -0.059/n \log [k/k']\} -\{0.059/n \log [I/I_0-I] -\{0.059/n \log k\} - \{0.059/n \log [L]$

$E_{1/2} = E^0_{Pb} -0.059/2 \log [k/k']$

For simplicity, let k know be assumed to remain the same for the complex as for the simple ion

Then, $E\ E_{1/2} -0.059/n \log [I/I_0-I] - 0.059/n \log k - 0.050/n \log[L]$

$E_{1/2}$ is the have wave potential of simple metal ion couple,

When $I=I_d /2$ for the complex, $E=E_{1/2}$

$(E_{1/2})_e =E_{1/2} -0.059/n \log k - 0.059 /n \log L$

The hafe wave potential shift due to complexation is delta $E_{1/2}$ versus log L will be produced the straight line.

Slope= $-0.059\, x /n$

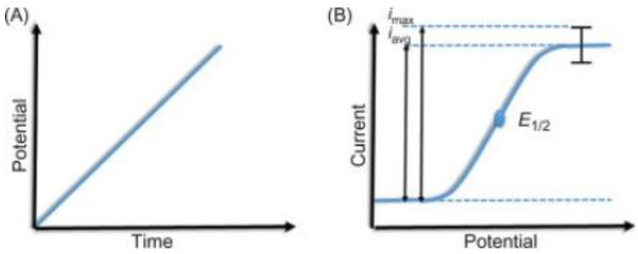
Therefore, the x number of the ligand bouned to the metal can be known.

Intercept = $-0.059/n \log k$

Therefor, the stability of constant k of the complex can be calculated.

Stability constant graph :

$E_{1/2}$ VS log L graph can be plotted the straight line



Continuous Variation Method (Job's Method)

This method is a variation of the spectrophotometric method and is used to determine the composition of a complex. This is mainly used for solutions where only one complex is formed.

Different steps of the procedure are:

1. Make 10 solutions of the complex containing metal ion and ligand in such proportions that the total volume of each solution is 10ml as shown below:

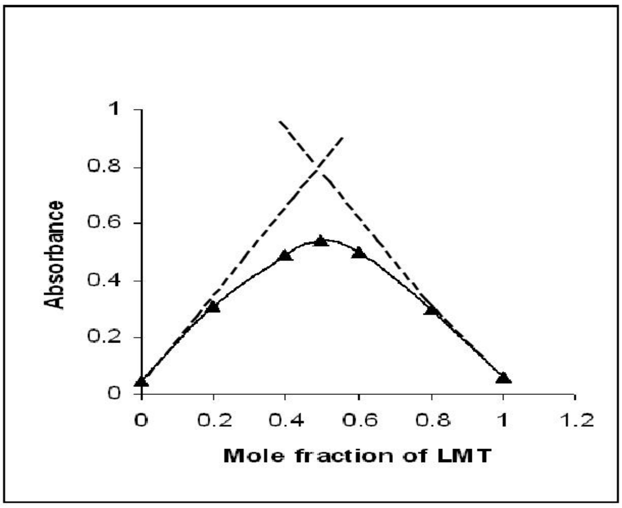
Solutions no. (10 solutions)	1	2	3	4	5	6	7	8	9	10
Volume of the metal ion(ml)	0	1	2	3	4	5	6	7	8	9
Volume of the ligand (ml)	10	9	8	7	6	5	4	3	2	1

   Thus we see that the sum of the concentration of the ligand, C_L and that of the metal ion, C_M is constant. Only their rations, $C_L : C_M$ are changed. Thus

$$\mathbf{C_L + C_M = C \qquad ---1}$$

   Where C is a constant.

2. Determine the optional densities of the solutions as prepared in step 1 with the help of a spectrophotometer as such a wavelength of light that the complex absorbs strongly and the metal ion and the ligand donot.
3. Draw a graph between the mole fraction of the ligand, m.f. (m.f. = C_L/C) and optical density (or absorbance). The graph obtained is of the type as shown in figure.



Point of maximum absorbance at which m.f. = C_L/C

When the legs of they curve are extrapolated, they cross each other at a point at which the absorbance is maximum.

If the formula of the complex is ML, then

$$\mathbf{n = C_L/C_M \qquad ----2}$$

Equation 1 can also be written as:

$$\mathbf{C_L/C + C_M/C = C/C = 1 \qquad ---3}$$

With the help of equation viz.,

$$\mathbf{m.f. = C_L/C \qquad ---4}$$

Equation 3 reduces to

$$\mathbf{m.f. + C_M/C = 1}$$

$$\mathbf{C_M/C = 1 - m.f. \qquad ---5}$$

Dividing equation 4 by 5 we get,

$$\mathbf{C_L/C*C/C_M = m.f./1-m.f.}$$

$$\mathbf{Or\ C_L/C_M = m.f./1-m.f.}$$

Or n = = m.f./1-m.f. See eqn 2 ----6

From the value of n as given by equation 6 we can determine the composition of the complex, ML_n.

LIMITATIONS:

- This method can be used when only one complex is formed under the experiment conditions.
- This method is used when there is no change is the total volume of the solutions containing metal ions and ligand.

Magnetic Property of Complexes: Spin-Orbit Coupling, Effect of Spin-Orbit Coupling on Magnetic Moments Quenching of Orbital Magnetic Moments.

Spin Orbit Coupling is the interaction of an electron's spin with its motion. It refers to the intertwining of an electron's inherent angular momentum (spin) and the angular momentum obtained from orbiting the nucleus. Spin Orbit Coupling is the ratio of the speed of an electron's spin to its orbital motion.

The total angular momentum for a system of electrons is denoted by the letter J. It is obtained by the coupling the resultant spin and angular momenta as per the relation.

The possible values of J are values between $L+S$ and $|L-S|$.

$J=L+S, L+S-1, L+S-2, ..., |L-S|$

Term of different L values denote different energies. For given values of L and S, several levels close together are possible. The number of such possible levels is called the multiplicity. The multiplicity is arrived at by the formula (2S+1).

Term Symbol

A term Symbol or spectroscopic term represents the energy level of microstate with same energy of a given electronic configuration. A full term symbol is as follows:

$$^{2S+1}L_J$$

Where,

J – Total angular momentum quantum number

2S+1 – Spin multiplicity

S	**J**	**Multiplicity**
0	L	1, Singlet
1/2	(L+1/2),(L-1/2)	2, doublet
1	L+1, L, L-1	3, Triplet

When L=0, the multiplicity can be only 1; that is, S terms can have only one value of J. All these information pertaining to the system of electrons is usually conveyed in a single symbol called as a term symbol:

Term symbol = ${}^{2S+1}L_J$

When L= 2 and S = 1, the term symbol becomes,

$(2\times1+1)2\ 3,2\ \text{or}1 = {}^{3}D$

As J= (2+1=3), (2+1-1=2), (2-1=1)

(D is the term letter for L=2). The three states of the triplets are ${}^3D_3$, ${}^3D_2$ and ${}^3D_1$.

Effect of Spin Orbit coupling on magnetic moment

When coupling of Spin and orbit to create a magnetic moment.

μeff due to spin-orbit coupling:

$$\mu\text{eff} = \mu s\,[1- \alpha\,\lambda/\Delta]$$

Where,

α is the constant depends on spectroscopic ground state of particular d election configuration. [For α=0 : S State d^5, α=2 : D State: d^1,d^5,d^6,d^9, α=4: F State: d^2,d^3,d^7,d^8].

Δ being the energy difference between the ground state and the excited state being mixed in (and hence this depends upon the ligand field strength of the system).

λ is related to the spin-orbit coupling constant. The constant λ is positive quantity for the first row transition metal ions having the configurations d^1 to d^5 and it is negative for those with more than the half-filled d^6 to d^9 shell (λ values: Ti^{3}+154, V^{3}+ 108, V^{2}+ 56, Cr^{3}+ 91, Cr^{2}+ 57, Mn^{2}+ 80, Fe^{3}+ 88, Fe^{2}+ -102, Co^{2}+ -177, Ni^{2}+ -315, Cu^{2}+ -829).

Since α and Δ are both positive quantities, it is seen that the observed magnetic moment is greater or less than μs as λ is negative or positive. The observed moment is lower or higher than the spin-only value in several cases.

Magnetic moment of octahedral complex of some first row transition metal ions:-

Metal ion	Configuration	μs, BM	μobs, BM
V^{4}+	$(t2g)^1$	1.73	1.68-1.78
V^{3}+	$(t2g)^2$	2.83	2.75-2.85
Cr^{3}+	$(t2g)^3$	3.88	3.70-3.90
Cr^{2}+	$(t2g)^3(eg)^1$	4.90	4.40-4.90
Fe^{2}+	$(t2g)^4(eg)^2$	4.90	5.10-5.70
Co^{2}+	$(t2g)^5(eg)^2$	3.88	4.80-5.20
Ni^{2}+	$(t2g)^6(eg)^2$	2.83	2.90-3.50

Quenching of orbital magnetic moment

Quenching of orbital magnetic moment refers to the phenomenon where the contribution of the electron's orbital angular momentum to the magnetic moment is significantly reduced or suppressed. This typically occurs in materials where the electron's orbital motion is restricted or influenced by the surrounding environment, such as in the presence of strong crystal fields or spin-orbit coupling.

In solid-state physics, quenching often happens in transition metal ions within crystal fields or ligands that cause the orbital angular momentum to average out. For example, in octahedral or tetrahedral crystal fields, the degeneracy of the orbitals is lifted, and the orbital magnetic moment is often quenched due to the combined effects of spin-orbit coupling and crystal field splitting.

The result is that the magnetic properties of the material are primarily due to the spin magnetic moment rather than the orbital magnetic moment. This concept is important in understanding the magnetic behavior of materials, especially in coordination chemistry and solid-state physics.

Kinetics and Mechanisms of Substitution Reactions of Octahedral and Square Planar Complexes

Inert and Labile Complexes

The metal complexes in which the rate of ligand displacement reactions is very fast and hence show high reactivity are called as labile Complexes and this property is termed as lability. On the other hand, the metal complexes in which the rate of ligand displacement reactions is very slow and hence show less reactivity are called as inert complexes and this property is termed as inertness.

Thermodynamic stability is the measure of the extent to which the complex will form or will be transformed into another complex when the system has reached equilibrium while kinetic stability refers to the speeds at which these transformations take place.

The kinetic stability of the complex depends upon the activation energy of the reaction. If the activation energy barrier is low, the reaction will take place at a higher speed. These types of complexes are also called as kinetically unstable. If the activation energy barrier is high, the substance will react slowly and will be called as kinetically stabilized or inert. There is no correlation between thermodynamic and kinetic stability. Thermodynamically stable products may labile or inert and the vice versa is also true.

Examples: $[Ni(CN)_4]^{2-}$, Its half lifetime ($t_{1/2}$) is 30 seconds and it is **Labile.**

$[Mn(CN)_6]^{3-}$, Its half lifetime ($t_{1/2}$) is 1 hours and it is **Inert.**

Lability and inertness on the basis of Valence bond theory:

According to the valence bond theory of chemical bonding, octahedral metal-complexes can be divided into two types.

1. **Outer orbital complexes:** These complexes have sp^3d^2 hybridization and are generally labile in nature. Valence bond theory proposed that the bonds in sp^3d^2 hybridization are generally weaker than that of $(n\text{-}1)\ d^2sp^3$ orbitals and therefore they show labile character. For example, octahedral complexes of Mn^{2+}, Fe^{2+}, Cr^{2+} complexes show fast ligand displacement.

2. **Inner orbital complexes:** Since d^2sp^3 hybrid orbitals are filled with six electron pairs donated by the ligands, d^n electron of metal will occupy d_{xy}, d_{yz} and d_{xz} orbitals. These d^2sp^3 hybrid orbitals can form both inert or labile complexes. In order to show lability, one orbital out of d_{xy}, d_{yz}, d_{xz} must be empty so that it can accept another.

On The Basis of Crystal Field Theory:

Octahedral complexes react either by Sn1 or Sn2 mechanism in which the intermediates are five and seven coordinated species, respectively. In both cases, the symmetry of the complex is lowered sown and due to this change in crystal field symmetry, the crystal field stabilization (CFSE) value also changes. The cases for lability and inertness are;

1. **Labile complexes** - If the CFSE value for the five or seven membered intermediate complex is greater than that of the reactant, the complex will be of labile nature as there is zero activation energy barrier.
2. **Inert complexes** - If the CFSE value for the five or seven membered intermediate complexes is less than that of the reactant, the metal complex will be of inert nature as loss of CFSE will become the activation energy barrier.

Hence the gain of CFSE will make the complex labile while the loss of CFSE will make the complex inert.

According to CFT,

- d_0, d_1, d_2 - Labile
- d_3 - Inert
- d_4(HS) - Labile ; (LS) - Inert
- d_5(HS) - Labile ; (LS) – Inert
- d_6(HS) - Inert ; (LS) - Inert
- d_7, d_8, d_9, d_{10} - Labile

All the Square planar complexes are Labile because they are nor sterically crowded so the ligand Substitution will occur from either upwards or downwards.

Examples;

$[PtCl_4]$ – Labile, Square planar

$[Fe(CN)_6]^{2-}$ - Inert, d_6 – low spin

$[Ni(CN)_4]^{2-}$ - Labile, d_8 and square planar.

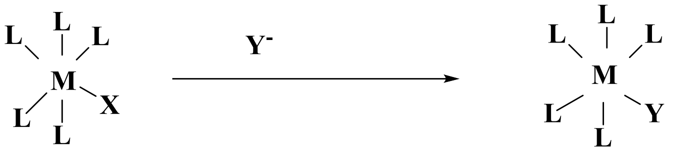
Associative and Dissociative Mechanistic Pathways for Substitution Reactions

In ligand substitution reactions, one or more ligands around a metal ion are replaced by other ligands without changing the oxidation state of central atom.

Eg,

$$[Ni(H_2O)_6]^{2+} \xrightarrow{(NH_3)_6} [Ni\ (NH_3)_6]^{2+}$$

General representation**,**



X=Leaving ligand

Y= Entering ligand

L_5=Ligands (inert in nature)

These reactions takes place by

- Dissociative mechanism
- Associative mechanism

Dissociative Mechanism:

- It is common in octahedral complexes.
- Here the bond between metal and leaving ligand dissociate, then the bond between metal and entering ligand is formed.

General Representation:

Step 1

$$[ML_5 - X] \xrightarrow[\text{R.D.S}]{\text{Slow}} [ML_5]$$

Coordination no : 6

Coordination no: 5
penta-coordinated intermediate

Step 2

$$[ML_5] \xrightarrow[\text{Fast}]{\text{Y}} [ML_5 - Y]$$

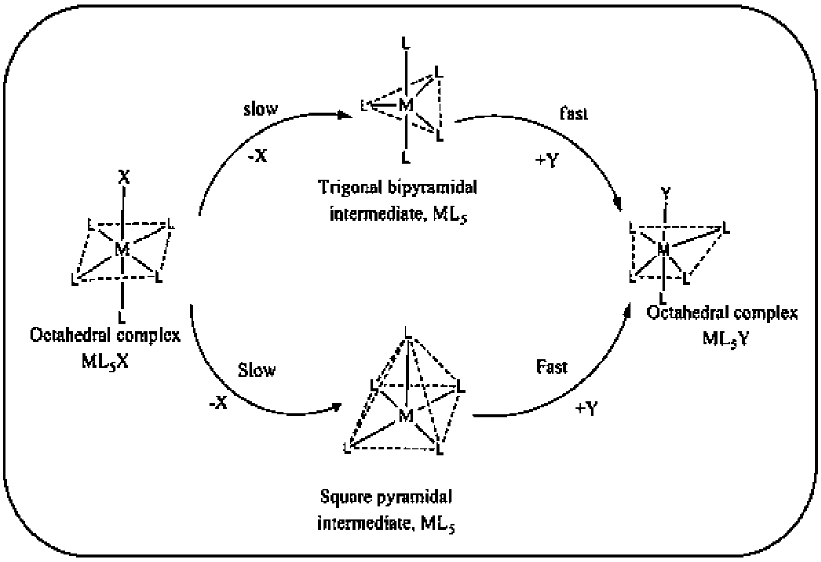
Coordination no : 6

Note: The coordination number of intermediate decreases. (I.e. lesser than the reactant).

Here the intermediate can have two geometries,

a. Trigonal bipyramidal
b. Square pyramidal

DIAGRAMMATIC REPRESENTATION OF DISSOCIATION



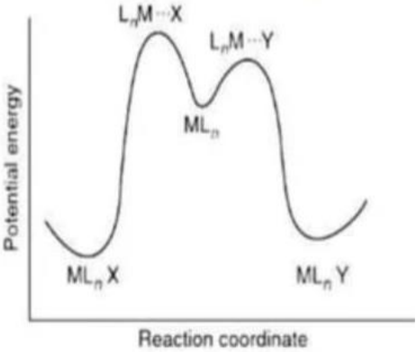
The rate of the dissociative mechanism depend only on reactants.

$$\text{Rate} = k_d\,[ML_5 - X]^1$$

Thus it follows 1st order kinetics **[SN^1 mechanism]**

Energy profile diagram:

Dissociative mechanism is favoured by Steric bulkiness. Incoming ligand has no effect on rate of reaction. Increase in entropy shows dissociative mechanism.



$$[Co(CN)_5(H_2O)]^{2-} \xrightarrow{-H_2O} [Co(CN)_5]^{2-} \xrightarrow{+\ I^-} [Co(CN)_5I]^{3-}$$

Coordination no :6 **Coordination no : 5** **Coordination no : 6**

Associative Mechanism [S_N^2 Mechanism]

- Associative mechanism is rarely seen in octahedral complexes and commonly seen in square planar complexes.
- In this mechanism, the bond between metal and incoming ligand is formed first and then bond between metal and leaving ligand is broken.

General Representation,

$$[ML_5\text{-}X] + \quad Y \longrightarrow L_5M\begin{smallmatrix}\nearrow X\\ \searrow Y\end{smallmatrix} \xrightarrow{-X} [L_5M\text{ - }Y]$$

Coordination no : 6 **Coordination no : 7 Hepta coordinated intermediate** **Coordination no : 6**

Note:

The coordination number of intermediate increases (greater than the reactant).Here the intermediate has two possible geometries,

- Pentagonal bipyramidal
- Monocapped octahedral or octahedral wedge

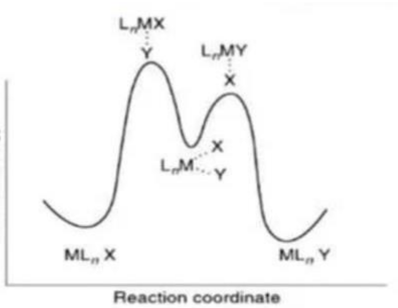
The rate of Associative mechanism depends on reactant and incoming ligand.

$$\text{Rate} = K_a[ML5 - X]^1\ [y]^1$$

Thus it follows 2nd order kinetics [SN2 mechanism]

It is unfavored by steric bulkiness in octahedral complexes.Incoming ligand influences the rate of reaction. Decrease in entropy shows associative mechanism.

Energy profile diagram



$$[Cr(H_2O)_6]^{3+} \xrightarrow{Y} [Cr(H_2O)_6Y]^{2+} \xrightarrow{-H_2O} [Cr(H_2O)_5Y]^{2+}$$

Coordination no : 6 **Coordination no : 7** **Coordination no : 6**

Associative mechanism is preferred by electron densities around metal centre. The above complex have electrophilic centre (as water is neutral ligand and have no effect on chromium).Thus this octahedral complex would involve associative mechanism**.**

Interchange Mechanism:

- In interchange mechanism,no stable intermediate is formed
- It proceeds by transition state.

General Representation,

$$[L_5M - X] \xrightarrow{Y} [Y\text{--------------}L_5M\text{-------------}X] \xrightarrow{-X^-} [ML_5Y] + X^-$$

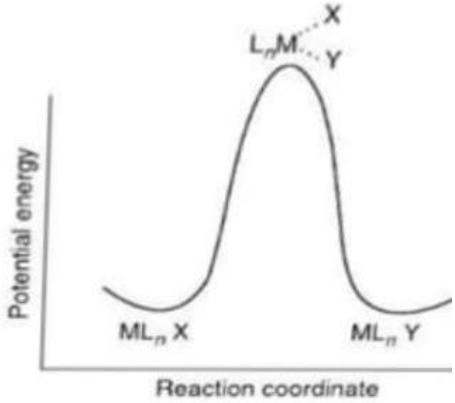
Transition State

Interchange mechanism can be classified into two types

1. Interchange Associative (I_a)
   Here M-X bond began to break before M-Y bond is fully formed.
   Eg) $[V(H_2O)_6]^{2+}$
2. Interchange Dissociative (I_d)
   Here M-Y began to form before M-X bond is fully broken.

Eg)$[Ni(H_2O)_6]^{2+}$

Energy profile Diagram



SNCB Mechanistic Pathway for Substitution Reactions

The SN1CB mechanism, or Substitution, Nucleophilic, first-order in the Conjugate Base mechanism, explains how many metal amine complexes undergo ligand exchange, or substitution, in coordination chemistry. This mechanism involves deprotonating a metal complex to form its conjugate base, which increases the electron density on the metal center and makes it easier to lose the leaving group ligand.

The SN1CB mechanism is often used to explain reactions that occur in non-hydroxylic solvents, like dimethyl sulphoxide. In these reactions, the acid-base properties of the complexes are more important than the nucleophilic properties of OH-, and the SN1CB mechanism is favored over the SN2 mechanism.

The SN1CB mechanism involves the following steps:

1.A polyamino metal halide reacts with aqueous base.

2.The base deprotonates the coordinated ammonia, increasing electron density on the metal center.

3.The halide dissociates simultaneously with the deprotonation.

4.Water binds to the complex that’s now coordinatively unsaturated,followed by proton transfer to create the hydroxy complex.

Kinetics of Sn1CB mechanism:

Rate-Determining Step:

(1) $[Co(NH_3)_5X]^{2+} + OH^- \rightleftharpoons [Co(NH_3)_4(NH_2)X]^+ + H_2O$ (equilibrium)

(2) $[Co(NH_3)_4(NH_2)X]^+ \longrightarrow [Co(NH_3)_4(NH_2)]^{2+} + X^-$ (slow)

(3) $[Co(NH_3)_4(NH_2)]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(OH)]^{2+}$ (fast)

Overall:

$$[Co(NH_3)_5X]^{2+} + OH^- \longrightarrow [Co(NH_3)_5(OH)]^{2+} + X^-$$

The rate-determining step (RDS) is the dissociation of the conjugate base to form the carbocation intermediate.The reaction rate is typically dependent on the concentration of the conjugate base formed in the first step.

Rate Law:

overall rate law for an SN1CB reaction can be expressed as:

[Rate] = k[[Conjugate Base]] Here, (k) is the rate constant for the dissociation step.

Factors Affecting the Rate:

Base Strength: The stronger the base, the faster the deprotonation step, leading to a higher concentration of the conjugate base.

Leaving Group Ability: The better the leaving group, the faster the dissociation step.

Solvent: Polar solvents stabilize the carbocation intermediate, which can increase the reaction rate.

Temperature: An increase in temperature generally increases the rate of the reaction.

Experimental Methods:

Spectrophotometry: Monitoring changes in absorbance as the reaction proceeds.

Conductometry: Measuring changes in electrical conductivity due to the formation of ions.

pH Measurement: Tracking changes in pH if the reaction involves proton transfer.

Evidence:

The SN1CB (Substitution Nucleophilic Unimolecular Conjugate Base) mechanism is a well-established reaction pathway, particularly in the context of organic and organometallic chemistry. Here are some pieces of evidence and research findings that support the existence and understanding of this mechanism:

1.Historical Studies on Carbanion Intermediates:

The SN1CB mechanism was first proposed based on studies of carbanion intermediates, particularly in reactions where a proton is abstracted to form a carbanion, which then dissociates to give a stable leaving group and a carbocation.

Research by Ingold and coworkers in the mid-20th century laid the groundwork for understanding nucleophilic substitution reactions, including the SN1CB pathway.

2. Kinetic Studies:

Rate Dependence on Base Concentration: Kinetic experiments often show that the reaction rate in SN1CB mechanisms is dependent on the concentration of the base, which supports the formation of a conjugate base intermediate.

First-Order Kinetics: Many reactions following the SN1CB mechanism exhibit first-order kinetics with respect to the conjugate base, which matches the theoretical rate law.

3. Spectroscopic Evidence:

UV-Vis and IR Spectroscopy: These techniques can be used to monitor the formation and consumption of intermediates in the reaction. For example, changes in absorbance corresponding to the formation of a carbocation or a leaving group can be observed, providing evidence for the SN1CB pathway.

NMR Spectroscopy: Nuclear Magnetic Resonance (NMR) can detect shifts in chemical environments that occur during the formation of intermediates, supporting the mechanistic steps.

4.Solvent effect:

Studies have shown that polar solvents stabilize the carbocation intermediate, which is crucial for the SN1CB mechanism. The reaction rate typically increases in more polar solvents, which is consistent with the mechanism's requirement.

5. Substrate Effects:

The mechanism has been observed in a variety of substrates, particularly those that can easily form stable carbanions or carbocations. The presence of electron-withdrawing groups in the substrate can enhance the rate of the SN1CB reaction by stabilizing the intermediate, further confirming the proposed mechanism.

6. Isotopic Labeling Experiments:

Isotopic labeling (e.g., using deuterium) can help trace the movement of atoms through the reaction mechanism. These experiments often confirm the deprotonation step as the first step in the mechanism, followed by dissociation.

These studies and pieces of evidence collectively support the existence and the understanding of the SN1CB mechanism in various chemical systems.

Acid Hydrolysis of Octahedral Complexes

The acid hydrolysis of octahedral metal complexes involves the substitution of ligands (usually water or anions) coordinated to the central metal ion by water molecules or other nucleophiles. This reaction is significant in coordination chemistry and can follow various pathways depending on the nature of the metal ion, the ligands, and the reaction conditions.

The acid hydrolysis of octahedral complexes typically involves the following steps:

1. Protonation of the Ligand:

In an acidic medium, the ligand coordinated to the metal ion can be protonated. This is particularly relevant when the ligand is a water molecule or a hydroxide ion.

$[M\text{-}L] + [H]^+ \rightarrow [M\text{-}LH]^+$

Here, M represents the metal center, and L represents the ligand (e.g., H_2O or OH^-).

2. Dissociation of the Protonated Ligand:

The protonated ligand becomes a better leaving group and dissociates from the metal center.

$[M\text{-}LH]^+ \rightarrow [M] + [LH]^+$

This leads to the formation of a vacant coordination site on the metal ion.

3. Substitution by Water:

The vacant site on the metal ion is rapidly occupied by a water molecule (or another nucleophile present in the solution).

$[M] + [H_2O] \rightarrow [M\text{-}H_2O]$

Here's an example:

$[Cr(NH_3)_6]^{3+} + 6H^+ \rightarrow Cr^{3+} + 6NH_4^+$

In this example, the hexaamminechromium(III) complex undergoes acid hydrolysis, where the six ammonia ligands (NH_3) are replaced by water molecules, releasing ammonium ions (NH_4^+) and forming the Cr^{3+} aqua ion.

Another example is:

$[Co(en)_3]^{3+} + 3H^+ \rightarrow Co^{3+} + 3H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$ (ethylenediamine)

In this case, the tris(ethylenediamine)cobalt(III) complex undergoes acid hydrolysis, where the ethylenediamine ligands are protonated and released, forming the Co^{3+} aqua ion.

Stereochemistry:

The stereochemistry of acid hydrolysis in octahedral complexes is an important aspect, particularly because octahedral complexes can exhibit different stereoisomers. The stereochemistry of the products depends on the nature of the ligands, the type of substitution, and whether the substitution process occurs with retention, inversion, or racemization of configuration.

In the context of octahedral complexes, stereochemical considerations usually involve:

1. **Retention of Configuration:** The spatial arrangement of the ligands around the metal ion remains the same after hydrolysis.
2. **Inversion of Configuration:** The spatial arrangement of the ligands changes (like a mirror image) after the hydrolysis.

3. **Racemization**: The hydrolysis results in a mixture of isomers, often leading to the loss of optical activity if the starting complex was optically active.

Example: Acid Hydrolysis of Cis- and Trans-$[Co(NH_3)_4Cl_2]^+$ Complexes

Complexes:

Cis-$[Co(NH_3)_4Cl_2]^+$: An octahedral complex where two chloride ligands are adjacent to each other.

Trans-$[Co(NH_3)_4Cl_2]^+$: An octahedral complex where the two chloride ligands are opposite each other.

Reaction:

In an acidic medium, these complexes can undergo hydrolysis where a chloride ion is replaced by a water molecule:

1. Cis-$[Co(NH_3)_4Cl_2]^+ + H_2O \rightarrow$ Cis-$[Co(NH_3)_4Cl(H_2O)]^{2+} + Cl^-$
   - In this case, the hydrolysis typically occurs with retention of configuration**. The resulting complex remains cis with respect to the ammonia ligands.

2. Trans-$[Co(NH_3)_4Cl_2]^+ + H_2O \rightarrow$ Trans-$[Co(NH_3)_4Cl(H_2O)]^{2+} + Cl^-$
   - Similarly, for the trans isomer, hydrolysis generally proceeds with retention of the trans configuration.

Stereochemical Considerations:

Cis to Cis and Trans to Trans: In these examples, the hydrolysis reaction does not cause a change in the relative positions of the ligands (cis remains cis, and trans remains trans). This indicates a retention of stereochemistry during the hydrolysis process.

No Racemization: Since the original complexes are symmetric and non-chiral (cis and trans forms), racemization isn’t a consideration in this particular reaction. However, if we were dealing with chiral octahedral complexes, racemization could be a possibility if the hydrolysis leads to a loss of stereochemical integrity.

Experimental Evidence:

1. Optical Activity:

- If a chiral complex were involved, one could measure optical rotation before and after hydrolysis to determine if racemization has occurred.

2. Spectroscopy:

- NMR and IR Spectroscopy: Can provide insights into the arrangement of ligands before and after hydrolysis, confirming whether the configuration has been retained or altered.

3. X-ray Crystallography:

- This method can be used to definitively determine the 3D structure of the complex before and after hydrolysis, allowing for a direct observation of stereochemical changes.

In acid hydrolysis of octahedral complexes like cis- and trans-$[Co(NH_3)_4Cl_2]^+$, the reaction generally proceeds with retention of stereochemistry, meaning that cis and trans configurations are preserved in the products. The stereochemical outcome of such reactions can be studied using various techniques, such as optical rotation measurements, NMR, IR spectroscopy, and X-ray crystallography.

Classification of Metal Ions Based on the Rate of Water Replacement Reaction and their Correlation to Crystal Field Activation Energy

When the water molecules in the coordination sphere are replaced with isotopically labelled bulk water. The reaction is called water replacement reaction.

Water replacement reaction depends upon the charge density.

If this is an Id reaction, M-X bond strength should correlate with reaction rate since most of the activation energy would be associated with bond breaking.statifies our expectation that the reaction rate depends on the kind of M-X bond bring broken. The entering group and leaving group data provide convincing evidence for a dissociative mechanism.

$$[M(OH)_2)_6]^{X+} + X^- \xrightarrow{K_a} [M(OH)_2)_5X]^{(X-1)+} + H_2O$$

Water replacement reaction:

Although it is probable if the reaction rates were known for all possible octahedral complexes a continuous series could be formed, it is still convenient to classify metal ions in four categories based on the rate of exchange of coordinated water:

CLASS 1: the exchange of water is extremely fast . first order exchange rate constants are on the order of 10^8 s^{-1}, which approaches the maximum possible rate constant. The complexes are bound by essentially electrostatic forces and include the complexes of the alkali metals and larger alkaline earth metals, except Be and Mg. Z^2/r ratio range up to about 10×10-^{28} C^2 m^{-1}.

CLASS2: The exchange of water is fast. First order rate constant range from 10^5tto 10^8 s^{-1}. Metal ions belonging to this group are the dispositive transition metals, Mg$^{\wedge 2+}$and tripositive lanthanides. These ions form complexes in which the bonding is somewhat stronger than in those of class 1ions,The Z^2/r values for ions in this category range from about 10 to 30×10^{28} $C^{\wedge 2}m^{-1}$.

CLASS 3:The exchange of water is slow compared with classes 1 and 2 , although fast on an absolute scale, with first order constant of 1 to 10^4 s^{-1}.The metal ions of this group are most of the tripositive transition metal ions and two very small ions,Al^{3+} and Gd^{3+} . The Z^2/r ratios are greater than about 30×10-^{28} C^2m^{-1}.

CLASS 4: The exchange of water is slow. These are only inert complexes. First order rate constants range from $10^{-1}$to 10^{-9} s^{-1} . These ions comparable in size to class 3 ions .Cr^{3+}, Ru^{3+}, Pt^{2+}..

A variety of methods is available for studying exchange reactions for classes 1,2,3 and 4.

Rate constants for the reaction Of $[Co(NH_3)_5(H_2O)]^{3+}$ With X^{n-} in water at 45°C.

X^{n-}	$k(M^{-1}s^{-1})$
NCS^-	1.3×10^{-6}
$H_2PO_4^-$	2.0×10^{-6}
Cl^-	2.1×10^{-6}
NO_3^-	2.3×10^{-6}

Rate constants for the reaction of $[Co(NH^3)^5X]^{m+}$ With H_2O

X^{n-}	$K(S^{-1})$
NCS^-	5.0×10^{-10}
$H_2PO_4^-$	2.6×10^{-7}
Cl^-	1.7×10^{-5}
NO_3^-	2.7×10^{-5}

Volume of activation exchange in [M(,NH3)5(OH2)]^3+

M	ΔV++,CM^3 mol^{-1}
Co^{3+}	+1.2 (300 K)
Cr^{3+}	-5.8 (298 K)
Rh^{3+}	-4.1 (308 K)
Ir^{3+}	-3.2 (344 K)

Volumes of activation for water replacement in hexa-aqua complexes of transition metal ions of the first row

M	ΔV++,CM^3 mol^{-1}
Ti^{3+}	-12.1
V^{3+}	-8.9
Cr^{3+}	-9.6
Fe^{3+}	-5.4

Activation Energy (AE):

Activation energy is defined as the energy required to convert the reacting complex into Unstable or activated complex (transition state or intermediate). Thus, activation energy is The energy necessary for forming activated complex from the reacting complex. Activated Complex does not represent a true molecule but represents only an imaginary molecule Which cannot be isolated. It has maximum energy and has very short life. Being unstable, The activated complex finally changes to the products. Activation energy (AE) is the Difference in energy between the reacting complex and activated complex, i.e.

A E = Energy of activated complex – Energy of reacting complex

Crystal Field Activation Energy (CFAE):

CFAE is defined as the change in crystal field stabilization energy (CFSE) when the reacting Complex is changed into intermediate, i.e.

CFAE = CFSE of intermediate – CFSE of the reacting complex

If the calculated value of CFAE is negative or zero or low, the reacting complex would Require less energy for its conversion into intermediate. On the other hand, calculated value Of CFAE is high, the reacting complex would require more energy for its conversion into Intermediate.

d* ion	**Sign of CFAE value**	**Labile or Inert**
d^0	0	Fast to react (Labile)
d^1	-	Fast to react (labile)
d^2		Fast to react (labile)

d^3		Slow to react (inert)
d^4(HS)		fast to react (labile)
d^4(LS)		Slow to react (inert)
d^5(HS).		Fast to react (labile)
d^5(LS)	+	Slow to react (Inert)
d^6(HS)		Fast to react (labile)
d^6(LS)	+	Slow to react (Inert)

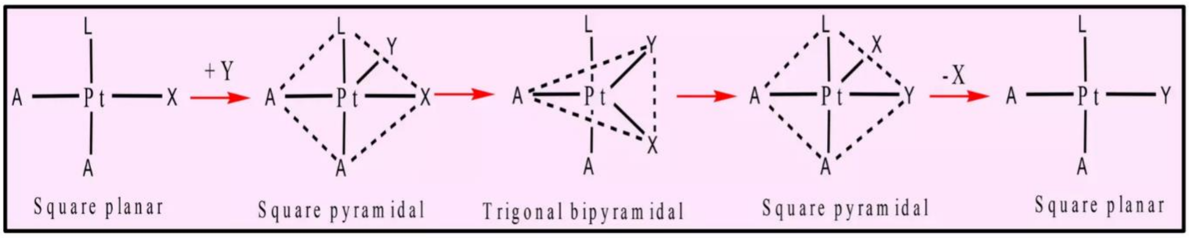
Substitution Reactions in Square Planar Complexes

Replacement or exchange of a ligand with another ligand without any change in oxidation state at the metal center or co-ordination number of metal ions.

$$\mathbf{[Pt\,(Cl_4)]^{2-} + NH_3 \longrightarrow [Pt\,Cl_3\,(NH_3)]^{-} + Cl^{-}}$$

Occurrences of square planar complex in low spin (Ni^{2+}, Pt^{2+}, Pd^{2+}, Rh^{+1}, Au^{+3}) d^8 metal ions. The metal ions must be low spin to become square planar. Pt complex is low spin and square planar, where energy increases down in the periodic table larger for the heavier member while Ni (II) most are high spin octahedral except for ligands high in spectrochemical series so [Ni $(CN)^4]^{2-}$ is square planar whereas [Ni $(Cl)^4]^{2-}$ is tetrahedral.

The most extensive work has been done on Pt (II) because it is stable, easy to synthesis, its rate is slow and both strong field ligand and weak field ligand gives square planar complex. Comparing Pt (II) the Ni (II) and Pd (II) has 10^6 - 10^7 faster reaction. The square planar complex has less steric effect due to lesser co-ordination number and the ligands can associate easily. It follows SN_1 associative pathway and co-ordination number is 4.



The reaction taking place in square planar complex are:

1. Dissociative reaction (SN1)

$$[MLnX] \longrightarrow [MLn] \longrightarrow [MLnY]$$

the co-ordination number of the intermediate is lesser than the starting material.

2. Associative reaction (SN2)

$$[MLnX] \longrightarrow [MLnXY] \longrightarrow [MLnY]$$

the co-ordination number of the intermediate is high than the starting material.

3. Interchange reaction (SN2)

$$[MLnX] + [Y] \longrightarrow [MLnXY] \longrightarrow [MLnY]$$

no intermediate and the simultaneous bond form of metal and entering group as well as the bond cleavage of metal and leaving group.

In general, the kinetic studies in square planar complexes has been carried out on the Pt(II), Ni(II), Pd(II) and Au(III) complexes.

$$\mathbf{[Pt\,(Cl_4)]^{2-} + NH_3 \longrightarrow [Pt\,Cl_3\,(NH_3)]^{-} + Cl^{-}}$$

For the reaction under pseudo-first order conditions, the concentration of Y is much larger than the Pt-complex. The usual from of the rate law is

$$-d/dt\,[PtLCl_3] = k1[PtLCl_3]\,[Y] - k2[PtLCl_2Y]\,[Cl]$$

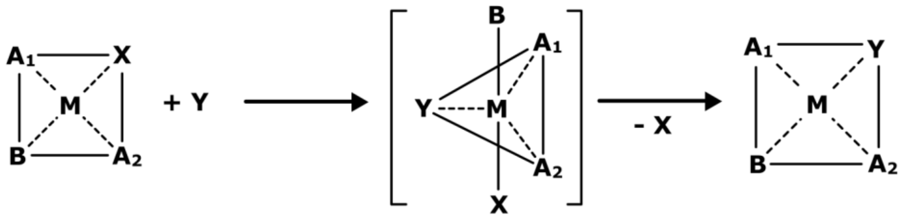
The above rate law suggests that substitution of Cl- by Y, follows two independent pathways. Since, reaction mostly dominates in the forward direction, the reaction rate for the first reaction path is given by

$$r = k\,[Pt\,Ln\,Cl4\text{-}n]\,[Y]$$

This indicate that the rate determine step is bimolecular and the mechanism involved is associative SN2 mechanism.

Stereochemistry

The SN2 Mechanism for the substitution reaction of square planar complexes follows retention of geometrical isomerism this may be illustrated as follows



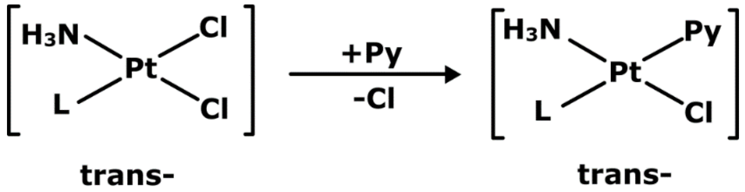
In the substitution of Square Planner complex, the entering ligand Y attacks the complex from one side of the plane with the formation of trigonal bipyramidal (TBP) transition state as shown in the above scheme. The three ligands (A1, A2 and Y) in its equatorial position while the two group (X and B) in its axial position. After removal of X, the TBP intermediate converted into new substituted square planner complex.

Factors affecting square planar complexes

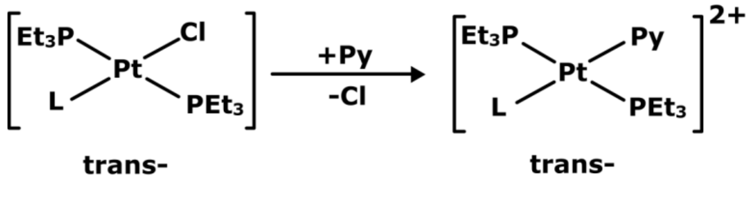
There are four kinds of factors affecting the substitution in square planner complex. The rate of exchange of ligands is governed by either the weakening of Pt-X bond in ground state or it can stabilize transition state. Combination of both the possibility somewhat influence the rate of reaction.

1. Trans effect

Trans effect is the ability of a group to direct substitution into its opposite trans position. The decrease of rate of substitution in trans Pt (II) complex is the decrease of trans effect. For example,



The relative rates of various L like $C_2H_4 > NO_2^- > Br^- > Cl^-$ increases as the trans effect increases, however activation energy decreases in the same way. The usual effect of trans effect on the rate has been observed in the following reactions.



In this reaction L like $H^- > CH_3^- > C_6H_5^-$ increases as the trans- effect of these ligands increases.

2. Effect of labile group

The labile group present in complex can directly affects the rate of substitution reactions.

$$[Pt\ (\ dien\ )X]^{+} + Y \longrightarrow [Pt(\ dien\ )Y]^{+} + X$$

The ease of substitution of X fallows the order: $Cl^{-} > Br^{-} > I^{-} > SCN^{-} > NO_2^{-} >$ CN. It has been observed that the replacement of halides is easier than other common ligands because of the weak strength of Metal-halide bond strength.

3. Effect of solvent

It has been observed that the coordination ability of the solvent can easily compete with the of substitution reactions. trans- $[Pt\ (\ py\ )_2Cl_2] + {}^{*}Cl^{-} \longrightarrow$ trans-$[Pt(\ py\ )_2(Cl)({}^{*}Cl)] +$ Cl. Some of the solvents have good coordinating ability hence these solvents don't affect the substitution of Cl- ions. Like DMSO, H_2O and ROH etc. While some of solvent having weaker coordinating ability like CCl_4, Benzene, acetone, DMF etc. In these solvents substitution reaction is dependent on the concentration of Cl- ions.

4. Effect of charge on complex

An increase in the positive charge on the complex specie decreases rate of substitution reactions. The decrease in reaction rate is observed as the charge of the complex increases, a dissociative nucleophilic substitution SN1 process seems to be operative.

Trans Effect - Theories of Trans Effect

Substitution reactions in square-planar complexes have been extensively studied using platinum (II) complexes.

Various ligands having different trans directing influence are arranged in an increasing order of their trans effect. This series is known as the trans effect series. This series is based on some qualitative and quantitative observations. This series is ,

$CN^{-} > C_2H_4 > CO > tu > NO_2^{-} > SCN^{-} > I^{-} > Br^{-} > Cl^{-} > py > NH_3 > OH^{-} > H_2O$

(tu-thiourea ; py-pyridine)

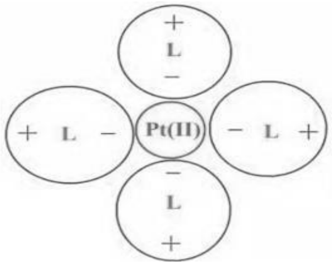
Trans effect may be defined as the labilisation of ligands trans to other trans-directing ligands.

Theories of Trans Effect:

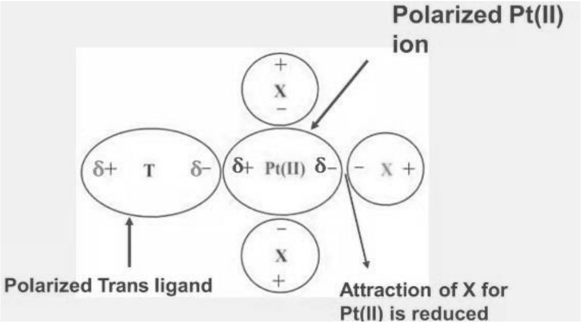
Several theories have been proposed for the explanation of the trans effect. Only two theories representing different approaches are outlined here.

1.The Polarization theory

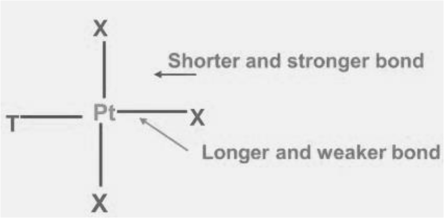
- This theory was proposed by grinberg (1927) in which a good trans-directing ligand was visualized as being more polarizable.



- According to this theory, the primary positive charge of Pt(II) induces a dipole in all the four ligands.
- If the four ligands are identical , then the dipoles induced by the metal ion cancel out each other and the resultant dipole is zero
- Here none of the four ligands shows trans effect.



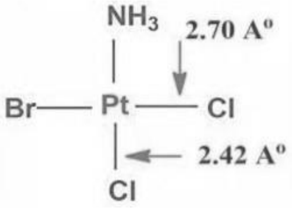
- If the four ligands are not identical as in , then the induced dipoles do not cancel out each other.
- The two X ligands which are similar and trans to each other balance each other. But the other two trans ligands, T and X, which are not similar, the induced dipoles do not balance each other.



- This figure represents the polarization of metal ion induced by a highly polarizable trans ligand, T in [Pt X_3 T) complex as compared to [Pt L_4] complex.
- Hence, the attraction of X for Pt(II) is reduced and the bond trans to T (Pt-X) is weakened and consequently lengthened. i.e., Pt-X bond trans to T is weaker and longer than Pt-X bonds that are cis to T .
- This facilitates the replacement of X by Y(entering ligand) at a point trans to T.

Evidence in favor of the Polarization theory :

- This theory predicts that trans effect is important only when the central metal ion itself is polarizable and large in size. Actually the order of importance of trans effect is Pt(II) > Pd(II) > Ni(II). Because, the size and polarizability decrease in the same order.



- If the ligand T is highly polarizable in [Pt X, T] complex, then Pt-X bond trans to T is longer than Pt-X bond cis to T. This is evident from the following example.

Merit:

This theory explain very well the trans effect of ligands that are present at the low end of trans effect series like H_2O, OH^-, NH_3, CI^- , Br^-, etc.

Defect:

This theory cannot explain the high trans-effect of the ligands like C_2H_4. CN^-, CO etc., which lie at the high end of the trans-effect.

2. **The π-bond theory :**

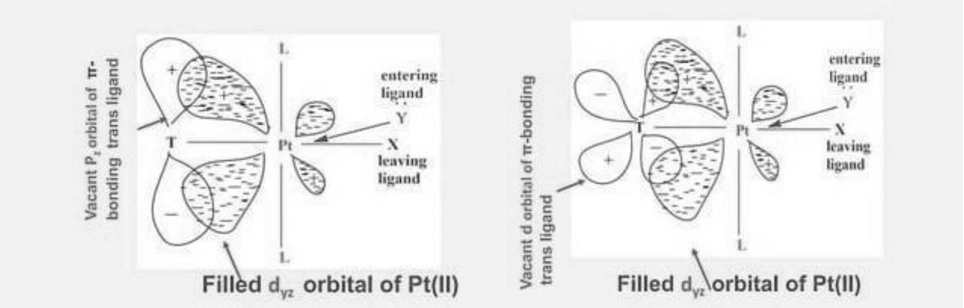
According to this theory, the vacant π or π orbitals of π - bonding ligands accept a pair of electrons from the filled d- orbitals of the metal (dyz or dx, orbitals) to form M L π -bond. (d π- ρπ overlapping or d π- d π- overlapping).

According to Orgel, the very good - acceptor ligands effectively withdraw electron density that will accumulate on the metal as a result of adding a fifth ligand (y), thereby stabilizing the 5-coordinate transition-state.

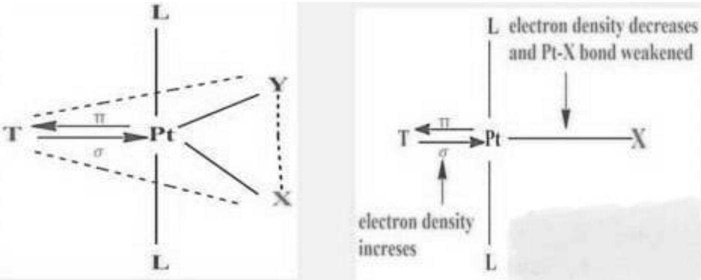
So, the energy of the 5-coordinate trigonal bipyramidal transition state is lowered which results in the lowering of energy of activation (Ea) of the substitution reaction. Thus, the rate of the ligand substitution is increased due to the presence of π- bonding trans ligands.

In the structure of TBP 5-coordinated intermediate, π- bonding trans ligand occupy the equatorial position and the two cis-inert ligands occupy the axial positions.

According to Chatt, the formation of M - L π-bond in the complex increases the electron density in the direction of T ligand and diminishes the electron density in the direction of X trans to T.



Thus, Pt-X bond trans to T is weakened. This facilitates the approach of the entering ligand Y with its lone pair in the direction of diminished electron density to form the 5- coordinated transition state complex, which on loosing X, yields the substituted complex.



Evidences in favour of the π -bonding Theory :

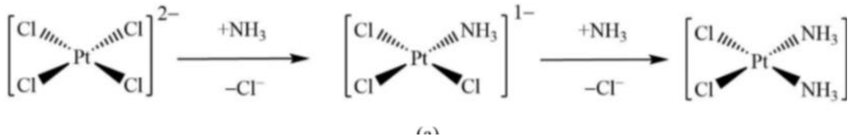
The Pt-X bond trans to the π - bonding C_2H_2 ligand in complexes of [Pt X3 (C_2H_4)] type has been found to be longer than that cis to it. Trans effect of C_2H_4> X^-

Merits of π – bonding theory :

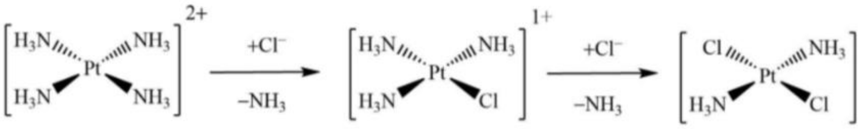
It explains the trans effect of π-bond acceptor ligands which lie at the high end of trans effect series.

Applications of Trans Effect in Synthesis of Square Planar Compounds

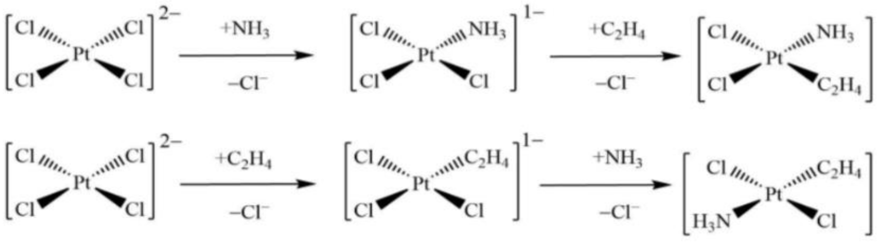
Preparation of Cis-isomer



Preparation of trans-isomers



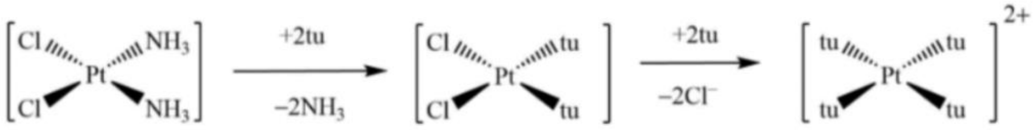
Preparation of Cis and Tras – isomers



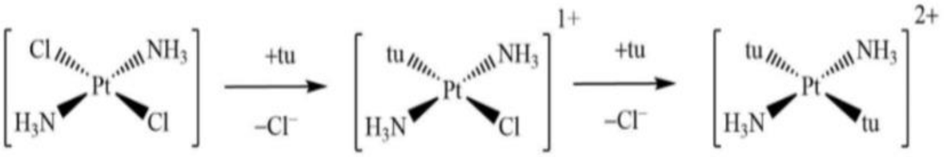
Kurnakov's test

Kunakov test contain cis platin and trans platin . cis platin are anti cancer d rug. Some times used to detect transplatin in samples of the drug cisplatin. In hot aquous solution the Cis compound react with aqueous thiourea to give a deeper yellow solution ,from yellow needles...

Cis-Platin



Trans- Platin



Electron Transfer Reactions in Octahedral Complexes

Electron Transfer:

Electron transfer reactions, also known as redox reactions, are chemical reactions that involve the transfer of electrons between atoms. In these reactions, one element loses electrons and undergoes oxidation, while another element gains electrons and undergoes reduction.

There are two mechanisms by which inorganic complexes transfer electrons. The outer sphere mechanism and the inner sphere mechanism. The outer sphere mechanism is important because of the analogy that can be drawn between electron transfer in metal complexes and electron transfer in metalloenzymes. The inner sphere mechanism is important because atom transfer (bond breaking/formation) can be concomitant with electron transfer. Both are important for photosynthesis.

Outer Sphere Electron Transfer:

- Outer sphere electron transfer occurs between complexes that do not undergo substitution.
- No new bonds are broken or formed.
- For throughout the reaction co-ordination sphere remains same.
- There is no bridging ligands needed.
- It is faster than inner sphere because the energetic demands are less.

Consider a general redox reaction,

$$M^{(a+1)+} L_x + M^{b+} L_y \longrightarrow M^{a+} L_x + M^{(b+1)+} L_y$$

Oxidant Reductant

Mechanism:

This mechanism involves three steps.

Step 1: Formation of precursor complex

$$M^{(a+1)+} L_x + M^{b+} L_y \xrightarrow{keq} [M^{(a+1)+} L_x \text{ IIIIII } M^{b+} L_y]$$

Precursor Complex

In this step the complexes come closer together to form a precursor complex

Step 2 : Relaxation to successor complex

$$[M^{(a+1)+} L_x \text{ IIIIII } M^{b+} L_y] \overset{K_{ET.}}{\longleftrightarrow} [M^{a+} L_x \text{ IIIIII } M^{(b+1)+} L_y]$$

Successor Complex

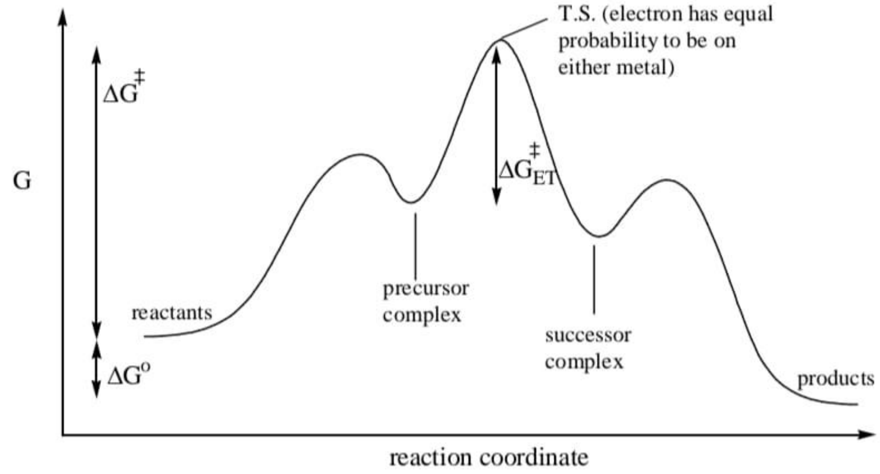
When the precursor complex formed the electron transfer takes place between the two complex. It is also known as activation/reorganisation of precursor complex.

Step 3: Dissociation of successor complex

$$[M^{a+}L_x \,\text{IIIIII}\, M^{(b+1)+}L_y] \xrightarrow{k_{diss}} M^{a+}L_x + M^{(b+1)+}L_y$$

In this step the successor Complex dissociated to give the product.

Formation of precursor complex and dissociation of successor complex are fast and Electron transfer slow.



Types:

The outer sphere electron transfer reaction are further classified into two types.

They are,

1. Self - exchange reaction
2. Cross reaction

1. Self - exchange reaction:

Self - exchange reaction are termed for electron transfer reaction in which the reacting species are identical but varies With an oxidation state.

An example of a self exchange reaction is,

$$[MnO_4]^- + [MnO_4]^{2-} \rightarrow [MnO_4]^{2-} + [MnO_4]^-$$

2. Cross reaction:

A cross reaction is a type of electron transfer reaction that involves two different metal ions exchanging.

An example of cross reaction is,

$$[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \longrightarrow [Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-}$$

Factors involves in the rate of the transfer reaction:

1. Ligand Effect

The nature of the ligands surrounding a transition metal ion can greatly affect the rate of redox reactions. Ligands that can accept electron density into empty orbitals stabilize higher oxidation states and thus can increase the rate of redox reactions.

So the л-acceptor ligands are increase the rate of the reaction.

Ex. CO, C_2H_4, CN^-, $P(Ph)_3$& bpy_3 .

2. Bond Length

Metal-ligand bond lengths will change when the oxidation state of the metal changes. The FrankCondon principle states that because nuclei are much more massive than electrons, an electronic transition occurs much faster than the nuclei can respond. Complexes must adjust their M-L bond lengths before electron transfer.

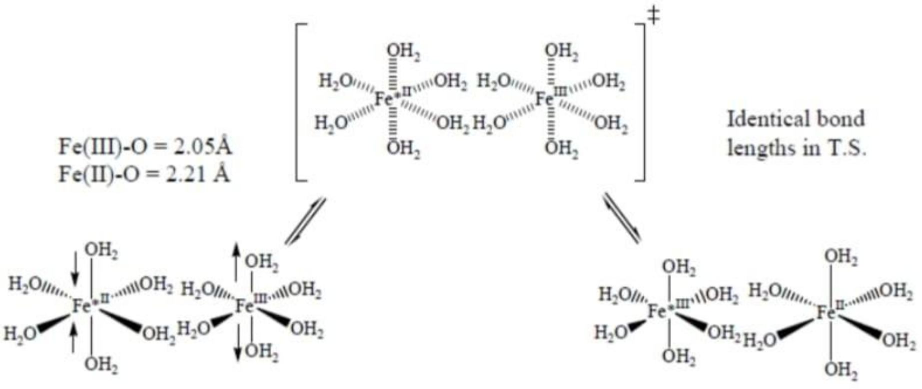


Fig. Transition state for outer sphere electron transfer

Example: Here Fe(III)-O and Fe(II)-O bond length are different in the reactant, but in the transition state identical bond length make the electron transfer possible.

3. Transition Order

Electron transfer happens more faster when transfer occurs between the same type of ligands. The increasing order of the electron transfer is

LS -- LS > HS -- HS > LS -- HS .

Where, LS refer to Low Spin ligands,

HS refer to High Spin ligands.

If the electron transition is occurring from e_g to e_g in Oh field large change in bond length (M-L) has to occur in sigma type of orbital, therefore the electron transfer would be Slow. Also the steric hindrance due to ligand is there.

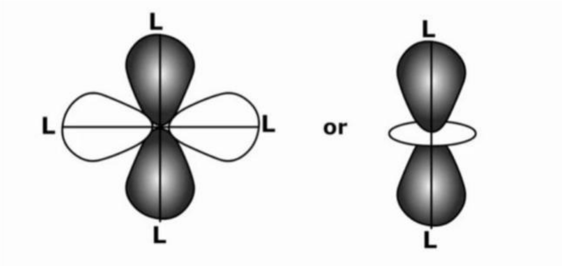


Fig. sigma type symmetry orbital $d_{x^2-y^2}$ *and* d_{z^2}

If the electron transition is occurring from t_{2g} to t_{2g} in Oh field t_{2g} is $\pi \rightarrow \pi^*$ transition occurs. So in t_{2g} to t_{2g} transition, only a small change in bond length. Thus 'Fast' electron transfer happens.

The increasing order of the electron transfer reaction

t_{2g} to t_{2g} > t_{2g} to e_g > e_g to e_g .

Marcus - Hush Theory :

Marcus Hush Theory (M-H Theory) was developed in 1956 by Rudolph A. Marcus which explains the fundamentals of the redox/ electron trasfer reaction in terms of the rate of moving electron from oxidant species (electron donor) to the reductant (electron acceptor). M-H Theory works as alternative Eyring's transition state theory for electron tranfer reactions where bond making or bond breaking does not occur.

The marcus Hush equation also known as the Marcus-DOS model, is a rate equation that describes the kinetics of electron tranfer reaction:

$$K_{12} = (K_{11}K_{22}K_{12}f)^{1/2}$$

It is the Marcus Hush equation and in this marcus related the cross reaction to the two self exchange reactions.

Where,

K_{12} = rate of the cross reaction

K_{11} & K_{22} = rate of the self exchange reaction

K_{12} = equilibrium constant of reaction

It does not have any unit

f = statistical & steric factor which is measure of correction of difference in free energy of the two reactants.

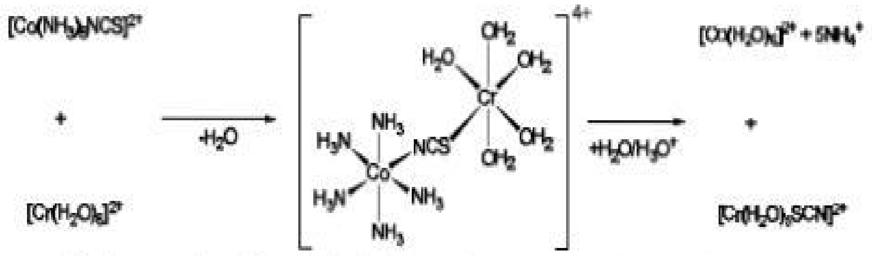
This value is nearly ≈ 1.

Inner Sphere Electron Transfer Reactions

Inner sphere electron transfer mechanism first suggested **Taube and co- workers**

- One of the reacting complex ion should be **inert** other ion should be **labile**
- **Reductant** will be labile **oxidant** will be inert
- There should be atleast one ligand (in one reactant) capable of binding simultaneously to two metal however transiently
- The attachment between O and R occurs **bridging ligand** (molecule atom or ion)
- In this mechanism, a ligand shared between the reductant and oxidant the inner (primary) **coordination sphere**
- The intermediate formed in the reaction is **binuclear**
- The rate – determining step is the **electron transfer** step and not the complex formation start .

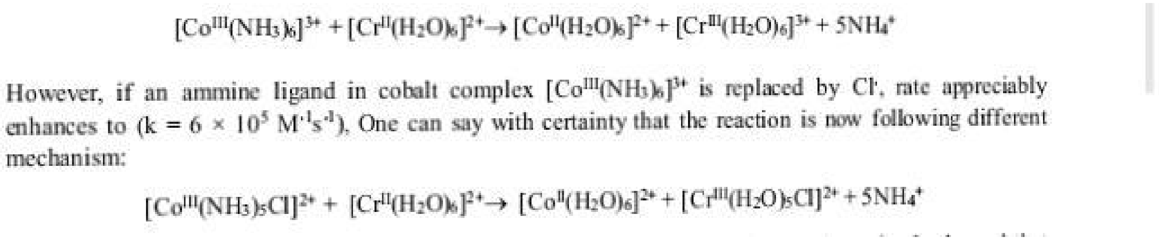
In this reaction there is a change in inner sphere of both the oxidant and reductant,if was examine reaction between [$Co(NH_3)_5NCS]^{2+}$ with $[Cr(H_2O_6]^2$ under **acidic condition**



The reaction is passes through intermediate bridged complex.the ligand NCS while linked to oxidant (co) concurrently established bond with the reductant (cr) metal center bridge the two metal.

Example:1

It is well known that reduction of [co(NH3)6]^3 with [cr(H20)6]^2+under **acedic condition** take place



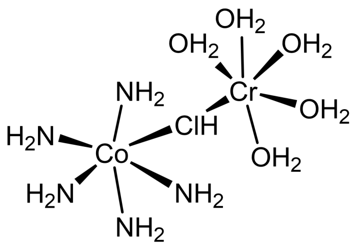
$$[Co^{III}(NH_3)_6]^{3+} + [Cr^{II}(H_2O)_6]^{2+} \rightarrow [Co^{II}(H_2O)_6]^{2+} + [Cr^{III}(H_2O)_6]^{3+} + 5NH_4^+$$

However, if an ammine ligand in cobalt complex $[Co^{III}(NH_3)_6]^{3+}$ is replaced by Cl^-, rate appreciably enhances to ($k = 6 \times 10^5$ $M^{-1}s^{-1}$). One can say with certainty that the reaction is now following different mechanism:

$$[Co^{III}(NH_3)_5Cl]^{2+} + [Cr^{II}(H_2O)_6]^{2+} \rightarrow [Co^{II}(H_2O)_6]^{2+} + [Cr^{III}(H_2O)_5Cl]^{2+} + 5NH_4^+$$

very slowly.

H **Taube** who was conferred on Nobel prize for his work on electron transfer reaction clearly showed that an inner sphere mechanism is operative in the reduction of [co(NH3)5cl]^{2}with [cr(H2o)6)2+,the cl ligand while still attached to co(III) replace an H2o at cr(II)to give an intermediate shown below and electron transfer follows



Mechanism of the inner sphere electron transfer mechanism:

The elementary steps involved in an inner sphere mechanism can be represented by:

The first step is the formation of precursor complex in this step the oxidant and reductant are brought close to each other via linkage by the bridged ligand so that electron transfer can take place

Ox- X + Red(H20)←→[Ox-X…Red]+H2

Second step involves **chemical activation, electron transfer and relaxation to the successor complex.**

In this step activation of the precursor complex occurs which is followed by electron transfer

[Ox-X...Red]←→[- Ox…X-Red+]

In the third step the **bridged species dissociation to separated product**

[- ox…X-Red+]+ H2O ←→ ox(H2O)-+RedX

It has been observed that such a reaction follows second order kineticsand for a reaction like the one

$$\mathrm{Ox\text{-}X + Red} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{[Ox\text{-}X\text{-}Red]} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{Ox^{\cdot} + RedX^{+}}$$

shown below

Rate of the reaction is given by the equation :

Rate=[k1 k3/ (k2+ k3).[Ox-X][Red]

Herek3 is overall rate constant for the second and third step.

It has been found that in some cases k3>>k2 and rate determining step is simply formation of the precursor complex.therefore,rate law reduce to Rate= k1[Ox-X[[Red].

However, there are many instances wherein rate determining step is rearrangement and electron transfer within the intermediate,or fission of the successor complex. This means that k3<k2 and the rate law becomes

Rate= Kk$_3$[Ox-X X][Red]

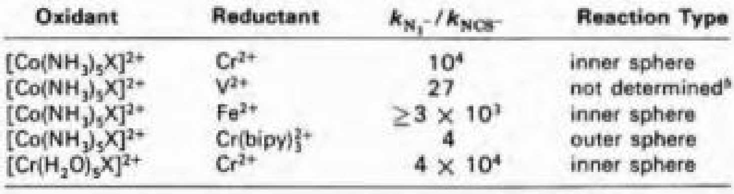
Nature of the Bridging Ligand in Inner Sphere Electron Transfer Reactions.

The nature of bridging ligand plays an important role in determining the rates of inner sphere electron transfer reactions. Haim recently pointed out, "The role of the bridging ligand [in an inner sphere mechanism] is ... dual. It brings the metal ions together (thermodynamic contribution) and mediates the transfer of the electron (kinetic contribution)." The thermodynamic contribution is related to the stability of the intermediate complex, and kinetic to factors such as oxidant-reductant reorganization and matching of donor and receptor molecular orbitals. As far as bridging ligands (BL) are concerned, both inorganic and organic ligands have extensively been utilized in the inner sphere electron transfer reactions. While studying electron transfer reactions one major problem is how to ascertain that reaction is following an inner or outer sphere mechanism? In this regard a simple test that can be applied in some of the cases is carrying out a reaction of the type:
utilizing the N_3 - or NCS- as bridge ligand X.

$$[Co^{III}(NH_3)_5X]^{2+} + [Cr^{II}(H_2O)_6]^{2+} \xrightarrow{H^+} [Co^{II}(H_2O)_6]^{2+} + [Cr^{III}(H_2O)_5X]^{2+} + 5NH^{4+}$$

For such a reaction the is $k^{os}_{N3-}/k^{os}_{NCS-} \approx 1$, while $k^{is}_{N3-}/k^{is}_{NCS-} >> 1$

It may be related to preferential formation of the intermediate in inner sphere mechanism by one bridging ligand or the other.

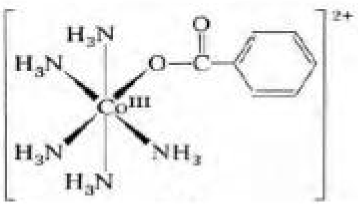


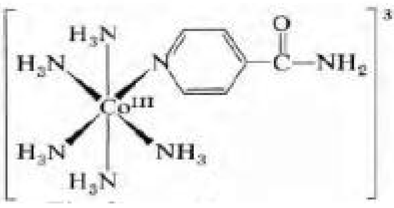
Oxidant	Reductant	$k_{N_3^-}/k_{NCS^-}$	Reaction Type
$[Co(NH_3)_5X]^{2+}$	Cr^{2+}	10^4	inner sphere
$[Co(NH_3)_5X]^{2+}$	V^{2+}	27	not determined[a]
$[Co(NH_3)_5X]^{2+}$	Fe^{2+}	$\geq 3 \times 10^3$	inner sphere
$[Co(NH_3)_5X]^{2+}$	$Cr(bipy)_3^{2+}$	4	outer sphere
$[Cr(H_2O)_5X]^{2+}$	Cr^{2+}	4×10^4	inner sphere

Table: Relative rates of reduction of azido and thiocyanato complexes

As NCS is an ambidentate ligand, it can form a bond with the metal centres through either end. When NCS^- is S-bound to a oxidant, $[Co(NH_3)_5SCN)]^{3+}$ nitrogen end of the ligand can be attacked by the reductant $[Cr(H_2O)6]$ 2+ and rate of this reaction is comparable to azide as the bridge (NCS- , $=1.9 \times 10^5\ M^{-1}s^{-1}$; N_3 - , $3.0 \times 10^5\ M^{-1}s^{-1}$). The bent S-bound thiocyanate can also be attacked by the reductant at sulphur atom directly bound to the oxidant metal ion because it possesses two lone pairs of electron. When attack occurs at S- bound to oxidant we call it adjacent and when remote N atom is attacked by the reductant we call it remote attack. Thus, both remote attack at nitrogen and adjacent at sulphur is possible, and notably, these occur at almost the same rates at least with $[Cr(H_2O)_6]^{2+}$ as the reducing agent.

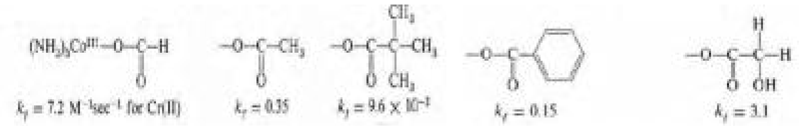
A lot of information has been acquired on inner sphere electron transfer reactions using organic bridging agents. It has been observed that rate of such reactions are controlled by: i) Bridge steric effects ii) the point of attack by reductant on the bridge, and ii) electronic structure of the bridge along with its reducibility. Most of such studies have been made on carboxylate complexes and amine complexes of the type:.



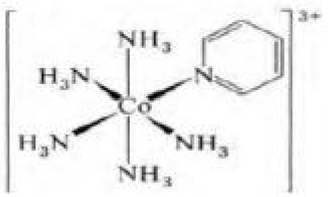


These follow second order kinetics and proposed mechanisms involve attack at a remote site rather than at the atom directly bonded to the oxidant metal center. The influence of steric crowing on rates of some reactions for $[Co^{III}(NH_3)_5X]^{2+}$ complexes as oxidant and $[Cr^{II}(H_2O)_6]$

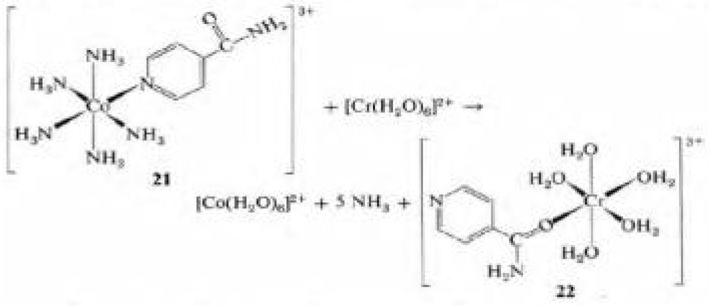
$^{2+}$ as reductant is shown below. In these reactions attack by the Cr(^{II}) ion occurs at the carbonyl oxygen of the carboxylate group. Notably, the rate constants for reduction by $[Cr(H_2O)_6]^{2+}$decreases with increasing steric bulk of the organic compounds.



Further, if another basic group is added on to the carboxylate moiety, chelation of the reductant [Cr(II) in this case] is possible, and the rate constant increases. Electron transfer is possible via attack at a site even more remote than the carboxylcarbonyl oxygen. It has been observed in the reactions of various Co(III) and Ru(III) complexes based on substituted pyridines. For example, $[CoIII(NH_3)_5(py)]^{2+}$ reacts relatively slowly with Cr(II)



(k = 4 × 10^{-3} $M^{-1}s^{-1}$) to give [Cr(H2O)6] 3+ by an outer sphere pathway. On the other hand, complex [CoIII(NH3)$_5$(isonicotinamide)]2+ reacts rather rapidly (k = 17.4 $M^{-1}s^{-1}$) with $[Cr(H_2O)_6]^{3+}$ to give 22 as the first Cr(III) product. This observation suggested that the attack of Cr(II) is at the remote carbonyl group in 21, not the -NR_2 group.



On the other hand, reductions of Co(III) and Cr(III) through simpler bridges such as Cl- occur by the concerted mechanism, because these species are not reducible. Thus, reductions through simple inorganic bridges are generally controlled by oxidant activation and the thermodynamics of the reaction

Photo-Redox Reactions in Complexes and their Applications

The photochemical cleavage of water into its elements has the distinction of being the most widely studied energy storage reaction. The reasons for this popularity are evident: the starting material is inexpensive, plentiful, and safe, and hydrogen is an attractive fuel. Since water does not absorb above 200 nm, however. some means of sensitizing. the reaction to solar radiation is required.

$$H_2O\,(l) \xrightarrow[\text{sensitizer}]{h\nu} H_2\,(g) + \tfrac{1}{2}O_2\,(g) \quad \text{———— (1)}$$

The basic strategy for sensitization that has evolved from the work of several investigators makes use of the excited state redox properties of transition metal complexes to effect the reduction (2) and oxidation (3) of water. The reduction potentials, E", for these half-cell reactions are -0.41 V and t0.82 V, respectively, at pH 7 and 760 torr pressure.

$$2e^- + 2H_2O = 2OH^- + H_2 \quad \text{----------- (2)}$$

$$2H_2O = 4H^+ + O_2 + 4e^- \quad \text{------------ (3)}$$

as the standard state for the gases. It should he noted that these processes involve multi electron changes. Here in lies a problem. Photo redox reactions of transition metal complexes generally occur with the transfer of only one electron per photon absorbed. Thus one is faced with the difficult task of driving two-electron (HZ production) and four-electron (02 ~reduction) reactions with one-electron redox processes in such a manner as 1,. avoid the formation of high energy radical intermediates. For example, any step in the production of H_2 that passes through the stage of the free hydrogen atom (a one-electron reduction product) pays an energy penalty of about 50 kcal. Consequently, another requirement for the efficient cleavage of water with reasonably low-energy photons is the presence of a charge-storage catalyst that mediates the multielectron changes that occur. In essence, the catalyst accumulates the proper number of electrons for delivery to the reactants and also stabilizes any intermediates formed. A few examples of photosensitizers and catalysts will now be considered.

One of the earliest reports of photochemical water splitting involved the photo redox reactions of cerium salts. Heidt and co-workers found that cerous perchlorate undergoes photooxidations in an acidic aqueous medium upon 254nm irradiation. The resulting ceric ion is capable of thermally or photochemically oxidising water.

$$Ce^{3+}\,(aq) + H^{+} \xrightarrow{h\nu} Ce^{4+}\,(aq) + \tfrac{1}{2}H_2 \quad \text{---------- (4)}$$

$$2Ce^{4+}\,(aq) + H_2O \xrightarrow{\Delta\ or\ h\nu} 2Ce^{3+}\,(aq) + 2H^{+} + \tfrac{1}{2}O_2 \quad \text{----------- (5)}$$

While interesting as a model, this system is of little practical value since, in addition to the high-energy radiation required, the quantum yield for reaction (4) is low and competitive absorption by Ce^{4+} occurs. Other aquated transition metal ions (e.g., Fe^{2+}, Mo_2^{3+}) that undergo photooxidation with production of H2 suffer similar problems.

Another approach to water splitting based upon photo redox chemistry is illustrated in Figure 1. Light initiates a bimolecular electron transfer reaction between an electron donor, D and acceptor A, resulting in the formation of the energy-rich species D^+ and A^-. The reducing power of A^- is then coupled to the reduction of H_2O (or H+) by a suitable catalyst, while the complementary process involving the catalysed oxidation of H_2O to O_2 is accomplished D^+.

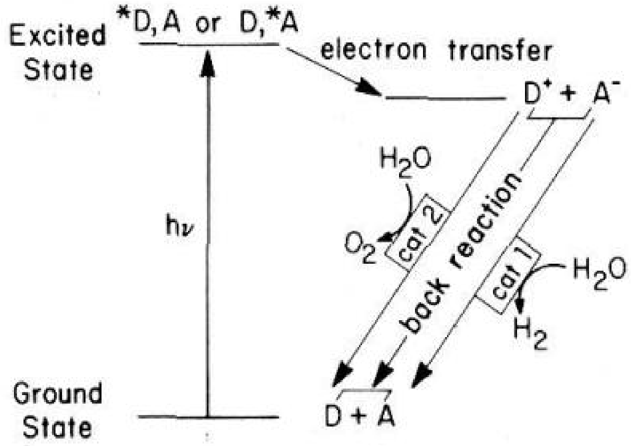


Figure 1

The principles light absorbing species, which can be either D or A, plays the role of a photosensitizer and must possess at least the following properties:

1) Appreciable light absorption in the solar energy wavelength region.

2) An excited state lifetime of sufficient length to allow bimolecular chemical reactions to compete with other deactivation processes.

3) Ability to undergo excited state electron transfer reactions with suitable quenchers.

4) Long-term stability under the photochemical reaction conditions.

The $Ru(bpy)_3^{2+}$ ion (bpy is 2,2'-bipyridine) satisfies these requirements and thus has enjoyed wide popularity as a sensitizer for photo redox reactions of the type shown in figure 1.

The complex displays an intense metal-to-ligand charge transfer absorption at 450 nm that extends well into the visible region. The state initially populated upon light absorption relaxes with near unit efficiency to the lowest excited state (hereafter designated as $*Ru(bpy)_3^{2+}$) which possesses a lifetime of 0.6 μs at 25'C in aqueous solution and an energy 2.1 eV above the ground state.

Both reductive quenching of * $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{+}$: and oxidative quenching to $Ru(bpy)_3^{3+}$ have been observed. Moreover, the coordinated 2,2'-bipyridyl ligands are inert to photo substitution in room temperature aqueous solution. The ground and excited state redox properties of $Ru(bpy)_3^{2+}$are summarized in Figure 2.

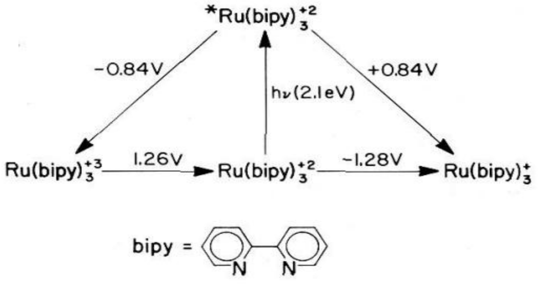


Figure 2

The formation of * $Ru(bpy)_3^{2+}$ it via light absorption can he likened to the creation of a separated electron-hole pair within the complex. As a consequence, * $Ru(bpy)_3^{2+}$ is expected to be both a stronger reductant and a stronger oxidant than the ground state by the excitation energy of 2.1 eV. Reductive quenching of * $Ru(bpy)_3^{2+}$ produces the powerful reductant, $Ru(bpy)_3^{+}$, while oxidative quenching generates the potent oxidant, $Ru(bpy)_3^{3+}$.

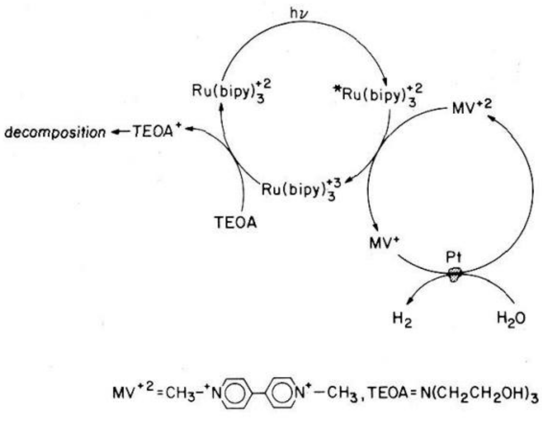


Figure 3: A system for the photochemical reduction of H_2O to H_2.

A prototype H_2 -evolving system is outlined in Figure 3. Light absorption by $Ru(bpy)_3^{2+}$ produces * $Ru(bpy)_3^{2+}$ it which then undergoes oxidative quenching by methyl viologen, MV^{2+}. The rapid back reaction between the photoproducts is hindered by reducing $*Ru(bpy)_3^{2+}$ hack to $Ru(bpy)_3^{2+}$ with the sacrificial reagent triethanolamine, TEOA. In the presence of colloidal platinum, the other photoproduct, MV^+, reduces H_2O to H_2 and is oxidized to the original dictation.

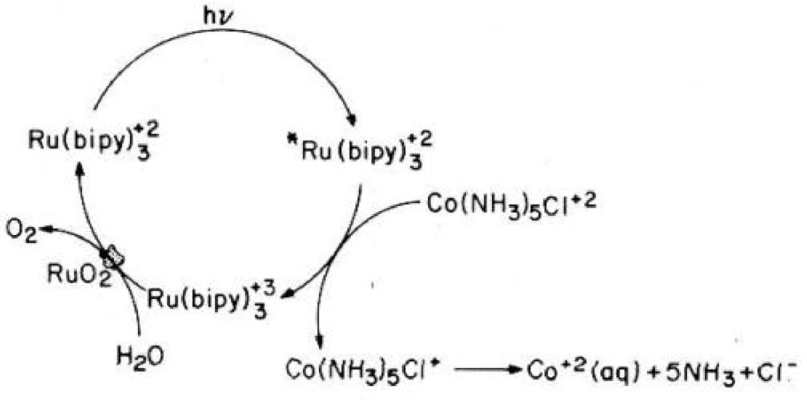


Figure 4: A system for the photochemical oxidation of H_2O to O_2.

The production of O_2 occurs in the system shown in Figure 4. Here the oxidative quenching of $*Ru(bpy)_3^{2+}$ by $Co(NH_3)_5Cl^{+2}$ generates $Ru(bpy)_3^{3+}$ and $Co(NH_3)_5C$\

l$^+$. The latter species decomposes rapidly and irreversibly to the weak reductant Co^{2+} (aq). The $Ru(bpy)_3^{3+}$ ion is a sufficiently strong oxidant (figure 1) to oxidize H_2O to O_2 in the presence of RuO_2 suspension.

Photo-Substitution Reactions in Complexes and their Applications

Photosubstitution reactions can be aquation, anation or ligand exchange.

I. Photoaquation reactions:

$$[Cr^{3+}L_6] \xrightarrow{h\nu} [Cr\,L_5(H_2O)]^{3+} + L$$

It involve heterolytic cleavage of Cr-L bond. For the specific case of Cr(III) complexes of O_h symmetry, efficient photochemical aquation reaction occurs when the $^4T_{2g}$ state lies significantly above the ^2E_g state. Efficiently decreases as the energy difference ΔE between these two states decreases. This happens for $[Cr(NH_3)_6]^{3+}$ on successive aquation. The system deviates from Oh symmetry and consequently Φ for aquation decreases from 0.3 for hexamine complex to less than 0.002 for $[Cr(NH_3)\ (H_2O)5]^{3+}$. Relative labilities of the ligand NH_3 and H_2O are reversed in the thermal and photochemical reactions.

$$[Cr(NH_3)_5(NCS)]^{2+} + H_2O \xrightarrow{hv} [Cr(NH_3)_5(H_2O)]^{3+} + NCS^-$$

$$[Cr(NH_3)_5(NCS)]^{2+} + H_2O \xrightarrow{hv} [Cr(NH_3)_4(NCS)]^{2+} + NH_3$$

Both 2t2g and 2eg states are photoactive. The ratio of Φ_{NH3}/Φ_{NCS-} is wavelength dependent, the ratio being 15 at 373nm (quartet band); 8 at 652nm (doublet band).

The photosensitization of this aquation can also be initiated by energy transfer from biacetyl and acridinium ion in the same solvent. The energy transfer reactions have helped to identifythe details of this aquation reaction:

(a) Biacetyl as sensitizer : phosphorescence quenched; fluorescence not affected, release of NH_3; No apparent degradation of biacetyl; $\Phi_{NH3}/\Phi_{NCS-} > 100$

(b) Acridinium ionas sensitizer : fluorescence quenched; both NH_3 and NCS^- released although NH_3 predominates; in presence of O_2, NCS^- release decreased, hence triplet stateof the sensitizer is involved; Φ_{NH3}/Φ_{NCS-}, 33 for quartet stat, 8 for doublet state.

Therefore it can beconcluded that NH_3 release occurs from $^4T_{2g}$ state and NCS^- from ^2E_g state.

$Co(NH_3)_6^{3+}$ is stable in aqueous solution whereas $[Co(NH_3)_2\ X]^{2+}$ undergoes moderately rapid substitution of water for the acid group X- , for example, nitrate:acetate is 103:1. The difference in behaviour between Cr(III) and Co(III) ammines may be due to necessity for energy of activation in the transition state for reaction with the later.

The photoaquation of $[K\ Cr(NH_3)_2\ (SCN)_4]$ (Reinnecke's salt) and $[Cr(urea)_6Cl_3]$ can be used as efficient actinometers between the range 316 and 750nm. For $[Co(CN)_6]^{3-}$ the photoreaction.

$$[Co\ (CN)_6]^{3-} \xrightarrow{hv} [Co(CN)_5(H_2O)]^{2-}$$

Photoanation Reaction :

Chromium(III) complexes also undergo photoanation reactions. When aqueous solutions of Cr(H2O)63+ are photolyzed in the wavelength range of 400-575nm in presence of Cl- or SCN- ion, replacement of a water molecule by the anionic ligand occurs:

$$[Cr\ (H_2O)_6]^{3+} + NCS- \xrightarrow{hv} [Co(CN)_5(H_2O)]^{2-}$$

$$[Cr\ (H_2O)_6]^{3+} + NCS- \xrightarrow{hv} [Co(CN)_5(H_2O)]^{2-}$$

The quantum yield are in the region of 10-4 for this photoanation reaction.

Photo-isomerisation Reactions in Complexes and their Applications

Photoisomerization:

Photoisomerization is the process through which a molecule or complex changes its isomeric form upon absorption of light. The isomers differ in the spatial arrangement of their atoms or groups. Many coordination complexes are photosensitive and reversible. For example, the complex of cis-bis(triphenylphosphine)platinum chloride is colourless while trans-bis(triphenylphosphine)platinum chloride is yellow in colour.

Photoisomerization of $PtCl_2(PPh_3)_2$

The process typically involves:

- Photon Absorption: The metal complex absorbs light, exciting an electron from a lower to a higher energy state.
- Formation of Excited State: The complex undergoes structural or electronic changes in the excited state.
- Isomerization: This excited state leads to a rearrangement of ligands or electronic configurations, resulting in a different isomer.
- Return to Ground State: The complex often returns to its ground state, retaining the new isomeric form.

In metal complexes, photoisomerization reactions generally fall into several distinct types based on the nature of the isomerization process and the structural changes involved. Here are the primary types:

Geometric Photoisomerization:

This type involves the rearrangement of ligands around the metal centre, leading to different spatial arrangements. Common forms include:

Cis-Trans Isomerization: Cis-trans photoisomerization is a type of geometrical isomerization where a molecule changes from a cis configuration (where substituents are adjacent) to a trans configuration (where substituents are opposite) upon exposure to light. This reaction is typically observed in octahedral or square planar complexes where the arrangement of ligands around the metal centre can be distinctly categorized as cis or trans.

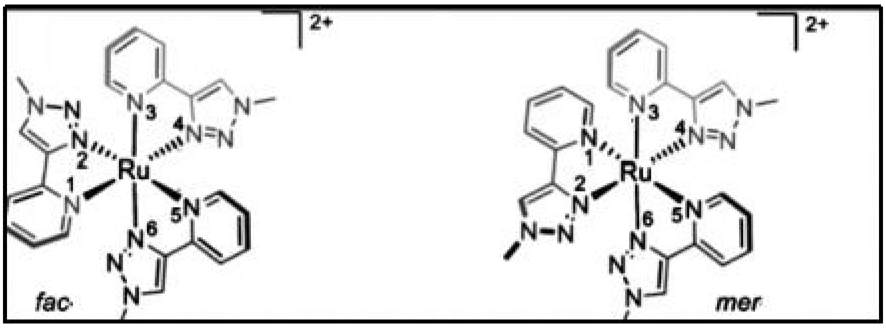
Example: cis-$[Ru(bpy)_2(OH)_2]^{2+}$ $\xleftrightarrow{h\upsilon}$ trans-$[Ru(bpy)_2(OH)_2]^{2+}$

Cis- $[Co(NH_3)_4Cl_2]^+$ $\xleftrightarrow{h\upsilon}$ trans- $[Co(NH_3)_4Cl_2]^+$

Fac-Mer Isomerization: The fac-mer photoisomerization reaction refers to the process by which a coordination complex undergoes a geometric change from a facial (fac) isomer to a meridional (mer) isomer, or vice versa, upon exposure to light. In the fac isomer, the ligands are positioned on the same face. In the mer isomer, the ligands are positioned along a meridian.

Example: mer- [Cr (III)(3,3'-dimethyl-1,1'-diaminopropane)$_3$] $\xleftrightarrow{h\upsilon}$ fac- [Cr (III)(3,3'-dimethyl-1,1'-diaminopropane)$_3$]

mer-$[Ru(pytz)_3]^{2+}$ $\xleftrightarrow{h\upsilon}$ fac-$[Ru(pytz)_3]^{2+}$



Electronic Photoisomerization:

Electronic photoisomerization reaction refers to a type of isomerization in which a molecule or complex undergoes a reversible change in its electronic configuration upon exposure to visible light. This reaction involves the transformation between electronic states as a result of photon absorption or illumination. This involves changes in the electronic configuration of the complex without significant changes in its geometric arrangement and changes in Spin State i.e., from high-spin to low-spin states and these are photosensitive spin crossover complexes.

Example: $[Fe(pyCH_2NH_2)_3]^{2+}$ (high spin) $\xleftrightarrow{h\upsilon}$ $[Fe(pyCH_2NH_2)_3]^{2+}$ (low spin)

Linkage Photoisomerization:

Linkage photoisomerization in coordination complexes refers to a photochemical reaction where a ligand within a metal complex undergoes a structural change upon absorbing light. This often involves the transformation of the ligand between different bonding states or isomeric forms.

An example of linkage photoisomerization is the photoisomerization of the $[Co(phen)_2(NO_2)]^{2+}$ complex. Here, phen refers to 1,10-phenanthroline, and the NO_2 ligand can switch between nitrito and nitro forms upon UV light exposure. It occurs through an intramolecular mechanism involving homolytic fission of $Co\text{-}NO_2$ bond and then recombination takes place.

Example: $[Co\ (NH_3)_5(NO_2)]^{2+} \xleftrightarrow{h\upsilon} [Co\ (NH_3)_5(ONO)]^{2+}$

$[Fe(bipy)_5(NO_2)]^{2+} \xleftrightarrow{h\upsilon} [Fe(bipy)_5(ONO)]^{2+}$

Applications:

Some key applications of photoisomerization reactions in metal complexes include:

- Molecular Switches: These complexes can act as switches that change states upon light exposure, useful in molecular electronics and smart materials.
- Catalysis: Photoisomerization can be employed to control catalytic activity. The ability to switch between isomers allows for modulation of the catalyst's function.
- Sensors: Photoisomerizable complexes can be used in sensors to detect light or other environmental changes by monitoring changes in their spectroscopic properties.
- Photodynamic Therapy: In medicinal chemistry, complexes that undergo photoisomerization can be used in targeted therapies where light triggers the release of therapeutic agents or active species.
- Optical Data Storage: The reversible nature of photoisomerization can be harnessed for storing data in optical media, where information is written and read using light.

Applications of Inorganic Photochemistry

Inorganic photochemistry is a field that explores the interactions of light with inorganic compounds, leading to various chemical transformations. These interactions are significant in a range of applications, from solar energy conversion to environmental cleanup. Photochemical reactions often offer a more sustainable and eco-friendly alternative to traditional chemical processes, especially when harnessed for energy conversion and pollution removal. This essay delves into some of the key applications of inorganic photochemistry, focusing on the photochemical conversion and storage of solar energy, the conversion of nitrogen to ammonia, and the use of titanium dioxide (TiO2) as a green photocatalyst in environmental remediation.

Photochemical Conversion and Storage of Solar Energy

Solar energy is one of the most abundant renewable energy sources available on Earth. However, its efficient conversion and storage pose significant scientific challenges. Photochemical processes are promising because they enable the direct conversion of solar energy into chemical energy, which can be stored and used on demand.

Photochemical energy storage often involves using light-absorbing inorganic complexes or materials that undergo chemical transformations when exposed to light. These transformations can generate high-energy products that store the absorbed energy as chemical potential. A major goal in this area is to achieve efficient photoinduced electron transfer, which is crucial for solar energy conversion. One of the widely studied materials in this regard is titanium dioxide (TiO2), which is used in dye-sensitized solar cells (DSSCs) due to its stability, low cost, and photocatalytic properties.

In photochemical water splitting, solar energy is used to split water molecules into hydrogen and oxygen. This process not only helps in storing energy in the form of hydrogen fuel but also addresses the need for clean energy. Catalysts based on transition metals such as ruthenium, iron, and cobalt complexes are often used to enhance the efficiency of these reactions. These complexes facilitate the transfer of electrons and aid in converting photon energy into chemical bonds, making them essential in photochemical applications for energy storage.

Photochemical Conversion of N_2 to NH_3

The photochemical conversion of nitrogen (N2) to ammonia (NH3) is an innovative approach to ammonia synthesis that mimics natural nitrogen fixation, which occurs in certain bacteria. Traditional methods of ammonia production, such as the Haber-Bosch process, are highly energy-intensive, requiring high temperatures and pressures. In contrast, a photochemical approach could enable the direct use of solar energy to drive the nitrogen fixation reaction under ambient conditions.

In photochemical nitrogen reduction, light-activated catalysts facilitate the activation and reduction of nitrogen molecules. Metal complexes, particularly those containing metals like iron and molybdenum, have shown promise in promoting the photochemical conversion of nitrogen to ammonia. By absorbing solar energy, these complexes can transfer electrons to nitrogen molecules, facilitating their reduction to ammonia. Recent research has also explored the use of semiconductor photocatalysts, which provide a surface for nitrogen fixation and can be activated under solar radiation. The development of efficient catalysts for this reaction remains a challenge, but progress in this area could lead to more sustainable methods of ammonia production.

TiO2 as a Green Photocatalyst in Removing Air and Water Pollutants

Titanium dioxide (TiO2) is one of the most widely studied and applied photocatalysts due to its efficiency, stability, and non-toxic nature. When exposed to ultraviolet (UV) light, TiO2 generates electron-hole pairs that can initiate oxidation-reduction reactions. These reactions make TiO2 highly effective in breaking down organic pollutants in both air and water.

In air purification, TiO2 photocatalysis can degrade volatile organic compounds (VOCs) and other air pollutants such as nitrogen oxides (NOx) and sulfur oxides (SOx). These pollutants are major contributors to urban air pollution and have adverse effects on human health. TiO2-based photocatalytic coatings are used in various applications, including self-cleaning surfaces and air-purifying filters, to improve indoor and outdoor air quality.

In water treatment, TiO2 can degrade organic contaminants, pathogens, and even some heavy metals under UV irradiation. The high oxidative potential of TiO2 allows it to decompose toxic compounds into harmless byproducts like carbon dioxide and water. This makes TiO2 an environmentally friendly solution for wastewater treatment, where conventional methods might fail to remove all pollutants effectively.

To enhance its applicability under visible light, modifications to TiO2, such as doping with non-metals or combining it with other semiconductors, have been explored. These modifications enable TiO2 to harness a broader spectrum of solar radiation, increasing its photocatalytic efficiency.