

1.3 Transition elements and coordination compounds

At a Glance to the Co-ordination Compounds

high-spin/ low-spin, Crystal field theory, weak-field ligand, strong-field ligand, spectrochemical series, crystal field stabilization energy (CFSE), pairing energy, Jahn–Teller distortion, π -donor ligand, π -acceptor ligand, 18-electron rule, ‘d–d’ transition, term symbol, Russell–Saunders coupling, Charge transfer absorption, MLCT, LMCT, selection rule:, Orgel diagram, Tanabe–Sugano diagram, Nephelauxetic effect, Magnetic susceptibility, Effective magnetic moment, Spin-only formula, spin–orbit coupling constant, Curie law, ferromagnetism, antiferromagnetism, ferrimagnetism etc.



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Key Statement

Basic Statement: Complex salt (1.3.4), Werner's Theory (1.3.5), Classification of ligands (1.3.8), IUPAC nomenclature of complex compounds (1.3.9), Chelate effect (1.3.15), Isomerism in complex compound (1.3.17), Ligand isomerism (1.3.20), Optical isomerism (1.3.33), Valence bond theory (VBT) (1.3.39), Factors affecting the magnitude of Δ_o (1.3.43), Spectrochemical series (1.3.44), High spin and low spin complexes (1.3.48), Jahn-Teller (J-T) theorem (1.3.51), Ligand field theory for octahedral complexes (1.3.60), MO diagram of octahedral complexes (ML_6) (1.3.61), MO diagram of tetrahedral complexes (ML_4) (1.3.62), Determination of the ground state term symbol of the metal ion by Hund's rule (1.3.81), Factors affecting the rates of direct electron transfer reactions (1.3.102)

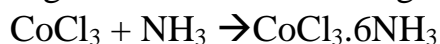
Standard Statement: Stability of the Complexes (1.3.11), Determination of stepwise stability constant and overall stability constant (1.3.13), Inner metallic complex (1.3.16), Ionisation isomerism (1.3.18), Linkage isomerism (1.3.21), Geometrical isomerism in square planar complexes (1.3.28), Optical isomerism in tetrahedral complexes (1.3.34), EAN rule (effective atomic number rule) (1.3.37), Crystal Field Stabilization Energy (CFSE) (1.3.49), Application of CFSE value (1.4.50), Condition for distortion (1.3.52), Orbital contribution (1.3.67), Selection rules (1.3.88), Ligands to metal charge transfer (LMCT) (1.3.94), Metal to ligand charge transfer (MLCT) (1.3.95), Electron transfer reaction in coordination compounds (1.3.100)

Advance Statement: Factors controlling the stability of complexes (1.3.12), Isomerism in octahedral complex (ML_6) (1.3.31), Optical isomerism in octahedral complexes (1.3.35), 18 electrons rule (1.3.38), Nephelauxetic effect (1.3.58), Curie equation (relationship between χ_M and μ) (1.3.77), Orgel diagram (1.3.89), Mechanism of one electron transfer reactions (1.3.101), Ligand substitution reactions in octahedral complexes (1.3.104)

Key Facts

1.3.1. If we the compounds available it may be in two types A. Compounds of first order for simple compound e.g., NaCl, NH₃, H₂O, CH₄ etc., B. Compounds of second order or addition compound.

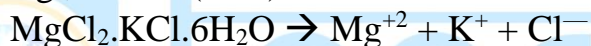
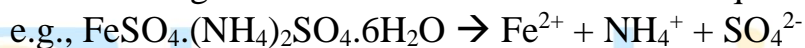
1.3.2. Addition compound: When two simple salts are mixing together in a same to molecular proportion a new crystals for called as addition compound.e.g.,



Again addition compounds are of two kinds A. Double Salt e.g., Mohr's salt, Allum etc., B. Complex Salt e.g., K₄[Fe(CN)₆], K₃[Fe(CN)₆], [Ni(CO)₄] etc.

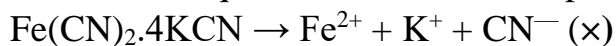
1.3.3. Double Salt: Addition compounds are those which lose their ideality in an aqueous solution.

Double salt gives all the constituents ion in an aqueous solution



That means if a chemically taste the constituents iron of double salts it will be positive.

1.3.4. Complex salt: Addition compound which retain their ideality in both solid and in aqueous state called complex salts.



Again complex salt are of two kinds according to their stability A. Perfect complex (whose stability is very high) B. Imperfect complex (whose stability is extremely low).

1.3.5. Werner's Theory:

A. Metal produces two types of balances, one is its primary valency or ionisable valency and another is called secondary valency or non ionisable valency.

B. Anion can satisfy only the primary valency but anion, neutral and cation (special case) satisfy the secondary valency.

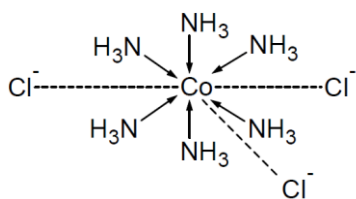
C. And can satisfy both the primary valency and secondary valency simultaneously, but the secondary valency is the predominant one.

D. The primary valency of metal indicates the oxidation state of the metal where the secondary valency indicates the coordination number of the metal.

E. The coordination number of metal is always fixed and there direct in a space in particular orientations i.e., C.N = 6 the structure is octahedral, and C.N = 4 the structure is tetrahedral.

Warner Structure:

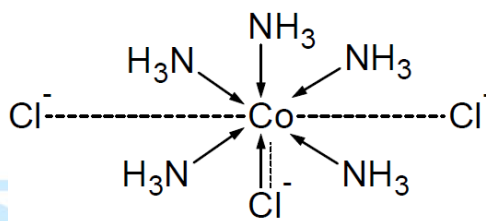
I. $\text{CoCl}_3 \cdot 6\text{NH}_3$:



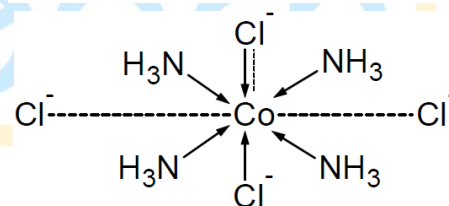
‘_____’: Secondary Valency

‘.....’: Primary Valency

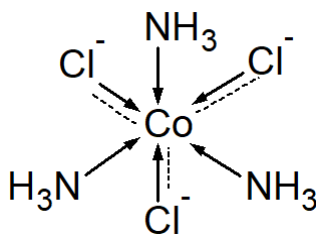
II. $\text{CoCl}_3 \cdot 5\text{NH}_3$:



III. $\text{CoCl}_3 \cdot 4\text{NH}_3$:

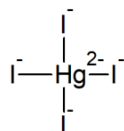


IV. $\text{CoCl}_3 \cdot 3\text{NH}_3$:



1.3.6. Drawback of

The primary valency and secondary valency are indistinguishable for many complexes.



Werner's Theory:

1.3.7. Modern Concept of writing of complex: Complex is always written in the third bracket.

e.g., $[\text{Ni}(\text{CO})_4]$, $\text{K}_4[\text{Fe}(\text{CN})_6]$

1.3.8. **Classification of ligands:** Ligands are classified according to the number of donor atom present in it.

A. **Monodentate ligand:** Ligand which has a only one donor atom/centre is called monodentate ligand. e.g., NH_3 / H_2O / CO / Cl^- etc.

B. **Bidentate ligand:** Ligands which have two donor atoms/centres are called bidentate ligand. e.g., 2,2-bipyridine(bpy), Ethylene diamine(en), Ethylene diphosphine (dipos), Propylene diamine (pn), Trimethylene diamine (tn), Butylene diamine (bn), Isobutylene dismine(i-bn), Tetramethyl ethylene diamine (tetrameen), O-phenanthroline or 1,10-phenanthroline(o-phen or phen), Acetylacetonato ion(acac⁻), Oxalato ion(ox²⁻), Benzoyl acetonato ion, Dimethyl glyoximato ion(DMG⁻), 8-hydroxyl quinolinato ion, Glycinato ion(gly⁻) etc.

C. **Tridentate ligand:** Diethyl triamine(dien), 2,2',2''-terpyridyl(terpy), Triaminopropane

D. **Tetradentate ligands:** Triethylene tetramine(trien), Triaminotriethylamine(tren).

E. **Pentadentate ligands:** Tetraethylene pentamine(tetraen), Ethylene diamine triacetate ion etc.

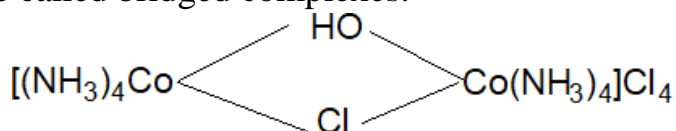
F. **Hexadentate ligand:** EDTA⁴⁻

G. **Ambidentate ligand:** Ligands which have different donor atom, but in forming complex, only one is attached with the metal atom is called ambidentate ligand. e.g., CN^-/NC^- , $\text{SCN}^-/\text{NCS}^-$, $\text{NO}_2^-/\text{ONO}^-$ etc.

H. **Flexidentate ligand:** Polydentate ligament may not use all the donor site in forming complex is called as flexidentate ligand. e.g., SO_4^{2-} , CO_3^{2-} etc.

I. **Bridging ligands and Bridged complexes:** When ligands are attached with two separate metals atoms, making a bridge between them. Such ligands are called bridging ligands and the complexes does formed are called bridged complexes.

e.g.,



1.3.9. IUPAC nomenclature of complex compounds:

Rules for naming of complex compound:

A. Cation named first followed by the anion indicate the oxidation number of the metal in the first bracket in Roman letter.

B. There is special ending for anionic complex the term '-ate' suffix is to be added up with the name of the metal.

Co- Cobaltate, Al- Aluminate, Cr- Chromate, Pd- Palladate, Hg- Murcurate, Au- Aurate, At- Argentate, Ni- Nickelate, Cu- Cuprate, Pt- Platinate, Fe- Ferrate, Mn- Manganate, BH_4^- -Borate etc.

C. There is a special ending for anionic ligand. The term '-O' suffix is to be added up with their name.

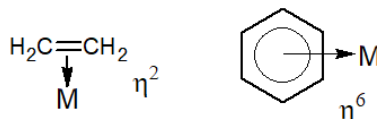
Cl^- - Chloro, OH^- - Hydroxo, SO_4^{2-} - Sulfato, NH_2^- - Amido, NH^{2-} - imido, ox^{2-} - oxalato, S^{2-} - sulfido, N_3^- - azido, N^{3-} - nitrido, gly- - glycinato, DMG- dimethylglyoxalato, CN^- - cyano, H^- - hydrido.

D. No special ending for neutral ligand. CO- carbonyl, H_2O - aqua, $\text{CH}_3\text{-NH}_2$ - methylamine, Py- pyridine.

E. There is a special ending for cationic ligand. The term '-ium' suffix is to be added up with the name. NO^+ - nitrosonium, H_3O^+ - hydronium.

F. When same ligand present more than one, the term prefix bi, tri, tetra, has to be consider but for few organic ligand the prefix bis, tris, tetrakis are added up. $(\text{H}_2\text{O})_5$ - pentaqua, $(\text{en})_2$ - bisethylenediamine.

G. For unsaturated ligand (C_2H_4 , C_6H_6) the term hapticity (η) is considered.



H. For 'bridged ligand' the term ' μ ' is considered.

1.3.10. Names:

❖ Cationic:

- $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ - Hexaamminecobalt(III)chloride.
- $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ - Pentaammineaquacobalt(III)chloride.

❖ Anionic:

- $\text{Li}[\text{AlH}_4]$ - Lithiumtetrahydridoaluminate(III).
- $\text{K}[\text{OsNCl}_5]$ - Potassiumpentachloronitridoosmate(VII).
- $\text{K}_3[\text{Fe}(\text{CN})_6]$ - Potassiumhexacyano-C-ferrate(III).

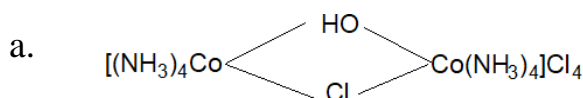
❖ Neutral:

- $[\text{Ni}(\text{CO})_4]$ - Tetracarbonylnickel(0)
- $[\text{Cr}(\text{C}_6\text{H}_6)_2]$ - Bis-(η^6 -benzene)chromate(0).

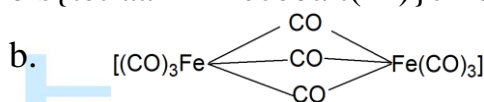
❖ Both cationic and anionic:

- $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]^-$
Tetraammineplatinum(II)tetrachloroplatinate(II).
- $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]^-$
Hexaamminecobalt(III)hexacyanochromate(III).

❖ Bridge complex:

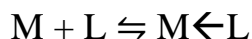


$\approx [\{\text{Co}(\text{NH}_3)_4\}_2(\mu\text{-OH})(\mu\text{-Cl})]\text{Cl}_4$ - μ -hydroxo- μ -chloro-bis{tetraamminecobalt(III)}chloride



$\approx [\{\text{Fe}(\text{CO})_3\}_2(\mu\text{-CO})_3]$ - Tri- μ -carbonylbis-{tricarbonyliron(0)}.

1.3.11. Stability of the Complexes:



The stability term in complexes coming two ways, 'thermodynamically stable' or 'kinetically stable'. Actually the complex is kinetically labile or inert whereas in thermodynamics sense the complex may be stable or unstable.

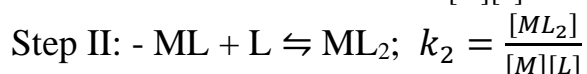
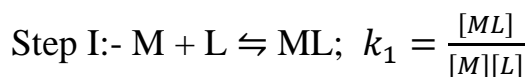
1.3.12. Factors controlling the stability of complexes:

- Nature of the metal ion: A metal whose ionic potential (Φ) is high, forms better complex than other.
Thus $\text{Li}^+ < \text{Be}^{+2} < \text{Al}^{+3}$ etc.
- Nature of the ligand: Generally a good Lewis base behaves as a good ligand. Polydentate ligands are much better than monodentate (chelate effect).
Bulky ligand forms less stable complexes due to steric effect.

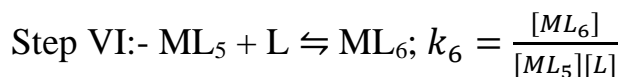
C. Nature of the solvent: A solvent with low dielectric constant is it better than others. Solvent having no donor atoms is better otherwise solvent will make Complex with the metal instead of ligand.

D. Effect of pH: A solution with low pH i.e., high concentration of H^+ iron is not favoured because ligaments are protonated easily and behave as a poor ligand.

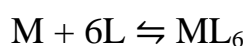
1.3.13. Determination of stepwise stability constant and overall stability constant:



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The overall stability constant for the reaction



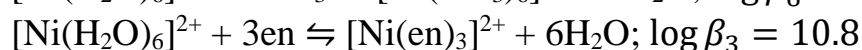
$\beta_6 = \frac{[ML_6]}{[M][L]^6}$

1.3.14. Relation between k_6 and β_6 :

$\beta_6 = \frac{[ML_6]}{[M][L]^6} = \frac{[ML_6]}{[ML_5][L]} \times \frac{[ML_5]}{[ML_4][L]} \times \dots \times \frac{[ML]}{[M][L]}$

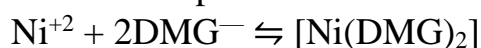
$\beta_6 = k_1 \times k_2 \times \dots \times k_6$

1.3.15. Chelate effect: Polydentate ligand form stable cyclic structure with the metal ion which are called chelate. Always chelate complexes are more stable than the non-chelate.



1.3.16. Inner metallic complex:

Few ligands mainly polydentate ligand simultaneously both the primary valency (oxidation state of the metal) as well as the secondary valency (co-ordination number of the metal) completely. So these are neutral and insoluble in polar solvent called as inner metallic complex.



1.3.17. Isomerism in complex compound:

If molecular formula be same and due to structural difference the molecules are said to be isomer and the phenomena is called isomerism. Incomplete isomerism may be classified as follows:

- i. Constitutional isomerism:
 - a) Ionisation isomerism
 - b) Hydrate isomerism
 - c) Ligand isomerism
 - d) Linkage isomerism
 - e) Coordination isomerism
 - f) Coordination position isomerism
- ii. Polytopal isomerism.
- iii. Spin state isomerism.
- iv. Stereoisomerism:
 1. Geometrical isomerism.
 2. Optical isomerism.

1.3.18. **Ionisation isomerism:** Two compounds having same molecular formula but gives different ions in aqueous solution called ionisation isomers and the phenomena is called ionisation isomerism.

Example, $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$

A and B a pair of constitution isomer

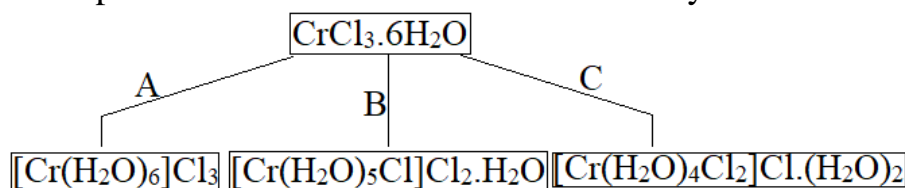
A=>on treatment with barium chloride gives white precipitate but no such a effect is found when treating with silver nitrate.

B=> on treatment with barium chloride gives no precipitate wild with silver nitrate gives white precipitate.

Thus by using the method that two isomers can be distinguished. Again by measuring the conductivity we can distinguish the compounds.

1.3.19. **Hydrate isomerism:** Compounds having the same molecular formula but the deposition of water is different called as hydrate isomers.

Example:



A => on treated with silver nitrate gives three moles of AgCl. On heating up to 100°C no water has been released that means it is tightly bounded.

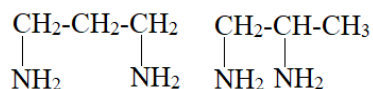
B => on treated with silver nitrate gives two moles of AgCl. On heating it easily lose water within 100°C . That means water is loosely bound.

C =>on treated with silver nitrate gives one mole of AgCl.

10 by using the above methods the complex isomers can be distinguished.

1.3.20. Ligand isomerism:

If ligands are isomers to each other when they form complexes always form a ligand isomer.



There is no chemical method to separate these two isomers only using spectroscopic method we can separate or distinguish them.

1.3.21. Linkage isomerism:

This is found only in case of ambidentate ligand i.e., metal to ligand donor atom is different. When such type of ligand form complexes these are called linkage isomers and the phenomena is called linkage isomerism.

Example, $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{+2}$ and $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{+2}$

These two isomers can be separated by using IR spectroscopy.

1.3.22. Coordination isomerism:

When both cation and anion form a complex the metal can exchange their position and form new isomer called coordination isomerism.

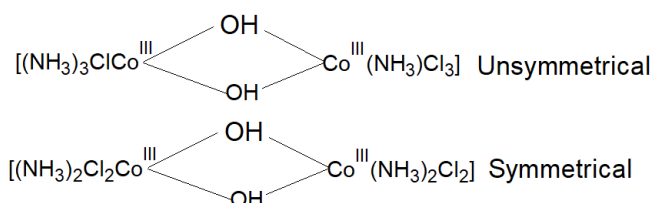
Example: $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

Here, A and B are coordination isomerism which can be distinguished by electrolysis.

1.3.23. Coordination position isomerism:

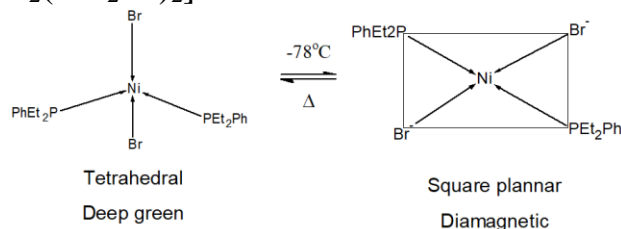
In a polynuclear complex ligand can exchange their position and form a new isomer called coordination position isomers.

Example:

**1.3.24. Polytopal isomerism:**

Compounds exhibits different magnetism at a different temperature due to the structural change called as polytopal isomerism.

Example: $[\text{NiBr}_2(\text{PEt}_2\text{Ph})_2]$



1.3.25. Spin state isomerism:

Compound which exhibit different magnetism at a different temperature due to the different number of unpaired electrons called spin state isomerism.

1.3.26. Stereoisomerism

Same molecular formula but the different arrangement in space called stereoisomerism.

1.3.27. Geometrical isomerism or *cis-trans* isomerism:

Complex type	Structure	No. Of geometrical isomer
ML ₂	Linear	-no-
ML ₃	Trigonal	-no-
ML ₄	Tetrahedral	-no-
ML ₄	Square planar	Two isomer; <i>cis</i> and <i>trans</i>
ML ₆	Octahedral	Have a geo-isomer

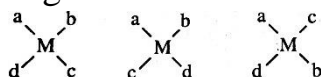
1.3.28. Geometrical isomerism in square planar complexes:

[Ma₄] → no geometrical isomers

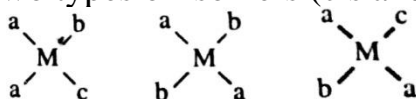
[Ma₃b] → no geometrical isomer

[Ma₂b₂] → two geometrical isomers; *cis* () and *trans* ()

[Mabcd] → three geometrical isomers



[Ma₂bc] → Two types of isomers (*cis* and *trans*)



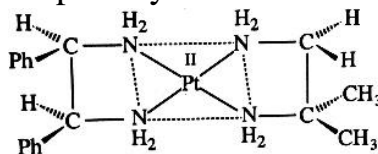
[M(AB)₂] → Two types of isomers (*cis* and *trans*)

Bridged binuclear square planar complexes of [M₂a₂b₄] → Three isomers (*cis*, *trans*, unsymmetric)

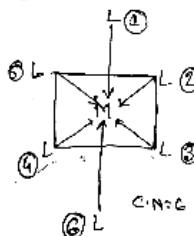
1.3.29. Optical isomer in Ma₄:

All square planar complexes are achiral (optically inactive) due to the presence of molecular plane of symmetry (σ).

Exception: In 1935, Mills and Quibell first prepared a square planar Complex which was optically active.



1.3.30. Octahedral complex $[ML_6]$:



Position: (1,6), (2,4), (3,5) all are trans position and rest are cis position.

1.3.31. Isomerism in octahedral complex (ML_6) :

- $Ma_6 \Rightarrow$ no geometrical isomer
- $Ma_5b \Rightarrow$ no geometrical isomer
- $Ma_4b_2 \Rightarrow$ two geometrical isomer
- $Ma_4bc \rightarrow$ Two geometrical isomers (cis and trans)
- Example: $[Co^{III}(NH_3)_4(H_2O)Cl]^{2+}$
- $Ma_3b_3 \rightarrow$ Two geometrical isomer.

The ligands of one type may form an equilateral triangle on one of the faces called as facial isomer. In the other isomer the ligands of one type occupy the positions such that two are opposite to each other, called meridional isomer.

Example: $[Cr(NH_3)_3Cl_3]$, $[Co(NH_3)_3(NO_2)_3]$, $[Cr(H_2O)_3F_3]$, $[Cr(NH_3)_3Cl_3]$, $[Rh(py)_3Cl_3]$, $[Ru(H_2O)_3Cl_3]$, $[Ir(H_2O)_3Cl_3]$, $[Pt(NH_3)_3Br_3]^+$, $[Pt(NH_3)_3I_3]^+$ etc.

- $Ma_2b_4 \rightarrow$ Two geometrical isomer.
- $Ma_2b_2c_2 \rightarrow$ Five geometrical isomer.
- Example: $[Pt^{IV}(NH_3)_2(py)_2Cl_2]^{2+}$
- $[M(AA)_2a_2] \rightarrow$ Two geometrical isomers (cis and trans)
- Example: $[Co(en)_2Cl_2]^+$, $[Co(en)_2(NH_3)_2]^{3+}$, $[Co(en)_2(NO_3)_2]^+$, $[Cr(en)_2Cl_2]^+$, $[Cr(C_2O_4)_2(H_2O)_2]^-$, $[Ir^{IV}(C_2O_4)_2Cl_2]^{2-}$ etc.
- $M(AA)_3 \rightarrow$ No geometrical isomer. All are cis, but chiral (OA).
- $M(AA)_2B_2 \rightarrow$ Two geometrical isomer.
- $[M(AA)_2ab] \rightarrow$ Two geometrical isomers (cis and trans)
- Example: $[Ru^{III}(C_2O_4)_2(py)(NO_2)]^{2-}$

- $[M(AA)_2b_2] \rightarrow$ Two geometrical isomers (cis and trans)
Example: $[Co^{III}(en)(NH_3)_2Cl_2]^+$, $[Co^{III}(C_2O_4)(NH_3)_2(NO_2)_2]^-$
- $M(AB)_3 \rightarrow$ Two geometrical isomer.
Example: $[Cr^{III}(gly)_3]$
- $Mabcdef \rightarrow$ 15 geometrical isomer. All are optically active.
Example: $[Pt(py)(NH_3)(NO_2)(Cl)(Br)(I)]$
- $[M(AB)_3]^{n\pm} \rightarrow$ show fac-meridional isomers.
Example: $[Co(gly)_3]$
- $[M(AB)_2a_2]^{n\pm} \rightarrow$ Five geometrical isomers.
Example: $[Co(gly)_2Cl_2]^-$
- Octahedral complexes containing optically active bidentate ligands \rightarrow Three geometrical isomers.
Example: $[Co^{III}(en)(pn)(NO_2)_2]^+$ ion forms two cis and one trans isomer.

1.3.32. **Distinguish between cis and trans isomers:** Following methods may be used to distinguish between cis and trans isomers.

- Dipole moment measurements.
- Infrared spectroscopy technique.
- Grinberg's method.

1.3.33. **Optical isomerism:** When the plane of a complex rotate in plane polarised light is called its optical activity and the complex possessing this property is said to be optically active. Optically active complexes are exist in two forms.

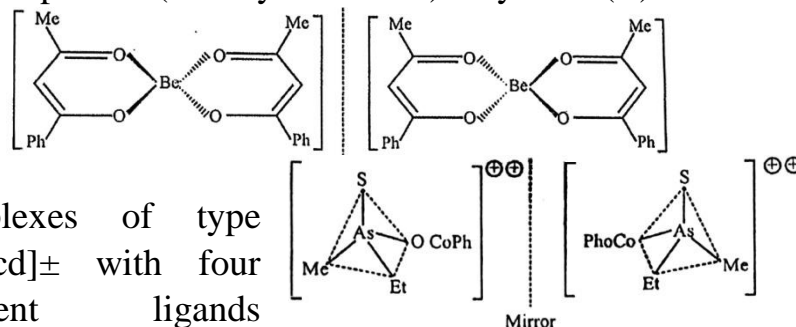
- One which rotates the plane of polarised light towards right is said to be dextro-rotatory or d-form(+).
- One which rotates the plane of polarised light towards left is called levo rotatory or l-form(-).

Condition for a molecule to show optical isomerism:

- The molecules which has a plane of symmetry are always optically inactive while those having no plane of symmetry are optically active and show optical isomerism.

1.3.34. Optical isomerism in tetrahedral complexes

- The complex bis(benzoylacetonato) beryllium (II) has been resolved



- Complexes of type $[Mabcd]^\pm$ with four different ligands exhibit optical isomerism. e.g.,

1.3.35. Optical isomerism in octahedral complexes:

- $[Ma_4b_2] \rightarrow$ They are optically inactive due to presence of symmetry and do not show optical isomerism.
- $[Ma_3b_3] \rightarrow$ The facial and meridional are optically inactive and hence do not show optical isomerism.
- $[Ma_2b_2c_2] \rightarrow$ Cis-isomer exists into optical isomers which are mirror image to each other. Trans-form is symmetrical and hence is optically inactive form.
- $[M(AA)_3] \rightarrow$ Due to absence of a plane or centre of symmetry, the octahedral complexes of this type are resolvable into dextro and levo forms.
- $[Mabcdef] \rightarrow$ They exist in 15 geometrical forms and each of which is optically active. Hence they exist in 30 stereoisomers.
- $[M(AA)_2a_2] \rightarrow$ The cis isomer does not have any plane or centre of symmetry and hence is optically active. On the other hand the trans isomer has a plane of symmetry and hence is optically inactive. Thus they have 3 optical isomers.
- $[M(AA)_2ab] \rightarrow$ The cis isomer have no centre of symmetry and thus optically active. The trans isomer contain plane of symmetry and hence optically inactive.

- $[M(AA)_2b_2] \rightarrow$ Cis isomer is optically active and hence gives optically active d- and l- forms. Trans isomer is optically inactive and hence does not give any optically active isomer.
- $[M(AB)_3] \rightarrow$ An octahedral complex of this type exists in cis and trans isomers. Each of these forms is optically active and hence it gives a pair of optical isomers.
- $[M(AA)_2(BB)] \rightarrow$ They exist in enantiomeric pair.
- $[M(AA)_2AB] \rightarrow$ They exist in enantiomeric pair.

1.3.36. **Nature of bonding in complex compounds:** different theories are used to explain the nature of metal-ligand bonding in a complex.

- Electronic theory of valency or EAN rule or 18 electron rule.
- Valence bond theory (VBT).
- Crystal field theory (CFT).
- Ligand field theory (LFT).

1.3.37. **EAN rule(effective atomic number rule):**

Sidgwick proposed EAN rule to determine the molecular formula of the complex. According to EAN rule, “a metal ion in a particular oxidation State will combine exactly that number of ligands, after gaining one electron pair from each ligand the total number of electron on metal is the nearest noble gas elements”.

e.g., for 3d series Elements the EAN is 36 (atomic number of Kr).

For 4d series Elements the EAN is 54 (atomic number of Xe).

For 5d series Elements the EAN is 86 (atomic number of Rn).

Limitation:

- This rule only determines the molecular formula but cannot predict the structure of the complex.
- $[Co(NH_3)_6]^{2+}$, $[Fe(CN)_6]^{3-}$ are stable although violets EAN rule.

Example:

- $[Co(NH_3)_6]^{3+}$ is a stable complex.
Electrons for $Co^{3+} = 24$
Electrons for $6NH_3 = 12$
Total electrons = 36 (EAN of Kr)
- The EAN rule is strictly valid for metal carbonyl compounds, e.g., Cr form $[Cr(CO)_6]$ where as Fe form $[Fe(CO)_5]$ and Ni form $[Ni(CO)_4]$.

- $[\text{Mn}(\text{CO})_5]$ does not exist but $[\text{Mn}_2(\text{CO})_{10}]$ is stable.

$[\text{Mn}(\text{CO})_5]$: Electron for Mn = 25

Electron for 5CO = 10

Total electrons = 35(unstable)

$[\text{Mn}_2(\text{CO})_{10}]$: Electros for Mn= 25

Electrons for 5CO = 10

Electron for one Mn-Mn bond = 1

Total electrons = 36(stable).

1.3.38. **18 electrons rule:** A metal ion contains 9 valence shell orbitals [(n-1)d, ns, np]. During formation of complex all valence shell orbitals are filled up by electrons i.e., required 18 electrons for closed shell configuration.

- 18 electron rule is only applicable for transition metal organometallic compound.
- The main group organometallic compound follow octet rule.
- Square planar complex follows 16 electron rule.
- The complexes which follow 16 and 18 electron rule are stable.
- Complex which follow 17 and 19 electron rule are paramagnetic.
- Complex which follows 17 electron rule is strong oxidizing agent.
- Complex which follows 19 electron rule is strong reducing agent.
- Rh(I), Pd(II), Pt(II), Au(III) form stable square planar complex which follow the 16 electron rule.

Example: $[\text{Ni}(\text{CO})_4]$:

Valence shell electron for Ni = 10

Electrons for 4CO = 8

Total electrons = 18

1.3.39. Valence bond theory (VBT):

Postulates of VBT:

- A metal atom ionization its appropriate oxidation State.
- In presence of various ligand field the inner metal d orbital electrons are rearranged and produce different number of unpaired electron.
- Hybrid metal orbitals overlap with the ligand orbitals containing a pair of lone pair.
- According to Pauling legends may be classified into two classes.

Strong ligands: CO, CN⁻ etc.

Weak ligands: F⁻, Cl⁻, Br⁻, H₂O etc.

Table: Hybrid orbitals for common co-ordination geometry

CN	Hybridisation	Orbitals involved	Bond angle(s)	Shape	Examples
2	sp	s and p _x	180°	Linear	[Ag(NH ₃) ₂] ⁺
3	sp ²	s, p _x and p _y	120°	Triangular planar	BCl ₃
4	sp ³	s, p _x , p _y and p _z	109°28'	Tetrahedral	CoCl ₄ ²⁻
4	d ³ s	s, d _{xy} , d _{yz} , d _{zx}	109°28'	Tetrahedral	MnO ₄ ⁻
4	dsp ²	s, p _x , p _y , d _{x²-y²}	90°	Square planar	[Ni(CN) ₄] ²⁻
	or sp ² d	s, p _x , p _y , d _{x²-y²}	90°	Square planar	[Cu(NH ₃) ₄] ²⁺
5	dsp ³	s, p _x , p _y , p _z , d _{z²}	90°, 120°	Trigonal pyramidal	Fe(CO) ₅
5	dsp ³	s, p _x , p _y , p _z , d _{x²-y²}	>90°, <90°	Square pyramidal	[Ni(CN) ₅] ³⁻
6	d ² sp ³	s, p _x , p _y , p _z , d _{x²-y²} , d _{z²}	90°, 90°	Inner orbital octahedral	[Fe(CN) ₆] ⁴⁻
6	sp ³ d ²	s, p _x , p _y , p _z , d _{x²-y²} , d _{z²}	90°, 90°	Outer orbital octahedral	[CoF ₆] ⁴⁻

*Actually VBT is totally based on magnetic orientation. Different state hybridization produce different number of unpaired electron of the metal i.e., gives different magnetic moment (μ)

$$\mu = \sqrt{n(n+2)} \text{ BM,}$$

When $n=0$, $\mu=0$, diamagnetic

When $n \neq 0$, $\mu \neq 0$, paramagnetic

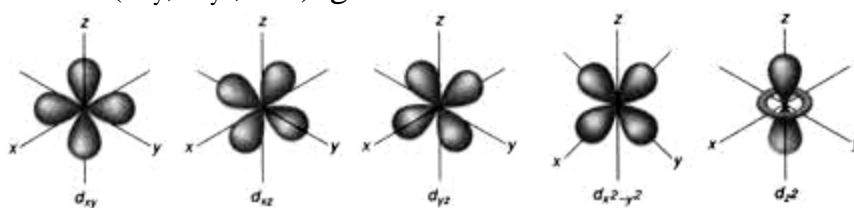
Limitation:

- This theory predicts the structure of the complexes, unable to explain the other properties like colour and spectra of the complexes.
- Although the VBT predict the approx magnetic moment, but actual magnetic moment cannot be explained by VBT or temperature dependent paramagnetism.
- Metal ion having a d^1 , d^2 , d^3 or d^9 system have a same number of unpaired electrons in presence of strong field or weak field. So these complexes either inner orbital or outer orbital cannot be predicted by VBT.

1.3.40. **Crystal field theory (CFT)** :H Bethe and Van Vleck proposed crystal field theory by considering the following features:

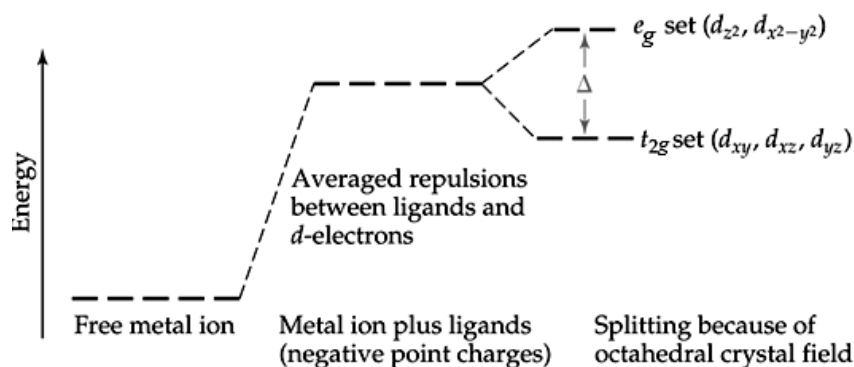
- Anionic ligand consider as point negative and neutral ligand considered as a point dipole where the negative pole is closer to the central ion.
- The nature of metal-ligand bonding is purely ionic i.e., 100% ionic in nature, there is no co-valency.
- In presence of various ligand fields metal d-orbitals loss their degeneracy and undergo splitting and produce new sets of d-orbitals.

Octahedral field: In an octahedral field, ligand approaches along the axis. So that two metal d orbitals ($d_{x^2-y^2}$, d_{z^2}) feel more repulsive force compared to the other three d orbitals (d_{xy} , d_{yz} , d_{xz}). The two orbitals ($d_{x^2-y^2}$) feel repulsive force as the lobes are directed along the axes. Since ligand also approaches along the axes, there is a electron-electron repulsion. The other three orbitals (d_{xy} , d_{yz} , d_{xz}) gets stabilization as the lobes are directed

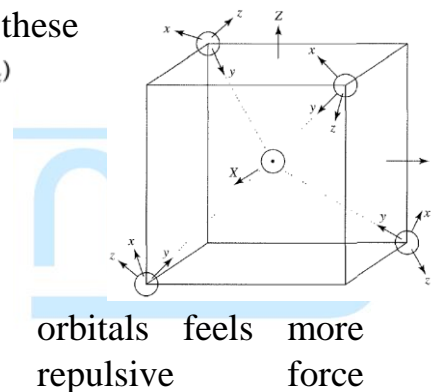
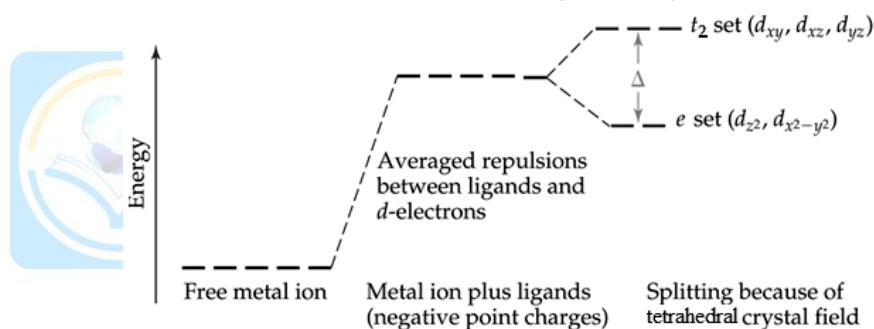


The shape of d orbital

between the axes.



Tetrahedral field: Here ligand approaches alternative corner of cube where metal is situated at the centre of a cube. The splitting of d orbital is just opposite to the octahedral field. Two orbitals ($d_{x^2-y^2}$, d_{z^2}) feel attractive force whereas other orbitals (d_{xy} , d_{yz} , d_{xz}) feel repulsive forces. Here three d orbitals (d_{xy} , d_{yz} , d_{xz}) are much closer to the ligand orbitals (difference of the bond angle only 90°). So these



compare to the other two ($d_{x^2-y^2}$, d_{z^2}).

1.3.41. Relationship between Δ_o and Δ_t :

$$\Delta_t = \frac{4}{9} \Delta_o$$

The magnitude of the Δ_o and Δ_t because of the following factors:-

- The higher number of ligands always feels repulsive forces.
- There is a direct repulsion for octahedral field (bond angle gap = 0°) but not for tetrahedral field (bond angle gap = 9°). Again $\frac{2}{3}$ rd force is lowered for tetrahedral field compare two octahedral field.

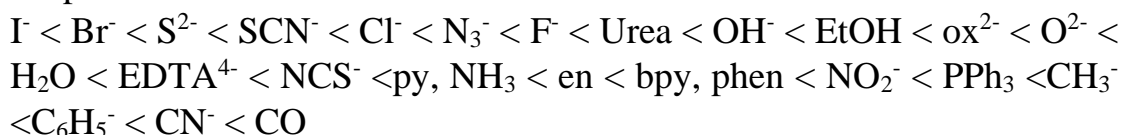
1.3.42. **The condition for the formation of tetrahedral complexes:** The CFSE value and bond energy data always favour the formation of octahedral complexes, but many complexes are tetrahedral. The following factors favour the formation of tetrahedral complexes:-

- Largest size ligands.
- Smaller size metal ion.
- High charge of ligand (anion).
- Low charge of the metal ion.

1.3.43. **Factors affecting the magnitude of Δ_o :**

- Higher the oxidation state of Central metal cation, having same number of d electrons, higher will be the value of Δ_o . The cations which have the higher oxidation State has larger value of Δ_o . For 3d series metal cation the value of Δ_o for M^{3+} complexes are roughly 50% larger than the values of M^{2+} complexes.
- Δ_o value decreases with increase in the number of d electrons.
- Δ_o for 5d > Δ_o for 4d > Δ_o for 3d
- Δ_o is high for stronger ligands and low for weaker ligands.
- In mixed ligand complexes the extent of splitting depends on the weighted average of the strength of various ligands.

1.3.44. **Spectrochemical series:** It is the order of splitting power of ligands to split the metal d orbitals.



1.3.45. **Jorgensen series:** $Mn^{2+} < Ni^{2+} < Co^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < Co^{3+} < Mn^{4+} < Mo^{3+} < Rh^{3+} < Pd^{4+} < Pt^{4+}$

1.3.46. **Mean pairing energy (PE):** It is the energy which is required to pair two electrons against electron- electron repulsion in the same orbital. PE is the pairing energy for one electron pair. It is generally expressed in cm^{-1} . Pairing energy depends on the principle energy level of d electrons.

1.3.47. **Calculation of total pairing energy of d^x ion:** If m is the total number of paired electrons in t_{2g} and e_g orbitals in d^x ion and PE is the pairing energy for one electron, then

$$\text{Total pairing energy for m electron pairs} = mPE \text{ cm}^{-1}$$

1.3.48. High spin and low spin complexes: The octahedral complexes of weak field ligand of d^4 , d^5 , d^6 and d^7 metal cations having the most unpaired electrons are called high spin (Hsp) complexes.

The octahedral complexes of strong field ligands, the energy gap Δ_o is greater than the energy required to pair electrons in the same orbital and the t_{2g} level is filled as far as possible. These complexes have lesser number of unpaired electrons or no unpaired electron. So these complexes are called low spin (Lsp) complexes.

- If $\Delta_o = PE$, the low spin and high spin complexes have equal energies.
- If $\Delta_o > PE$, electrons tend to pair and complexes are low spin complexes.
- If $\Delta_o < PE$, electrons tend to remain unpaired and hence complexes are high spin complexes.

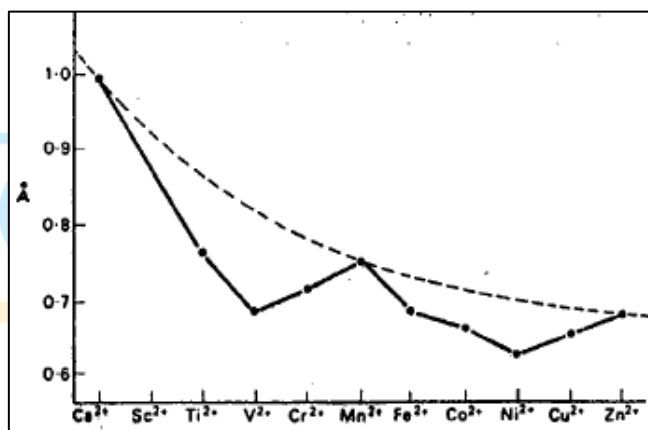
1.3.49. Crystal Field Stabilization Energy (CFSE): The CFSE may be defined as, the net energy of a complex which stabilized the complex relative to the hypothetical energy state. In the octahedral complexes, the d orbital of the central metal cation are split into two sets of different energy level (t_{2g} is used for lower energy and e_g is used for higher energy). The difference in energy between these two sets is Δ_o or Dq . The energy of t_{2g} set is lowered by $4Dq$ and the energy of e_g set is increased by $6Dq$ relative to the hypothetical energy state.

	High spin		Low spin	
d^1	$t_{2g}^1 e_g^0$	$0.4 \Delta_o$	$t_{2g}^1 e_g^0$	$0.4 \Delta_o$
d^2	$t_{2g}^2 e_g^0$	$0.8 \Delta_o$	$t_{2g}^2 e_g^0$	$0.8 \Delta_o$
d^3	$t_{2g}^3 e_g^0$	$1.2 \Delta_o$	$t_{2g}^3 e_g^0$	$1.2 \Delta_o$
d^4	$t_{2g}^3 e_g^1$	$0.6 \Delta_o$	$t_{2g}^4 e_g^0$	$1.6 \Delta_o$
d^5	$t_{2g}^3 e_g^2$	$0.0 \Delta_o$	$t_{2g}^5 e_g^0$	$2.0 \Delta_o$
d^6	$t_{2g}^4 e_g^2$	$0.4 \Delta_o$	$t_{2g}^6 e_g^0$	$2.4 \Delta_o$
d^7	$t_{2g}^5 e_g^2$	$0.8 \Delta_o$	$t_{2g}^6 e_g^1$	$1.8 \Delta_o$
d^8	$t_{2g}^6 e_g^2$	$1.2 \Delta_o$	$t_{2g}^6 e_g^2$	$1.2 \Delta_o$
d^9	$t_{2g}^6 e_g^3$	$0.6 \Delta_o$	$t_{2g}^6 e_g^3$	$0.6 \Delta_o$
d^{10}	$t_{2g}^6 e_g^4$	$0.0 \Delta_o$	$t_{2g}^6 e_g^4$	$0.0 \Delta_o$

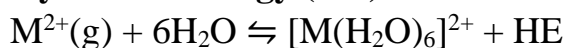
1.3.50. Application of CFSE value:

- Variation of ionic radii of transition metal ion in an aqueous solution:** In the gaseous state the radius of metal ion decreases with increasing nuclear charge, but in the aqua solution there is an irregular decrease because of their different CFSE value. Generally metal ions form octahedral hydrated complex $[M(H_2O)_6]^{2+}$. Here H_2O is a weak field ligand and prefers high spin complex. For d^1, d^2, d^3 the electron goes to the t_{2g} level, where lobes are directed between the axes. So, there is no direct repulsion but for d^4 and d^5 system, the electron goes to e_g level ($t_{2g}^3 e_g^1$ or $t_{2g}^3 e_g^2$) i.e., there is a direct repulsion when an electron is present in the e_g level. Here the metal ligand bond length increases as well as the radius of the metal ion also increases. Systems like d^0, d^5, d^{10} having no CFSE, these are placed in a straight line curve.

Curve:



- Hydration energy (HE) of transition metal ion :**



The amount of energy released when one mole of gaseous metal ion dissolves completely in water is called its hydration energy. Hydration energy depends on its ionic charge density i.e., the ratio of the cationic charges and its radius.

HE \propto cationic charge density \propto cationic charge/cationic radius.

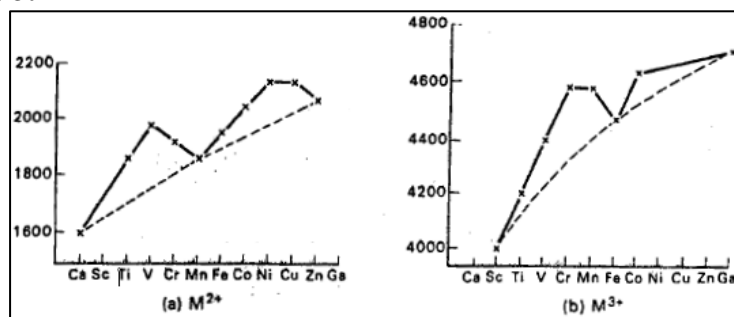
The HE of $[V(H_2O)_6]^{2+}$ is the highest one because of its highest CFSE value.

$$CFSE = (\Delta H_{exp} - \Delta H_{cal}).$$

Curve:

(U)

of



• Lattice energy of divalent chemicals transition metal ion

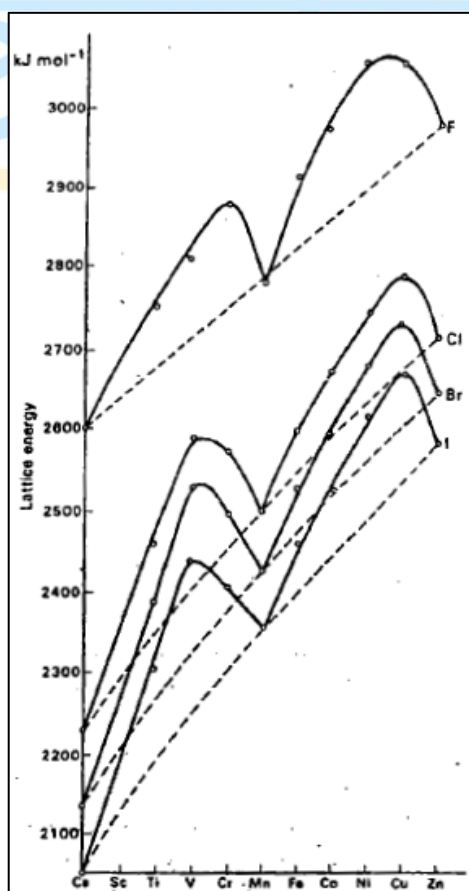
(MCl_2):

$U \propto z_+ z_-$

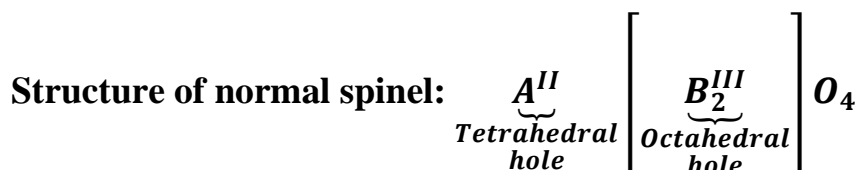
$U \propto 1/r$

The experimental lattice energy increases with increase in CFSE and decrease in size of cations. Since CFSE for V^{2+} (d^3) and Ni^{2+} (d^8) is maximum, show the lattice energy for this is maximum and shown Maxima in the curve.

Curve:

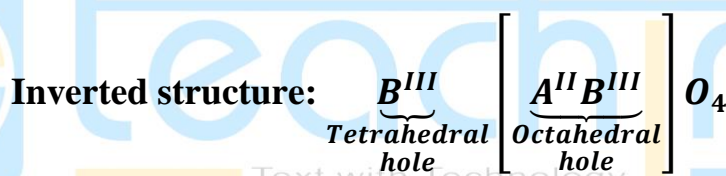


- Structure of spinel compounds:** The mixed oxides having a general formula $A[B_2]O$ is called **Spinel** where A is the divalent metal ion and B is the trivalent metal ion. Generally spinels are solid, so they have a close packing structure and creates two different types of holes i.e. tetrahedral hole (CN = 4) and octahedral hole (CN = 6). For normal spinel the trivalent metal ion (B^{3+}) always placed into the octahedral hole whereas divalent metal (A^{2+}) always placed into the tetrahedral hole.



Example: $MgAl_2O_4$, $MgCr_2O_4$, $NiCr_2O_4$, Co_3O_4 etc.

Structure of inverted spinel: In many cases half of the trivalent metal ion (B^{3+}) is replaced by the divalent metal ion (A^{2+}) and produce Inverted spinel structure.



Example: Fe_3O_4 , $CrFe_2O_4$, $NiFe_2O_4$, $MgFe_2O_4$. Calculation of CFSE of different metal ion (A^{2+}/B^{3+}) give the correct prediction of the structure of the spinel.

Note:

A^{2+} containing d^0 , d^5 , d^{10} having no CFSE always placed into the tetrahedral hole i.e., always forms normal spinel.

B^{3+} contains d^0 , d^5 , d^{10} electrons having no CFSE in the octahedral field, whereas divalent cation having some CFSE. So there is a chance to form inverted spinel.

- **Stereochemistry of complexes:** CFSE value predict why Cu^{2+} ion forms square planar complexes rather than tetrahedral or octahedral complexes in both the fields, as Cu^{2+} ion has a much higher CFSE value in a square planar configuration than in octahedral or tetrahedral configuration.

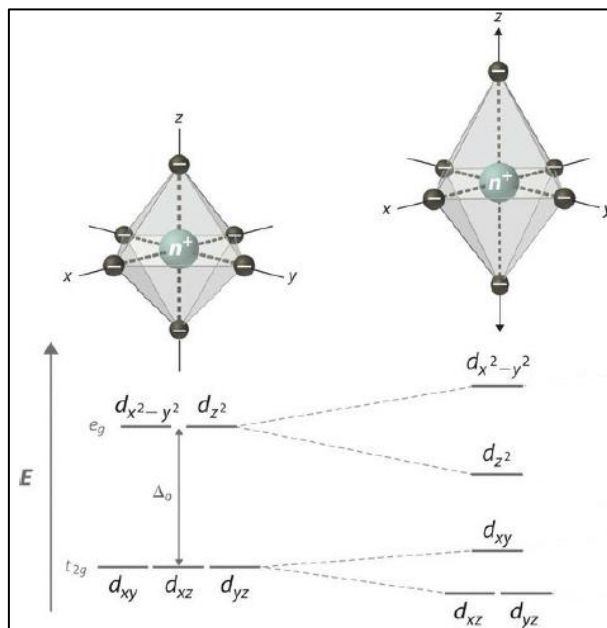
Most of the four coordinated complexes of Ni^{2+} ion are square planar rather than tetrahedral $[\text{NiX}_4]^{2-}$ is an exception, $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$.

- **Stabilization of oxidation state of metal ion:** CFSE value explains why certain oxidation states are preferential stabilized by coordination with certain ligands. The following two examples are discussed below:-

a) Although H_2O is a weak ligand should be expected to co-ordinate with Co^{2+} and Co^{3+} ions to form the high spin octahedral complexes such as $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ respectively. But experiments show that H_2O stabilizes Co^{2+} ion and not Co^{3+} . Thus $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is more stable than $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$. This is due to the fact that $\text{Co}^{2+}(\text{d}^7)$ has higher value of CFSE in weak octahedral configuration than $\text{Co}^{3+}(\text{d}^6)$ be in the same configuration.

b) If we consider the coordination of NH_3 molecules with Co^{2+} and Co^{3+} ions, it may be seen that, NH_3 is a strong ligand stabilizes Co^{3+} ion by forming $[\text{Co}(\text{NH}_3)_6]^{3+}$ rather than Co^{2+} ion. This is due to the fact that Co^{3+} spin (d^6) has much higher value of CFSE in strong octahedral configuration than Co^{2+} ion (d^7) in the same configuration.

1.3.51. **Jahn-Teller(J-T) theorem:** “Any non-linear molecule (octahedral) in a degenerate electronic state will be on stable and undergo splitting to lower the symmetry, energy and they remove the degeneracy also”.



1.3.52. **Condition for distortion:** When t_{2g} and e_g orbitals are unequally filled up there is a distortion i.e., if t_{2g} and e_g orbitals both are equally filled up or symmetrically filled up there is no distortion.

No distortion condition: $t_{2g}^0 e_g^0 / t_{2g}^3 e_g^0 / t_{2g}^3 e_g^2 / t_{2g}^6 e_g^0$ (Lsp) / $t_{2g}^6 e_g^4$

Weak distortion condition: t_{2g} sets of orbitals are unequally but e_g orbitals are equally filled up.

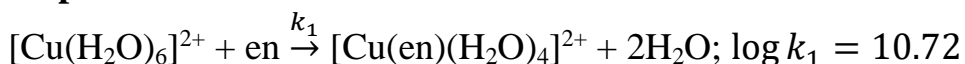
$d^1(t_{2g}^1 e_g^0) / d^2(t_{2g}^3 e_g^0) / d^4(t_{2g}^4 e_g^0)$ Lsp / $d^5(t_{2g}^5 e_g^0)$ Lsp / $d^6(t_{2g}^4 e_g^2)$ Hsp / $d^7(t_{2g}^5 e_g^2)$ Hsp.

Strong distortion condition: Here e_g shapes of orbitals are unequally filled up and t_{2g} orbitals are equally or unequally that does not affect at all in the distortion.

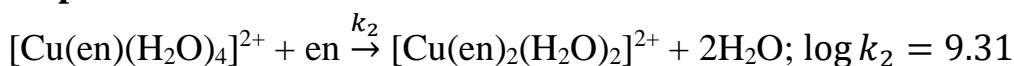
$d^4(t_{2g}^3 e_g^1)$ Hsp / $d^7(t_{2g}^6 e_g^1)$ Lsp / $d^8(t_{2g}^6 e_g^2)(d_{z^2}, d_{x^2-y^2})$

1.3.53. **Experimental evidence in favour of distortion:**

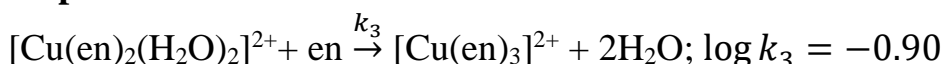
Step I:



Step II:



Step III:



1.3.54. Why the stability constant order $K_1 > K_2 > K_3$?

- Coulombic attractive force decreases gradually with increasing the coordination number of the complexes.
- Statistical factors: When successive ligand comes to form a complex, the rate always decreases because the active site decreases.

1.3.55. Type of distortion:

- Static distortion (measurable distortion)
- Dynamic distortion (non measurable distortion)

Static distortion: At all condition i.e., low temperature, high temperature the distortion is found. Then the distortion is called as static distortion. (Unsymmetrical e_g orbitals).

Dynamic distortion: At low-temperature the complex is distorted but at high temperature the complex is undistorted then it is called as dynamic distortion (unsymmetrical t_{2g} orbitals, perfect octahedral).

1.3.56. Note:

- All d^1 system have tetragonal compressed structure.
- All d^2 system have tetragonal elongated structure.
- Most of the complexes in which e_g orbitals are unsymmetrical field has tetragonal Z-out structure.
- High spin d^6 system has Z-in structure.
- $d^4(\text{Hsp}) \rightarrow \text{Z-out}$
- $d^4(\text{Lsp}) \rightarrow \text{Z-in}$

1.3.57. Limitation of crystal field theory:

- This theory consider the metal- ligand bonding is purely ionic (100% ionic), there is no co-valency in the metal- ligand Bond. Actually this is nothing but over stabilization.
- This theory gives too much important to the metal d -orbitals only, ignore the effect of the other valence orbitals s and p type.
- Why the enemy ligands (OH^- , F^- , Cl^-) are placed in the bottom end (weak field) of the spectrochemical series, there is no proper justification.
- CFT fails to explain charge transfer spectra of the complexes.
- CFT cannot explain the properties of the complexes where π Bond present along with σ Bond (π acid complex).
- CFT cannot explain Nephelauxetic effect.

1.3.58. **Nephelauxetic effect:** The electron-electron repulsion is more in the atomic orbitals (smaller size). When metal form complex, the electron-electron repulsion decreases due to the increase of the size of molecular orbitals which is called as Nephelauxetic effect. This effect gives direct proof for covalent character.

1.3.59. **Ligand field theory:** The electrostatic crystal field theory and the molecular orbital theory where combined into a more complete theory called ligand field theory.

1.3.60. **Ligand field theory for octahedral complexes:** Molecular orbitals are formed by the linear combinations of metal and ligand atomic orbitals having the same symmetry. The linear combinations of ligand orbital or ligand group orbitals (LGO's) with the metal orbitals along the octahedral axes. Thus legend orbitals overlap with those metal orbitals which lie on the axes. The ligand orbitals must match the symmetries of metal orbitals which are available for bonding. The central metal cation contains ns, np and (n-1)d orbitals. These orbitals are divided by O_h (octahedral symmetry) into four sets.

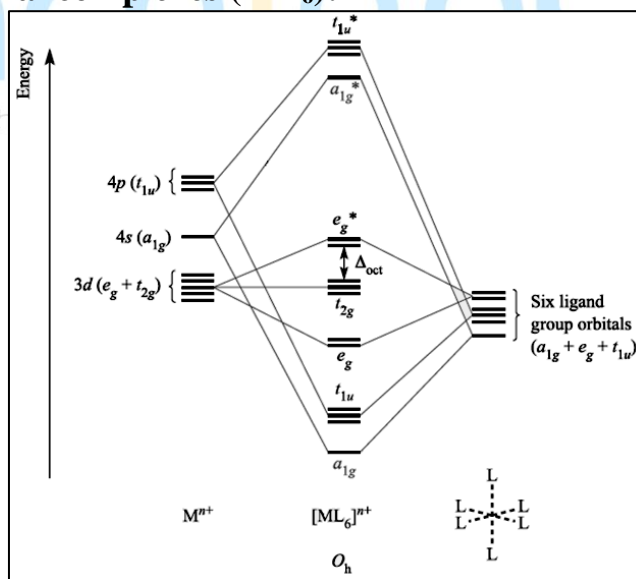
1.3.61. **MO diagram of octahedral complexes (ML_6):**

Valence shell: (n-1)d, ns, np

Symmetry: $t_{2g} + e_g, a_{1g}, t_{1u}$

σ symmetry: $e_g + a_{1g} + t_{1u}$

π symmetry: t_{2g}

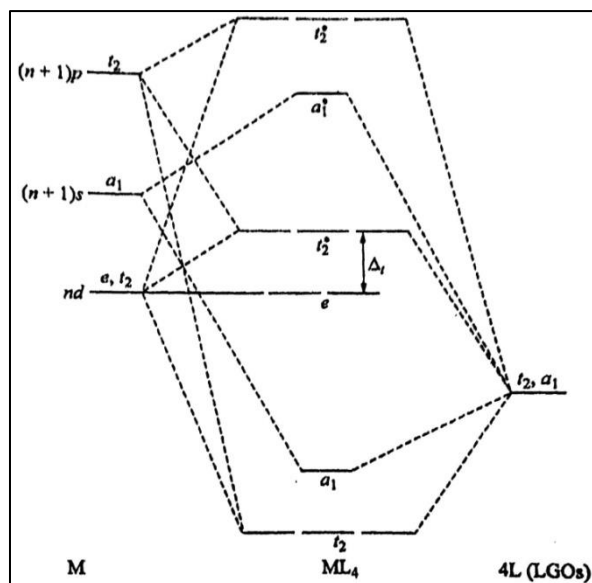


1.3.62. **MO diagram of tetrahedral complexes (ML_4):**

Valence shell: (n-1)d, ns, np

σ symmetry: $t_2 + a_1$

π symmetry: e



1.3.63. **NH₃ is a stronger ligand field than H₂O:** Here NH₃ is only a σ donor i.e., presence of one lone pair there is no scope to form a π bond along with its sigma bond. But in H₂O, the central O contains two lone pairs i.e., H₂O is a σ donor as well as π donor ligand, which reduces the Δ_o values and holds the bottom end in the spectrochemical series.

1.3.64. **OH⁻ is a weaker ligand field than H₂O:** Here OH⁻ is a better π donor (higher electron density) compared to the H₂O. So it decreases the Δ_o value more due to the formation of π bond.

1.3.65. **Magnetic properties:** Paramagnetism arises due to the presence of unpaired electrons in the species (molecule, atom, ion). Due to the motion of electrons in its own axis, some spin is developed. The resultant spin angular momentum (μ) is determined quantitatively by

$$\mu_s = 2\sqrt{s(s+1)}\text{BM}$$

$$\text{Actually } \mu_s = g\sqrt{s(s+1)}\text{ BM,}$$

Where g is Gyromagnetic ratio = $2.00129 \approx 2$

S = resultant spin angular momentum.

$S = \frac{1}{2} \times n$, n is the number of unpaired electron.

1.3.66. Magnetic substances:

- Diamagnetic ($\mu = 0$, $n = 0$)
- Paramagnetic ($\mu \neq 0$, $n \neq 0$)
 - i) Ferromagnetic ($\mu \gg 1$)
 - ii) Antiferromagnetic

$$\text{Spin only value } \mu_s = 2\sqrt{s(s+1)}$$

$$\mu_{\text{experimental}} \gg \mu_s$$

1.3.67. Orbital contribution: Electrons are placed in a specific orbital.

When degenerate orbitals are equally filled up, then orbital momentum is developed because electron can transfer from one orbital to the other orbital very easily by simple rotation. In the free metal ion the d_{xy} and $d_{x^2-y^2}$ orbitals, one can transform to the other by simple rotation 45° around the Z-axis. But in a complex, the metal d-orbitals lost their degeneracy i.e., d_{xy} and $d_{x^2-y^2}$ lie in a different plane. Show the orbital momentum is quenched in complexes.

In spite of that the two degenerate orbital like d_{yz} and d_{zx} may transfer one to other by rotation of 90° through Z-axis.

In octahedral complex d_{yz} and d_{z^2} form t_{2g} set and for tetrahedral these are t_2 set.

When t_{2g} sets of orbital is unequally filled up, some orbital momentum is developed.

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)} \text{ BM}$$

$$\mu_{\text{exp}} = \mu_{S+L}$$

When $\mu_L = 0$ (no orbital contribution)

$$\text{Then, } \mu_{S+L} = \sqrt{4S(S+1)} \text{ BM i.e., } \mu_{\text{eff}} = \mu_s$$

Orbital contribution present in the following electronic configuration:

$d^1(t_{2g}^1 e_g^0)$ / $d^2(t_{2g}^2 e_g^0)$ / $d^4(t_{2g}^4 e_g^0)$ Lsp / $d^5(t_{2g}^5 e_g^0)$ Lsp / $d^6(t_{2g}^4 e_g^2)$ Hsp / $d^7(t_{2g}^5 e_g^2)$ Hsp

Mathematical expression: $\mu_{eff} = \mu_s \left(1 - \frac{\alpha\lambda}{\Delta}\right)$

μ_s = Spin only magnetic moment.

α = constant where value depends on the spectroscopy term symbol of the metal ion.

$$\begin{aligned}\alpha &= 0 \rightarrow d^0, d^5, d^{10} \\ &= 2 \rightarrow d^1, d^4, d^6, d^9 \\ &= 4 \rightarrow d^2, d^3, d^7, d^8\end{aligned}$$

λ = Spin orbital coupling constant whose value is positive for less than half filled but it is negative for more than half filled.

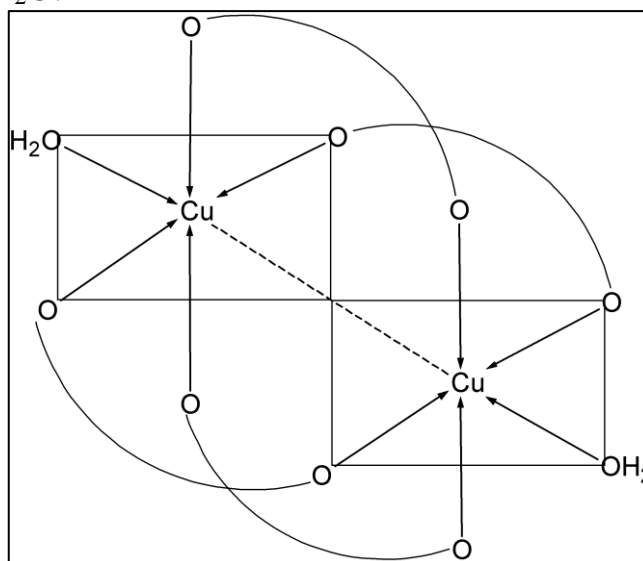
Δ_o = CFSE in octahedral field

1.3.68. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is a paramagnetic as H_2O is a weak field ligand and $\Delta_o < \text{PE}$. But $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic as CN^- is a strong field ligand. So $n = 0$ and $\mu = 0$. Thus $\Delta_o > \text{PE}$.

1.3.69. $\text{K}_3[\text{CoF}_6]$ is paramagnetic but $\text{K}_2[\text{NiF}_6]$ is diamagnetic. Although F^- is a weak field ligand but the oxidation state of the metal ion is too large. Show the Δ_o value is high and overcome the PE ($\Delta_o > \text{PE}$) i.e., low spin arrangement is the favourable one.

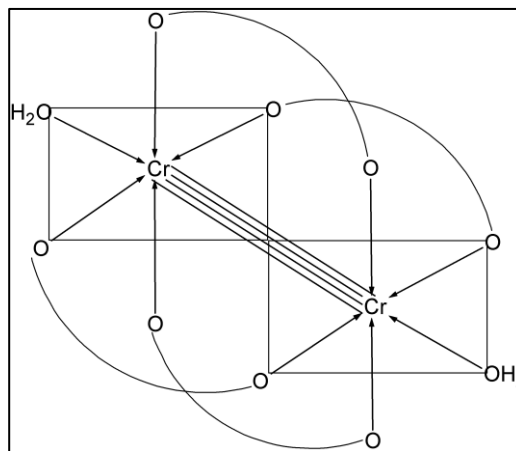
1.3.70. **Dimerization of $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$:** The driving force for dimerization is to their suitable coordination number of each metal ion. In the dimeric structure the odd electron of each metal composer and form delta type bond(weak interaction). So part of time dimeric structure feel diamagnetism and overall reduces the dipole moment value in $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$.

Structure:



1.3.71. $\text{Cr}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ is diamagnetic in nature due to the formation of quadruple Bond ($\text{BO} = 4$) in the dimeric structure $\text{Cr}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$.

Structure of the dimer:



All the odd electron participates in the bonding level ($1\sigma + 2\pi + 1\delta$). Since there is no free odd electron in the dimeric structure i.e $\text{Cr}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$ is diamagnetic.

1.3.72. **Magnetic induction (B):** When the sample is placed in the external magnetic field (H) the density of lines of force is somewhat different from the applied field strength called magnetic induction.

$B = H + 4\pi I$, where I is the intensity of magnetism.

1.3.73. **Magnetic permeability:** It is the ratio of the density of lines of force in presence of magnetic field and in the vacuum.

$$P = \frac{B}{H} = \frac{(H + 4\pi I)}{H}$$

$P = 1 + 4\pi\left(\frac{I}{H}\right) = 1 + 4\pi K$ where, K is volume magnetic susceptibility.

$P > 1 \rightarrow$ paramagnetic

$P < 1 \rightarrow$ diamagnetic

1.3.74. **Gram magnetic susceptibility (χ_g)**

$$\chi_g = \frac{K}{\rho}$$

1.3.75. **Molar magnetic susceptibility (χ_M)**

$$\chi_M = \chi_g \times M$$

1.3.76. **Curie law:** The magnetic susceptibility of a substance is inversely proportional to its absolute temperature.

$$\chi_M \propto 1/T$$

$$\chi_M = C/T \quad (C = \text{Curie's constant})$$

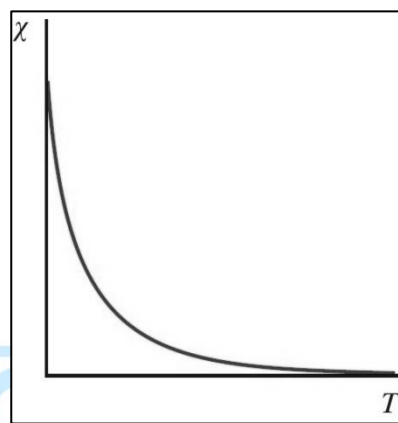
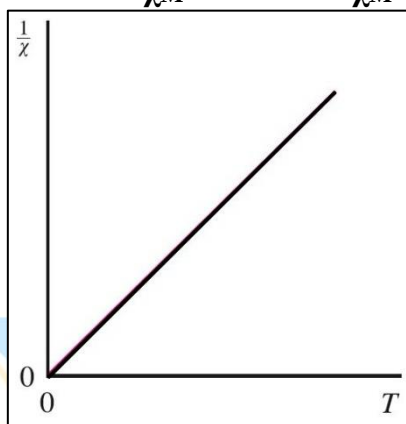
1.3.77. **Curie equation (relationship between χ_M and μ):**

For paramagnetic substance

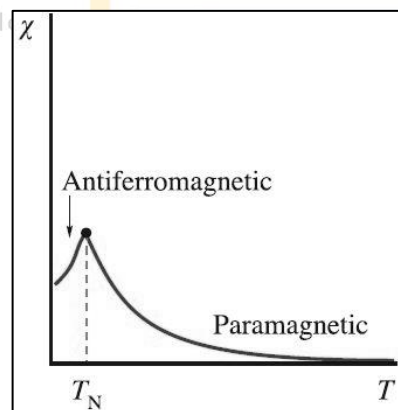
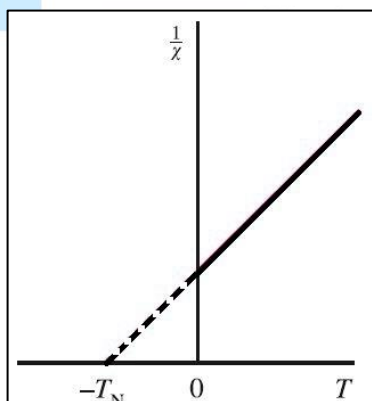
$$\mu_{eff} = 2.84\sqrt{\chi_M \cdot T} \text{ BM}$$

T = Absolute temperature.

1.3.78. **Plot of χ_M vs T or $1/\chi_M$ vs T:**



1.3.79. **Modification of Curie law (Weiss's law) :**



For antiferromagnetic substances there is a specific temperature, below this temperature the χ_M value decreases with decreasing temperature. Above the specific temperature the substances behaves as a simple paramagnetic.

1.3.80. **Microstates:** The different arrangement of electrons in orbitals having slightly different energy is called microstates.

$$\text{Number of microstates} = \frac{n!}{r!(n-r)!}$$

Where, n = twice the number of orbitals.

And r = the number of electrons.

Example: For d^2 configuration $n = 10$, $r = 2$

$$\text{Number of microstates} = \frac{10!}{2!(10-2)!} = 45$$

1.3.81. Determination of the ground state term symbol of the metal ion by Hund's rule:

- The ground state is characterised by the highest spin multiplicity ($2S + 1$) where S is the resultant spin momentum ($S = \frac{1}{2} \times n$) where n is the number of unpaired electron.
- The ground state is characterized by the highest orbital multiplicity (highest L value).

$$L = \sum ml$$

L	0	1	2	3	4	5
Symbol	S	P	D	F	G	H

- For less than half filled, the lowest J value in its ground state ($J = |L - S|$) and for more than half filled, the highest J value in its ground state ($J = |L + S|$)

Mode of writing: $(2S+1)L_J$

1.3.82. Splitting of spectroscopic terms into Mulliken symbols in octahedral field:

S \rightarrow A_{1g}

P \rightarrow T_{1u}

D \rightarrow $T_{2g} + E_g$

F \rightarrow $T_{1g} + T_{2g} + A_{2g}$

G \rightarrow $A_{1g} + E_g + T_{1g} + T_{2g}$

H \rightarrow $E_u + {}^2T_{1u} + T_{2u}$

I \rightarrow $A_{1g} + A_{2g} + E_g + T_{1g} + {}^2T_{2g}$

1.3.83. Splitting of spectroscopic term symbol into Mulliken symbols in tetrahedral field:

$$S \rightarrow A_1$$

$$P \rightarrow T_1$$

$$D \rightarrow E + T_2$$

$$F \rightarrow A_2 + T_1 + T_2$$

$$G \rightarrow A_1 + E + T_1 + T_2$$

$$H \rightarrow E + T_1 + T_1 + T_2$$

$$I \rightarrow A_1 + A_2 + E + T_1 + T_2 + T_2$$

1.3.84. Convention of using g and u subscript: If the point group of the environment has no centre of symmetry the g and u subscript are not used but when environment possesses centre of symmetry the subscript are determined by types of orbitals. All atomic orbital for which l is even (S, D, G) being centrosymmetric and hence g character and for all atomic orbitals for which l is odd that means (P, F, H etc) are non-centrosymmetric and u subscript are used.

1.3.85. Hole formalism concept: The relation between d^n and d^{10-n} term splitting in the same symmetry ligand field is called hole formalism.

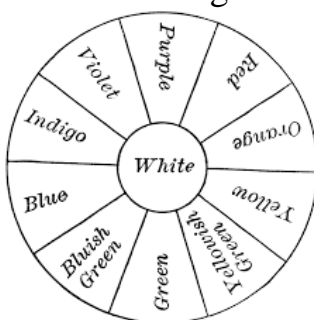
The spectra of d^1 is inverted to the d^9 spectra and similarly the d^2 spectra is inverted to the d^8 spectra as these are related through hole formalism concept.

General relation:

$$d^n(\text{oh}) = d^{10-n}(\text{Td})$$

$$d^n(\text{Td}) = d^{10-n}(\text{Oh})$$

1.3.86. Absorption of light: To explain the colours of coordination compounds, we are dealing with the phenomenon of complementary colours. If a compound absorbs light of one colour, we can see the complement of that light passes through light, the colour the complement of can conveniently be pairs on opposite sides of the colour wheel shown below.



colour. Such as, when white a substance that absorbs red observed is green. Green is red. Complementary colours remembered as the colour sides of the colour wheel

1.3.87. **Beer Lambert absorption law:** The beer Lambert law may be used to describe the absorption of light at a given wavelength by an absorbing species in solution.

$$A = \epsilon_0 \cdot c \cdot l$$

Where, A = Absorbance

ϵ_0 = molar extinction coefficient ($\text{mol.lit}^{-1}.\text{cm}^{-1}$)

l = path length through solution (cm)

c = concentration of absorbing species (mol.L^{-1})

1.3.88. **Selection rules:** The electronic transition is guided by the two fundamental selection rule.

- Laporte orbital selection rule ($\Delta l = \pm 0$)
- Spin selection rule ($\Delta S = 0$)

Selection rule \rightarrow Allowed/Forbidden

The intensity of the colour depends on the type of transition. If the transition follow both the selection rules i.e., allowed type the intensity of the colour is high.

Laporte orbital selection rule: Transition involved the change of subsidiary quantum number (Δl) is ± 1 .

d-d transition of electron: In a complex metal d-orbitals lost their degeneracy and split into a two sets of orbitals e.g. for octahedral t_{2g} and e_g set and for tetrahedral t_2 and e sets. Show the colour is appear due to the transition of electron into the t_{2g} set to e_g set.

d-d transition is laporte forbidden but many complexes are deeply coloured. colour of the complexes developed the transition lie in the UV region appear as a colourless due to the d-d transition of electron.

Relaxation of Laporte rule: We know that the metal ligand lead contains some covalent character i.e. metal orbital (d) overlap with ligand orbital (p). Show in a complex there is a 'd-p' mixing. The percentage of mixing depends on the symmetry of the complexes e.g., for octahedral complexes there is a centre of symmetry i.e. poor 'd-p' mixing but for tetragonal complex there is no centre of symmetry i.e. large 'd-p' mixing. So the transition in the $d(t_{2g})$ to $d(e_g)$ is not strictly true because the percentage of p is different in this two sets. Show transition of electron for t_{2g} to e_g means different 'd-p' level to other 'd-p' level i.e. $\Delta l \neq 0$. More d-p mixing means more Laporte allowed (found in tetrahedral complex) appear deep colour. When % of 'd-p' mixing small, the complex is light colour pale colour.

Spin selection rule ($\Delta S = 0$): During transition of electron, the total number of unpaired electrons (n) remain same i.e. same spin multiplicity $\Delta S = 0$.

Singlet \rightarrow Singlet (allowed)

Triplet \rightarrow Triplet (allowed)

Singlet \rightarrow Triplet (forbidden)

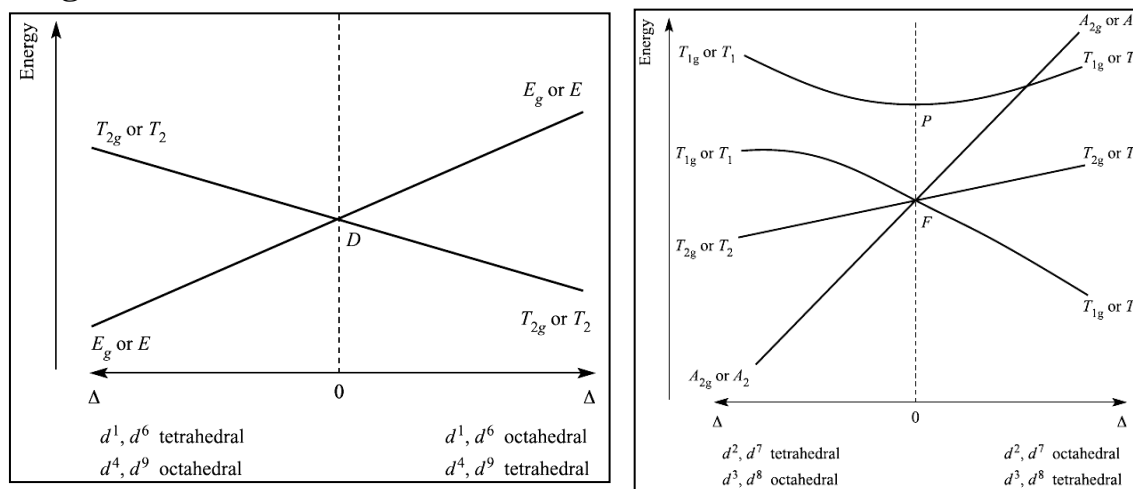
Triplet \rightarrow Singlet (forbidden)

Laporte (orbital)	Spin	Type of spectra	$\epsilon(\text{L.mol}^{-1}\text{cm}^{-1})$	Example
Allowed	Allowed	Charge transfer	1000	$[\text{TiCl}_6]^{2-}$
Partly allowed, Some d-p mixing	Allowed	d-d	500	$[\text{CoBr}_4]^{2-}$, $[\text{CoCl}_4]^{2-}$
Forbidden	Allowed	d-d	8-10	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{V}(\text{H}_2\text{O})_6]^{3+}$
Partly allowed, some d-p mixing	Forbidden	d-d	4	$[\text{MnBr}_4]^{2-}$
Forbidden	Forbidden	d-d	0.02	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

1.3.89. Orgel diagram: If the exemption is made that the Racah parameter (B) has the same value in complex that it has in the free ion, then the energy of the each level may be plotted out for various value of Δ_o as the variable. This type of energy level diagrams constructed are usually known as Orgel diagram.

These diagrams are used for interpretation of electron spin absorption bands of crystal field in electronic spectra of tetrahedral and octahedral transition metal complexes.

Orgel diagrams are useful in interpretation of spin allowed electronic transitions of tetrahedral and high spin octahedral complexes but not for low spin octahedral complexes. In all d^1 , d^2 , d^3 , d^8 , d^9 metal ions octahedral complexes, Orgel diagrams can be used as they give identical energy States.

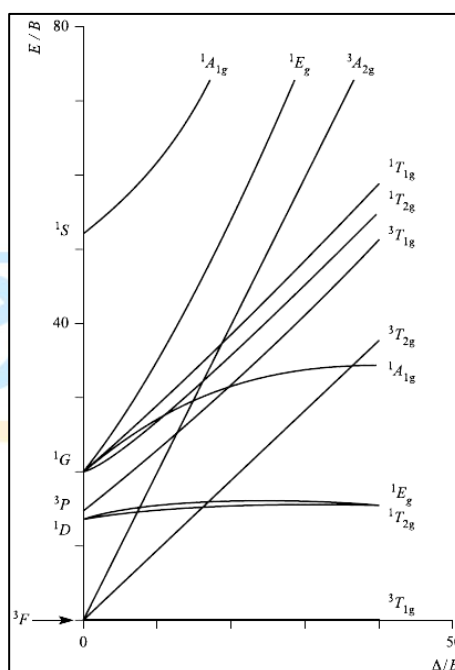
Diagram:

1.3.90. Tanabe sugano diagram: Orgels are simple to use but suffer from a limitation that they can be used to interpret the electronic spectra of only weak field complexes. Since these diagrams are concerned only with the weak field, the splitting of spectral terms of highest multiplicity as a function of Dq only are considered. High energy terms of other multiplicity and hence the levels arising from them have no place in the Orgel diagram. In order to make any such diagram to be universal use, they have to be constructed in such a way that they could be used for crystal field of any strength and for all metal ions of a particular configuration. When the crystal field become stronger than the inter electronic repulsion for strong field complexes, the ground state changes after some critical field strength for some configuration (not all). The Tanabe Sugano diagram while incorporating all the spectral terms hold good for both the weak and strong fields complexes and have the following characteristics:-

- In Tanabe Sugano diagrams the energy of the states arising from various terms divided by 3 are plotted against Dq/B . E can be obtained as an Orgel diagram and B from emission spectrum of the metal ion. Therefore diagram can be used for any metal with a particular configuration.
- The energy of the ground state is fixed at zero and hence as a horizontal line in the diagram so that the energies of the higher energy levels can be measured vertically.

- For a d^1 , d^2 , d^3 , d^8 and d^9 configuration the ground state remain same for both weak and strong crystal field for the remaining d^n ($n = 4, 5, 6, 7$) configuration the ground level of high spin multiplicity changes (term crossing) at some critical field strength and a state of lower multiplicity (of a higher energy term) becomes the ground state. Thus there is a break in original ground state and a sharp change in the slopes of all the lines at $Dq/B = 2.8$ (d^4 , d^5); 2.0 (d^6); 2.2 (d^7).
- Some of the lines Tanabe Sugano diagrams are shown as curved rather than as straight lines, because of the interaction between the levels of same spin and orbital multiplicity.

Diagram:



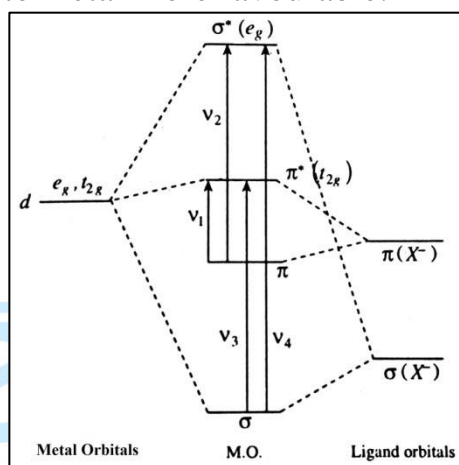
- 1.3.91. **Vibronic coupling:** In this process vibrational wave function combines with the electronic wave function i.e. in this process electron transition takes place with vibrational excitation. So, thus the pure d-d transition does not happen.
- 1.3.92. **Charge transfer spectra:** An electronic transition between orbitals that are centred on different atoms is called charge transfer transition and absorption band is usually very strong. When the transition is charge transfer type the colour is always dark because the transition follow both the selection rules.

1.3.93. Types of charge transfer spectra:

- Ligand to metal charge transfer (LMCT)
- Metal to ligand charge transfer (MLCT)
- Metal to metal charge transfer (MMCT)
- Inter ligand charge transfer

1.3.94. **Ligands to metal charge transfer (LMCT):** If the migration of electron is from ligand to the metal, then the charge transfer is called ligand to metal charge transfer. When the metal has relatively high ionization energy so that it would have empty orbitals at early low energy, the electron transfer from ligand to metal is more favourable.

MO diagram:

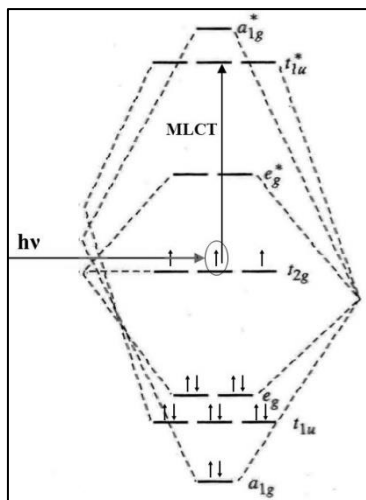


Example:

- $\text{CdS} \rightarrow$ cadmium yellow
- $\text{HgS} \rightarrow$ Vermilion
- $[\text{Pb}_3(\text{SbO}_4)_2] \rightarrow$ Naples yellow
- $\text{PbO} \rightarrow$ Massicot
- $\text{PbCrO}_4 \rightarrow$ Chrome yellow
- $\text{Fe}_2\text{O}_3 \rightarrow$ red and yellow ochres
- $\text{MnO}_4^- \rightarrow$ Deep purple
- $\text{HgI}_2 \rightarrow$ red
- $\text{BiI}_3 \rightarrow$ Orange red
- $\text{PbI}_2 \rightarrow$ yellow

1.3.95. **Metal to ligand charge transfer (MLCT):** If the migration of electron is from metal to ligand, then charge transfer is called metal to ligand charge transfer. Charge transfer processes in the opposite direction from metal to ligand are favoured in complexes that have occupied metal centred orbitals and back and low lying ligand Central orbitals.

MO diagram:



Example: phen, bipy,
 $[\text{Ru}(\text{bipy})_3]^{2+}$

dithiolene,

1.3.96. Metal to metal charge transfer (MMCT) (via bridge ligand field):

Example:

- $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6] \rightarrow \text{Prussian blue} \rightarrow \text{deep blue}$
- $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6] \rightarrow \text{Turnbull's blue.}$
- $[(\text{NH}_3)_5\text{Ru}-\text{Pyz}-\text{Ru}(\text{NH}_3)_5]^{5+}$, where Pyz is bringing pyrazine ligand \rightarrow Creutz-Taube ion
- Red lead $\rightarrow \text{Pb}_3\text{O}_4$.

1.3.97. Interligand charge transfer: The legend itself may have a chromophore and steel another type of absorption band, an inter ligand man may be observed. These bands sometimes be identified by comparing the spectra of complexes with the spectra of free ligands. Not all the ligands exist in three states, some ligand owe their existence to the ability of metal atom to stabilize molecules that are otherwise highly unstable.

1.3.98. Colour of the complex:

- Originates mainly due to d-d transition of electron (presence of d orbital electron).
- In many cases colour originates due to the charge transfer transition of electrons (absence of d orbitals).

1.3.99. Some examples of charge transfer spectra:

- In the +1 state of Cu most of the simple compound and complex is a diamagnetic and colourless as the ions have a d^{10} configuration. Cu_2O is yellow or red, Cu_2CO_3 is yellow and CuI is brown. In all these cases the colour arises from the charge transfer bands and not from d - d spectra.
- There are blue proteins which contain copper. They act as an electron transfer agents by means of a $\text{Cu}^{2+}/\text{Cu}^+$ couple. Their colour is much more intense than would be expected for d-d spectra. Such as plastocyanin and azurin.
- HgI_2 exist in red and yellow forms and the colour is due to the charge transfer.
- The permanganate ion has an intense purple colour. This colour is due to the charge transfer as Mn has d^0 configuration and not from d-d spectra.
- $\text{Cr}_2\text{O}_7^{2-}$ is an orange solid. This colour is due to the charge transfer.
- CrO_4^{2-} is yellow solid and CrO_3 is a bright Orange solid.
- V_2O_5 is orange or red coloured due to the charge transfer.

1.3.100. Electron transfer reaction in coordination compounds: These are the reaction in which the transfer of an electron from one account to other atom occurs and the oxidation state of some atoms change. This type of reaction may be divided into the following two classes:-

- The process in which the electron transfer results in no net chemical change are called as electron exchange process.

Examples: $[\text{Fe}(\text{CN})_6]^{3-} - [\text{Fe}(\text{CN})_6]^{4-}$; $[\text{Co}(\text{en})_3]^{3+} - [\text{Co}(\text{en})_3]^{2+}$; $[\text{Fe}(\text{dipy})_3]^{3+} - [\text{Fe}(\text{dipy})_3]^{2+}$; $[\text{Co}(\text{NH}_3)_6]^{3+} - [\text{Co}(\text{NH}_3)_6]^{2+}$ etc. They can be followed only indirectly, for example isotropic labeling or by NMR.

- Those in which there is net chemical change.

Example: $[\text{Cr}(\text{NH}_3)_5\text{X}]^{2+} - [\text{Cr}(\text{H}_2\text{O})_6]^{2+}$; $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+} - [\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ etc, where $\text{X} = \text{F}^- , \text{Cl}^- , \text{Br}^- , \text{I}^- , \text{SO}_4^{2-} , \text{NCS}^-$ etc. This can be followed by many standard chemical and physical methods.

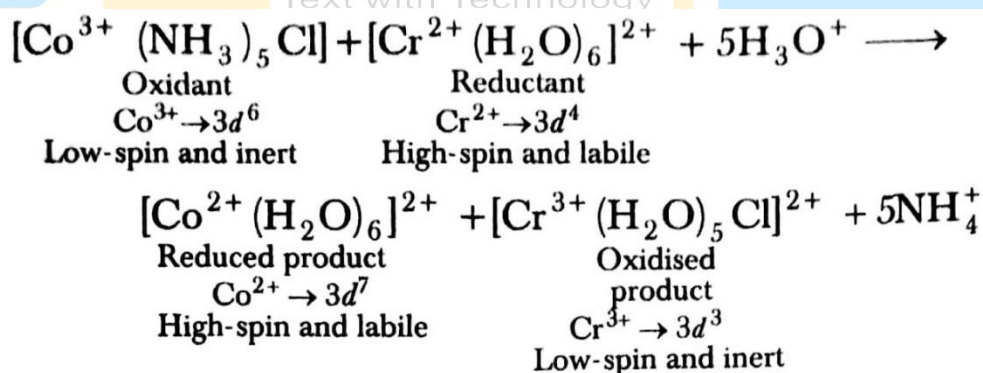
1.3.101. **Mechanism of one electron transfer reactions:** The mechanism of the one electron transfer reactions are two types:

- Bridge or inner sphere mechanism.
- Electron transfer or outer sphere mechanism.

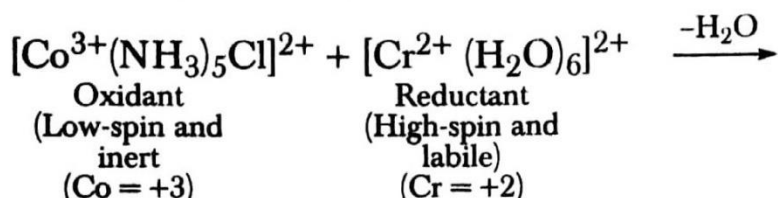
Inner sphere mechanism: These mechanisms are electron transfer reactions in which concomitant electron transfer and ligand transfer occur. In this reactions and intimate contact between oxidant and reductant is required. This type of requirement is fulfilled when a bridge activated complex is formed as a result of an intimate attachment between the oxidant and reductant. This activated complex has at least one ligand and which is common to the co-ordinates fear of both the reacting complexes and this form bridge between them. Does the name inner sphere mechanism is given. It is also called as ligand bridged atom transfer or bridged activated complex mechanism.

Taube and his coworkers have shown that oxidation of aqueous Cr(II), $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ by pentammine cobalt (III) chloride, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{3+}$ in acidic medium represented by the equation

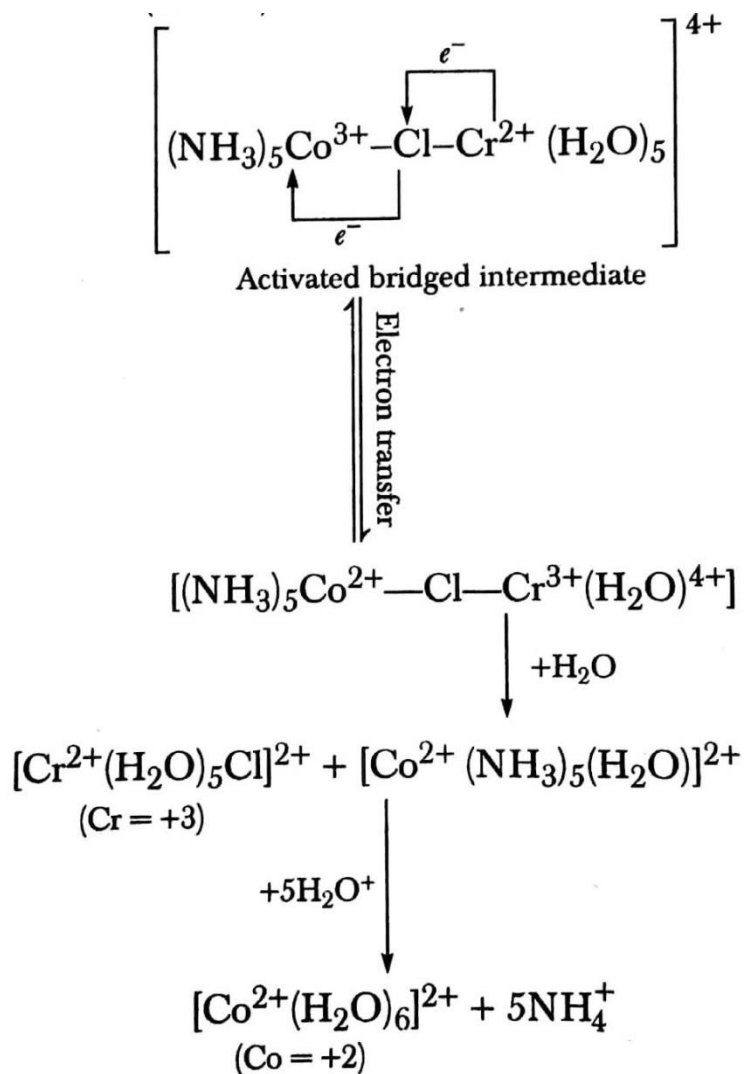
Similar



can be explained by this mechanism as follows :

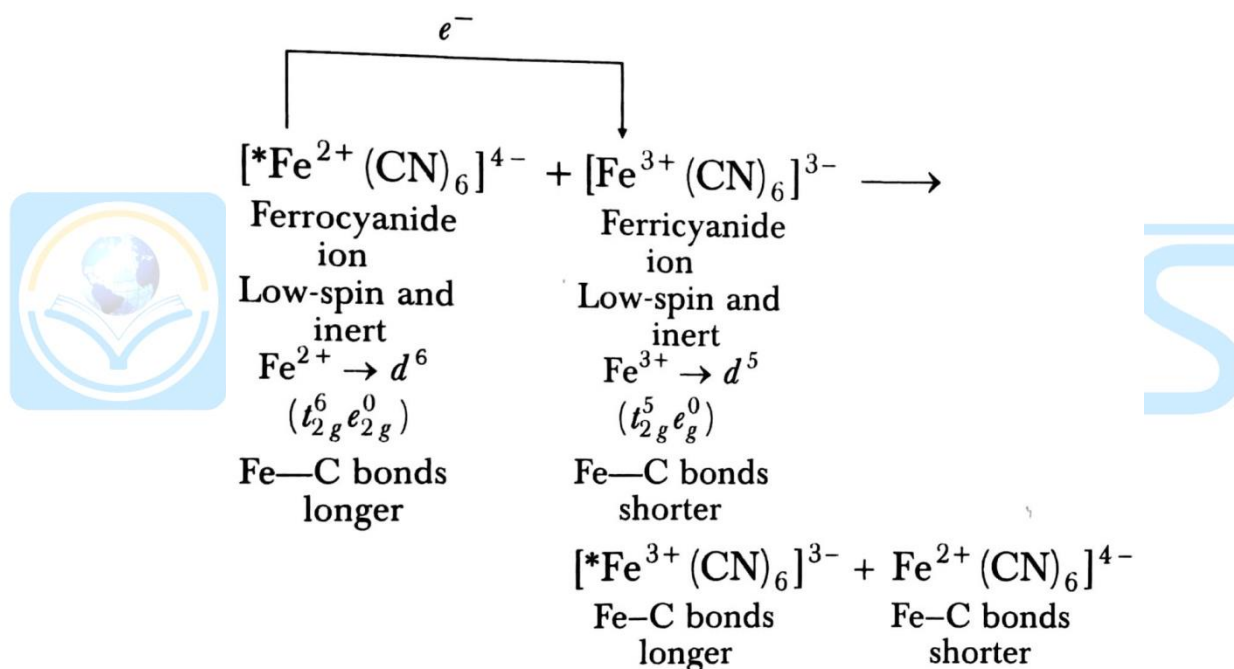


mechanism has been suggested for the following general reaction:



$[\text{Co}(\text{NH}_3)_5\text{X}]^{2+} + [\text{Cr}(\text{H}_2\text{O})_6]^{2+} + 3\text{H}_3\text{O}^+ \rightarrow [\text{Co}(\text{H}_2\text{O})_6]^{2+} + [\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+} + 5\text{NH}_4^+$
 Here X = F⁻, Cl⁻, Br⁻, I⁻, SO₄²⁻, NCS⁻, N₃⁻, PO₄³⁻, CH₃COO⁻ etc. with these ligands which form bridges the rates of these reactions increase in the order : SO₄²⁻ < Cl⁻ < Br⁻. The ions which perform bridges most readily and provide the best path for electron produce fastest reactions.

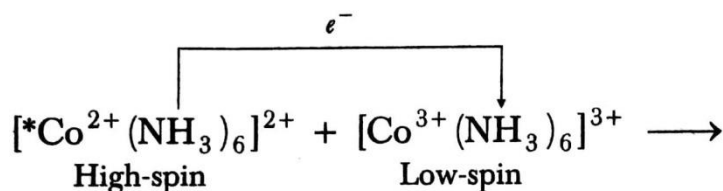
Outer sphere mechanism: This is the electron transfer reaction in which only the formal valence States of the metal ions involved change. These reactions occur by direct electron transfer and the electron effectively hops from one species to the other and the ligands act as electron conduction media. Electron transfer can occur by a mechanism which involves movement of an electron from the outside of a ligand in one coordination sphere over the outside of a second sphere. This mechanism is appropriate with large conjugated ligands like phenanthroline and bipyridine. In this process direct transfer of an electron occurs. In this reaction very light electrons move much more rapidly than much heavier atoms. In order to understand its effect let us assume the transfer of an electron from $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ to $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$.



There is no heat change associated with this electron transfer reaction. An electron transfer reaction is only occurring when the vibrations within the two anions have made them of identical geometries and electronic configuration. Then the products and the reactance in this process would be equivalent and no energy would be produced as a result of the electron transfer. When both the reactant are in earth as in the present case the close approach of the metal atoms is impossible and hence the electron transfer takes place by tunneling or outer sphere mechanism. In this process the complex retains its full coordination shell in activated complex so that there is no ligand common to either central metal atom

and an electron is relieved to pass through both the coordination shells. Outer sphere electron transfer reactions are more rapid for complexes containing ligands such as ortho phenanthroline and CN^- ion then for corresponding complexes with ligands like H_2O or NH_3 .

The electron transfer reaction between $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}^{\text{II}}(\text{NH}_3)_6]^{2+}$ are given below:



Outer sphere exchange reactions between complexes having different Central metal ions with different oxidation State are usually faster than

outer sphere exchange reaction between the complexes of the same metals with different oxidation State. e.g., $[\text{Os}^{\text{II}}(\text{dipyl})_3]^{2+}$ - $[\text{MoV}(\text{CN})_8]^{3-}$ for such type of reactions when excited states of the products are converted into ground States, the energy decreases as the free energy of the reaction. Thus for such reactions the structure of the transition state is more like that of the reactants and consequently the activation energy is decreased and the rate is increased.

There is a number of electron transfer reactions such as those of $[\text{Co}^{\text{II}}(\text{NH}_3)_4\text{X}]^{2+}$ with $[\text{Co}^{\text{II}}(\text{CN})_6]^{2-}$, where $\text{X} = \text{F}^-$, CN^- , NO_3^- and NO_2^- and that of Cr^{2+} with $[\text{IrCl}_6]^{2-}$ in which the electron transfer takes place by both inner sphere mechanism and outer sphere mechanism.

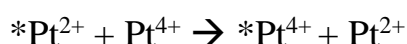
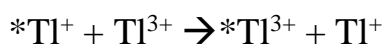
1.3.102. Factors affecting the rates of direct electron transfer reactions:

The factors affecting the rates of direct electron transfer reactions are given below:

- **Electrostatic repulsion between ions of like charges:** Due to the electrostatic repulsion the energy of activation increases. the increase in activation energy tends to decrease the rate of exchange of electrons.

- **Identity and concentration of the cations present in solution:** In some cases the rate constants for the electron transfer reactions have been found to depend on the Identity and concentration of the cations present in the solution. An increase in the concentration of the cations increases the rate but certain cations are particularly effective. the general effect can be attributed to the formation of iron pairs which then decrease the electrostatic contribution to the activation energy.
- **Conductivity of the legends:** With increasing the conductivity of the ligands the electron transfer proceed more readily between the two complexes. Electron transfer between a variety of similar CN-complexes has been found to be rapid and the same is true for the the highly conducting complexes viz. $[M(\text{phen})_3]^{n+}$ and $[M(\text{bipy})_3]^{n+}$ relative to $[M(\text{en})_3]^{n+}$ and $[M(\text{NH}_3)_6]^{n+}$.
- **Reorganization energy:** The Bond lengths in MnO_4^- and MnO_4^{2-} the former and the activated complex for exchange between these mast involve a stretched MnO Bond in MnO_4^- . Slow reactions are expected when the accident and the reductant have greatly different Bond lengths, geometry or solvation shells. For octahedral complexes the bond lengths are changed drastically when e_g electrons are involved in the transfer as compared to t_{2g} electrons in the d-orbitals.
- **Free energy change in the reaction:** When the negative free energy change for the overall reaction is greater, the faster will be the reaction.

1.3.103. Two electron transfer reactions: The reactions in which two electrons are transferred are known. e.g., the reaction:

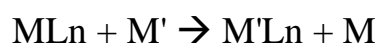


1.3.104. **Ligand substitution reactions in octahedral complexes:** Few important types of substitution reactions are given below:

- **Nucleophilic or ligand substitution(SN) reaction:** In these reactions a nucleophile in a coordination complex is replaced by another nucleophile.



- **Electrophilic or metal substitution (SE) reactions:** In these type of reactions and electrophile in a coordination complex is replaced by another electrophile.

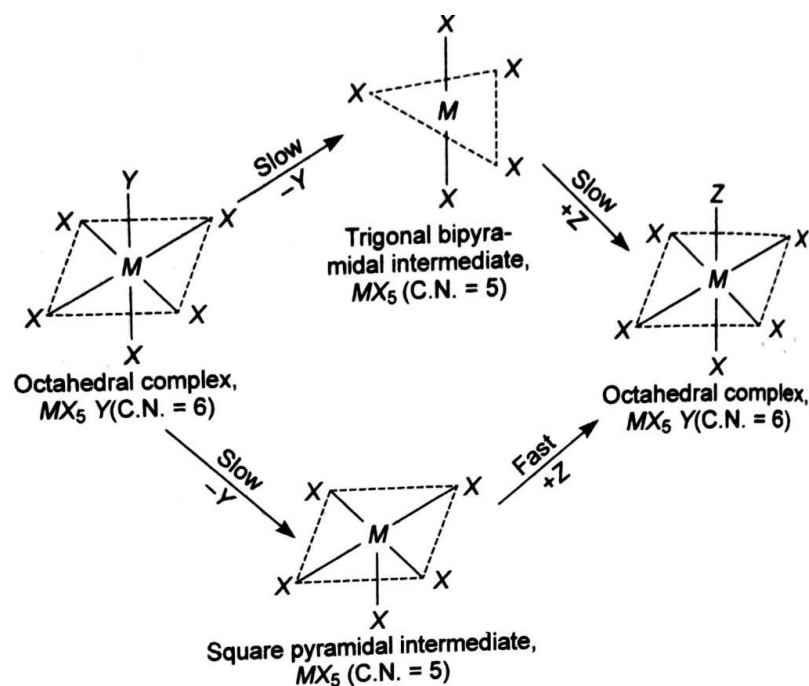


Although SE reactions, such as that between Hg^{2+} and $[Co^{II}(NH_3)_5Cl]^+$ are known, there much less than SN reactions and hence, will not be considered here.

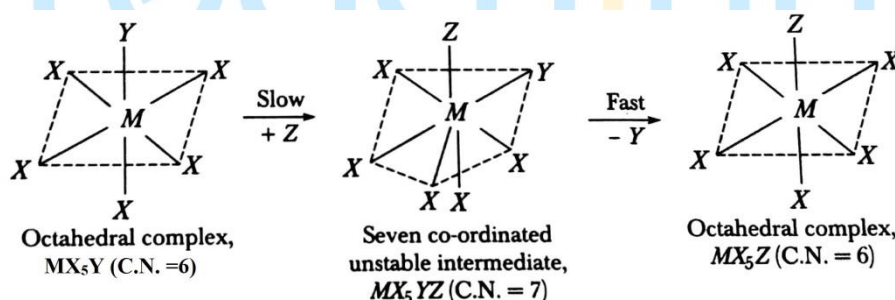
1.3.105. **Mechanism of nucleophilic substitution reactions in octahedral complexes:** Two types of different ports of nucleophilic substitution reaction have been suggested;

- **SN¹ or dissociation mechanism:** SN¹ indicates substitution (S) nucleophilic (N) uni molecular for first order (1) reaction. The reaction is nucleophile due to the incoming ligand seeks a positive centre, the metal ion. For a general ligand substitution reaction in an octahedral complex this mechanism can be shown as following:





- **SN^2 or association for displacement mechanism:** SN^2 stands to indicate substitution (S) nucleophilic (N) bimolecular or second order (2) reaction. This reaction proceeds through the two steps



1.3.106. Hydrolysis reactions: These are the substitution reaction in which a ligand is replaced by a water molecule or by OH^- groups. The reaction in which an Aqua complex is formed as a result of the replacement of a ligand by water molecules are called acid hydrolysis or equation reactions. The reactions in which a hydroxyl complex is formed by the replacement of a ligand by OH^- group are called base hydrolysis reactions. Acid hydrolysis reactions occur in neutral and acid solutions ($pH < 3$) while base hydrolysis reactions occur in basic solution ($pH > 10$). For intermediate pH range the reaction is referred to just as hydrolysis reactions.

Example:Acid hydrolysis reaction:

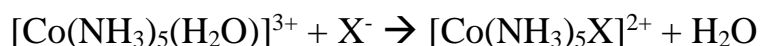
- $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+} + \text{Cl}^-$
- $[\text{Co}^{\text{III}}(\text{en})_2\text{ACl}]^+ + \text{H}_2\text{O} \rightarrow [\text{Co}^{\text{III}}(\text{en})_2\text{A}(\text{H}_2\text{O})]^{2+} + \text{Cl}^-$

A = OH^- , Cl^- , NCS^- , NO_2^-

Base hydrolysis reaction:

- $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + \text{OH}^- \rightarrow [\text{Co}(\text{NH}_3)_5(\text{OH})]^{2+} + \text{Cl}^-$

1.3.107. **Anation Reactions:** These are the reactions in which an ecology and from an Aqua complex is replaced from the coordination shell by some anion.



Thus we find that an anation reaction is the reverse of acid hydrolysis reaction.



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Q. If L is a neutral monodentate ligand, the species, $[\text{AgL}_4]^{2+}$, $[\text{AgL}_6]^{2+}$ and $[\text{AgL}_4]^{3+}$, respectively are

- (a) paramagnetic, paramagnetic and diamagnetic
- (b) paramagnetic, diamagnetic and paramagnetic
- (c) diamagnetic, paramagnetic and diamagnetic
- (d) paramagnetic, diamagnetic and diamagnetic

Ans. In $[\text{AgL}_4]^{2+}$ and $[\text{AgL}_6]^{2+}$, the oxidation state of Ag is +2 i.e., $4d^9$ electronic system, hence there present unpaired electron. i.e., paramagnetic.

But, in $[\text{AgL}_4]^{3+}$ the oxidation state of Ag is +1 i.e., $4d^8$ electronic system with dsp^2 hybridization i.e., square planar geometry. So, pairing of electrons is occurred i.e., diamagnetic.

Correct option is (a).

Q. The ligand(s) that is (are) fluxional in $[(\eta^5 - \text{C}_5\text{H}_5)(\eta^1 - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ in the temperature range 221–298K, is (are)

- (a) $\eta^5 - \text{C}_5\text{H}_5$ (b) $\eta^1 - \text{C}_5\text{H}_5$ (c) $\eta^5 - \text{C}_5\text{H}_5$ and CO (d) $\eta^1 - \text{C}_5\text{H}_5$ and CO

Ans. $[(\eta^5 - \text{C}_5\text{H}_5)(\eta^1 - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2] \xrightarrow{221-298\text{K}} [(\eta^5 - \text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]$

Correct option is (b).

Q. $[\text{CoL}_6]^{3+}$ is red in colour whereas $[\text{CoL}'_6]^{3+}$ is green. L and L' respectively corresponds to,

- (a) NH_3 and H_2O (b) NH_3 and 1, 10-phenanthroline
- (c) NH_3 and 1, 10-phenanthroline (d) H_2O and NH_3

Ans. $[\text{CoL}_6]^{3+} \rightarrow \text{red colour} \rightarrow \text{absorbs green light}$

$[\text{CoL}'_6]^{3+} \rightarrow \text{green colour} \rightarrow \text{absorbs red light}$

Energy of green light is higher than that of red light.

Therefore, L is strong field and L' is weak field ligand ($\text{NH}_3 > \text{H}_2\text{O}$).

Correct option is (a).

Q. The oxidation state of Ni and the number of metal-metal bonds in $[\text{Ni}_2(\text{CO})_6]^{2-}$ that are consistent with the 18-electron rule are

- (a) Ni(–II), 1 bond (b) Ni(IV), 2 bonds (c) Ni(–I), 1 bond (d) Ni(IV), 3 bonds

Ans. Let x be the number of M-M bond

As per 18-electron rule number electrons per Ni atom is,

$$\underbrace{11}_{\text{Ni}} + \underbrace{(2 \times 3)}_{\text{CO}} + \underbrace{x}_{\text{M-M}} = 18$$

Hence, $x=1$

Correct option is (c).

Q. In its electronic spectrum, $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ exhibits two absorption bands, one at 17,800 (ν_1) and the second at 25,700 (ν_2) cm^{-1} . The correct assignment of these bands, respectively, is

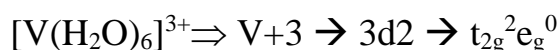
- (a) $\nu_1 = {}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, $\nu_2 = {}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$

- (b) $\nu_1 = {}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$, $\nu_2 = {}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{P})$

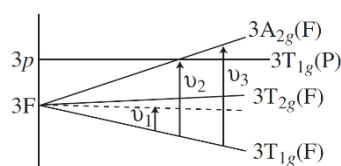
- (c) $\nu_1 = {}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$, $\nu_2 = {}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$

- (d) $\nu_1 = {}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$, $\nu_2 = {}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$

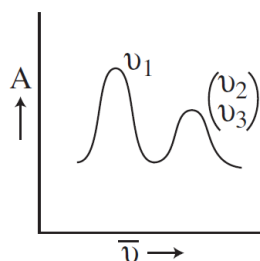
Ans.



${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{A}_{2g}(\text{F})$ – not observed low intensity and high energy portion of spectrum.



Observed spectrum



$$v_1 = {}^3T_{1g} (F) \rightarrow {}^3T_{2g} (F)$$

$$v_2 = {}^3T_{1g} (F) \rightarrow {}^3T_{1g} (P)$$

Correct option is

(a).

Q. Identify the correct statement about $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$

- (a) All Ni-O and Cu-O bond lengths of individual species are equal
- (b) Ni-O(equatorial) and Cu-O(equatorial)
- (c) All Ni-O bond lengths are equal whereas Cu-O (equatorial) bonds are shorter than Cu-O(axial)bonds
- (d) All Cu-O bond lengths are equal whereas Ni-O(equatorial) bonds are shorter than Ni-O(axial)bonds.

Ans.

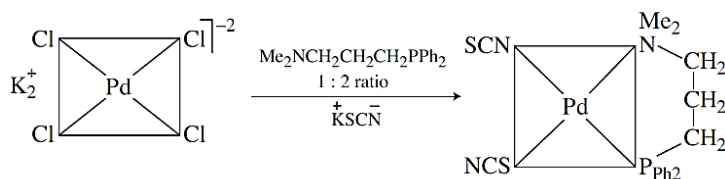
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is d^8 system and have regular octahedral geometry (all Ni-O bond lengths are equal). Whereas $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is d^9 system, shows **large John-Teller distortion** with Z_{out} (tetragonally elongated). Therefore, Cu-O (equatorial) bonds are shorter than Cu-O (axial) bonds.

Correct option is (c).

Q. A 1 : 2 mixture of $\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ and KSCN with $\text{K}_2[\text{PdCl}_4]$ gives a square planar complex A. Identify the correct pairs of donor atoms trans to each other in complex A from the following combinations.

- (a) P, N
- (b) N, S
- (c) P, S
- (d) N, N

Ans.



On warming, S-bonded isomer is converted to the N bonding isomer, which is presumably slightly more stable. So, P opposite to N and S opposite to N.

Correct option is (a).

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Q. The hapticities 'x' and 'y' of the arene moieties in the diamagnetic complex $[(\eta^x - \text{C}_6\text{H}_6)\text{Ru}(\eta^y - \text{C}_6\text{H}_6)]$ respectively are

- (a) 6 and 6 (b) 4 and 4 (c) 4 and 6 (d) 6 and 2

Ans. $[(\eta^x - \text{C}_6\text{H}_6)\text{Ru}(\eta^y - \text{C}_6\text{H}_6)]$ – diamagnetic Ru – 8e⁻ in valence shell, want 10 more e⁻ for 18e⁻ system, so hepticity will be 4 and 6.

$x = 4, y = 6$.

Correct option is (c).

Q. The rate of the reaction $\text{Ni}(\text{CO})_4 + \text{PPh}_3 \xrightarrow{h\nu} [\text{Ni}(\text{CO})_3(\text{PPh}_3)] + \text{CO}$ depends on

- (a) Concentration of both the reactants (b) Concentration of $\text{Ni}(\text{CO})_4$ only
(c) Concentration of PPh_3 only (d) The steric bulk of PPh_3

Ans. $\text{Ni}(\text{CO})_4 + \text{PPh}_3 \xrightarrow{h\nu} [\text{Ni}(\text{CO})_3(\text{PPh}_3)] + \text{CO}$ 18 e⁻s complex.

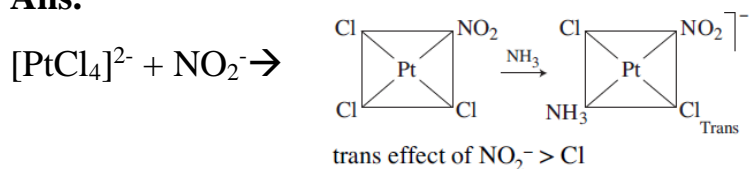
For substitution, it must follow dissociative mechanism (S_N^1). Hence, it depends only on $\text{Ni}(\text{CO})_4$ concentration.

Correct option is (b).

Q. In the following reaction $[\text{PtCl}_4]^{2-} + \text{NO}_2^- \rightarrow \text{A} \xrightarrow{\text{NH}_3} \text{B}$, compound B is

- (a) *trans*- $[\text{PtCl}_2(\text{NO}_2)(\text{NH}_3)]^-$ (b) *cis*- $[\text{PtCl}_2(\text{NO}_2)(\text{NH}_3)]^-$
(c) *trans*- $[\text{PtCl}_2(\text{NH}_3)_2]$ (d) *cis*- $[\text{PtCl}_2(\text{NO}_2)_2]^{2-}$

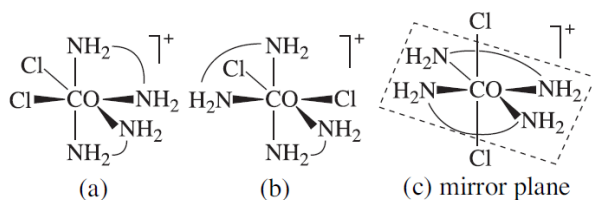
Ans.



Correct option is (a).

Q. The number of stereo-isomers of $trans-[CoCl_2(triethylenetetraamine)]Br$ is

- (a) One (b) Two (c) Three (d) Four



Ans. Correct option is (c).

Q. An aqueous solution of $[Mn(H_2O)_6]^{2+}$ complex is pale pink in colour. The probable reasons for it are

- (A) Presence of ${}^6A_{1g}$ ground state
 (B) Disallowed transition by spin selection rule
 (C) Presence of ${}^2T_{2g}$ ground state
 (D) Charge transfer transition

The correct answer is

- (a) A and B (b) A and C (c) B and C (d) C and D

Ans.



$$2s + 1 = 6, L = 0 (s)$$

Spin selection rule, $\Delta s = 0$

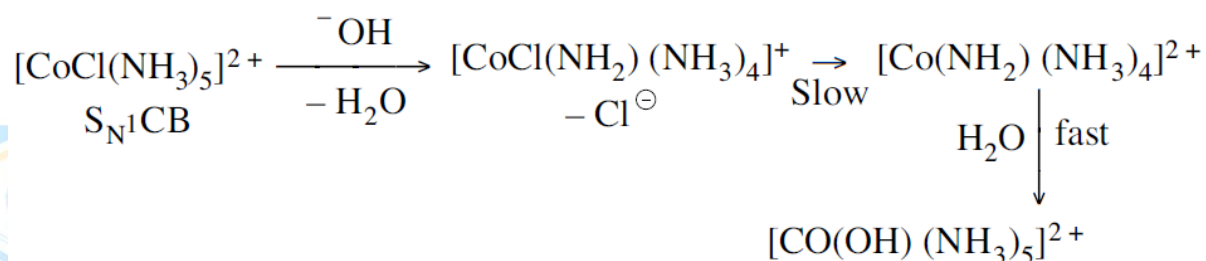
$6s^- \rightarrow {}^6A_{1g}$ ground state, violated and disallowed transition charge transfer impossible and ${}^2T_{2g}$ is not ground state.

Hence, A & B are correct.

Correct option is (a).

(D) S_N1_{CB} mechanism in both the complexes

Ans.

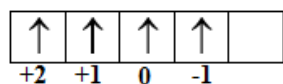


Correct option is (a).

Ans. $[\text{MnF}_6]^{3-} \Rightarrow \text{Mn}^{+3} \Rightarrow$

↑	↑	↑	↑	
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$$\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} = 4.9BM$$



Correct option is (a).

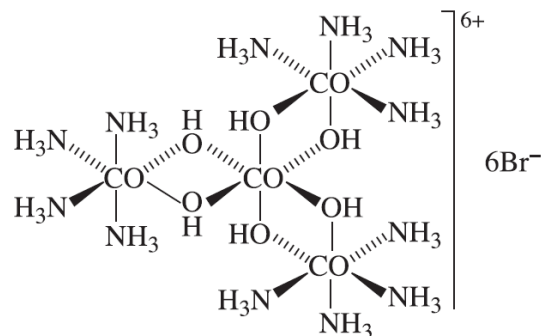
Q. The three dimensional structure of compound $[\text{Co}(\text{Co}(\text{NH}_3)_4(\text{OH})_2)_3]\text{Br}$ has

- (a) Twelve Co—O and twelve Co—N bonds (b) Ten Co—O and ten Co—N bonds
(c) Fourteen Co—O and ten Co—N bonds (d) Twelve Co—O and ten Co—N bonds

Ans. Inorganic optically active complex—

12Co—O and 12 Co—N bonds

Correct option is (a).



Q. The spin-only (μ_s) and spin plus orbital (μ_{s+L}) magnetic moments of $[\text{CrCl}_6]^{3-}$ are

- (a) 3.87 BM and 5.20 BM (b) 2.84 BM and 5.20 BM
(c) 3.87 BM and 6.34 BM (d) 2.84 BM and 6.34 BM

Ans. $[\text{CrCl}_6]^{3-} \Rightarrow \text{Cr}^{+3} \Rightarrow$



$$\mu_s = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}$$

$$\mu_{s+L} = \sqrt{n(n+2) + L(L+1)} = \sqrt{3(3+2) + 3(3+1)} = \sqrt{15 + 12} = 5.20 \text{ BM}$$

NET JUNE 2015

Q. In transition metal phosphine ($\text{M} \rightarrow \text{PR}_3$) complexes, the back-bonding involves donation of electrons from

- (a) $\text{M}(^3t_{2g}) \rightarrow \text{PR}(\sigma^*)$ (b) $\text{M}(^3t_{2g}) \rightarrow \text{PR}_3(\pi^*)$
(c) $\text{M}(e_g) \rightarrow \text{P}(d)$ (d) $\text{PR}_3(\pi) \rightarrow \text{M}(t_{2g})$

Ans. $\text{M}(t_{2g}) \rightarrow \text{PR}_3(\sigma^*)$

Phosphines (PR_3) primarily function as Lewis base, interacting with metal as σ donor Ligand. PR_3 can accept electron density from metal into P—C (σ^*) Antibonding orbital having π symmetry.

Correct option is (a).

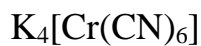
(d) $[\text{RhCl}(\text{PPh}_3)_5]$, 18



Q. Among the complexes, (A) $K_4[Cr(CN)_6]$, (B) $K_4[Fe(CN)_6]$, (C) $K_3[Co(CN)_6]$ and (D) $K_4[Mn(CN)_6]$, Jahn-Teller distortion is expected in

- (a) A, B and C (b) B, C and D (c) A and D (d) B and C

Ans. J. T. distortion occurs where there is unsymmetrical filling of electrons in t_{2g} or e_g orbital.



Cr = + 2 O.S. low spin complex $Cr(II) = d^4 t_{2g}^4 e_g^0$ (unsym)

$K_4[Fe(CN)_6]$ low spin complex $Fe(II) = d^6 t_{2g}^6 e_g^0$ (symmetrical)

$K_3[Co(CN)_6]$ low spin complex $Co(III) \Rightarrow d^6 t_{2g}^6 e_g^0$ (symmetrical)

$K_4[Mn(CN)_6]$ low spin complex $Mn(II) \Rightarrow d^5 t_{2g}^5 e_g^0$ (unsym)

Hence only A and D is having unsymmetrical filling, hence undergo distortion.

Correct option is (c).

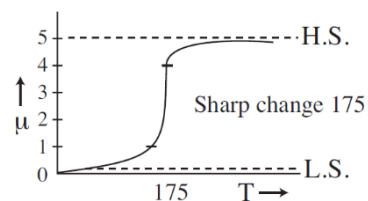
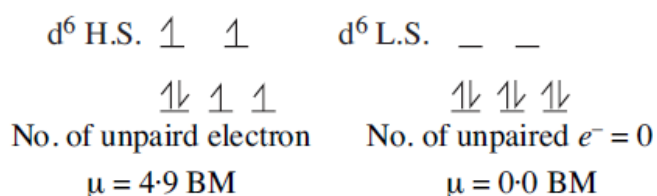


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Q. The complex $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ (phen=1,10-phenanthroline) shows spin cross-over behaviour. CFSE and μ_{eff} at 250 and 150K, respectively are

- (a) $0.4\Delta_o$, 4.90 BM and $2.4\Delta_o$, 0.00 BM
 (b) $2.4\Delta_o$, 2.90 BM and $0.4\Delta_o$, 1.77 BM
 (c) $2.4\Delta_o$, 0.00 BM and $0.4\Delta_o$, 4.90 BM
 (d) $1.2\Delta_o$, 4.90 BM and $2.4\Delta_o$, 0.00 BM

Ans. $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ O.S. of Fe = + 2Fe(II) = d^6 High spin – low spin equilibria or spin cross-over



$$\text{CFSE } \Delta = (-0.4p + 0.6q)$$

Where p = No. of e^- s in t_{2g} orbital, q = No. of e^- s in e_g orbital

$$\Rightarrow d^6 \text{ H.S. } \Delta = (-0.4 \times 4 + 0.6 \times 2)$$

$$= -1.6 + 1.2 = -0.4 \Delta_o$$

$$\Rightarrow d^6 \text{ L.S. } \Delta = -0.4 \times 6 = -2.4 \Delta_o$$

Correct option is (a).

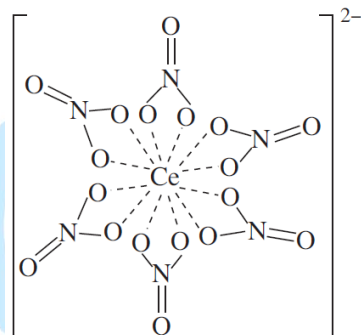
Q. Consider the following statements for $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6] \cdot \text{Z}$

- (A) Coordination number of Ce is 12
- (B) Z is paramagnetic
- (C) Z is an oxidising agent
- (D) Reaction of Ph_3PO with Z gives a complex having coordination number 10 for Ce.

The correct statements are

- (a) A, B and C (b) B, A and D (c) B, C and D (d) A, C and D

Ans. $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ complex NO_3 is bidentate ligand and structure is Icosahedron *i.e.*, coordination number of Ce is 12.



In Ce^{+4} more stable $\text{Ce} = 4f^4 5d^1 6s^2$; $\text{Ce}(\text{IV}) = 4f^0 5d^1 6s^0$ *i.e.*, Z is diamagnetic Ce^{+4} is a strong one electron oxidizing agent. Ce^{+4} used in redox process.

Correct option is (d).

NET DEC 2015

Q. Using crystal field theory, identify from the following complex ions that shows same μ_{eff} (spin only) values

- (A) $[\text{CoF}_6]^{3-}$, (B) $[\text{IrCl}_6]^{3-}$, (C) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$,

- (a) A and B (b) B and C (c) A and C (d) A, B, and C

Ans.

Unpaired electrons

$$[\text{CoF}_6]^{3-} \Rightarrow d^6 (\text{H}_{\text{sp}}) \Rightarrow t_{2g}^4 e_g^2 \quad 4$$

$$[\text{IrCl}_6]^{3-} \Rightarrow d^6 (\text{L}_{\text{sp}}) \Rightarrow t_{2g}^6 e_g^0 \quad 0$$

$$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} \Rightarrow d^6 (\text{H}_{\text{sp}}) \Rightarrow t_{2g}^4 e_g^2 \quad 4$$

Correct option is (c).

Q. The correct statement for Mn–O bond lengths in $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ is

- (a) All bonds are equal
- (b) Four bonds are longer than two others
- (c) Two bonds are longer than four others
- (d) They are shorter than the Mn–O bond in $[\text{MnO}_4]^-$

Ans. $[\text{Mn}(\text{H}_2\text{O})_6]^{2+} : \text{Mn}^{+2} \Rightarrow d^5$

↑	↑	↑	↑	↑
---	---	---	---	---

All energy levels are equally filled up as water is a weak field ligand, and hence no Jahn-Teller distortion is observed i.e., all bonds are in equal distance.

Correct option is (a).

Q. Identify the complex ions in sequential order when ferroin is used as an indicator in the titration of iron(II) with potassium dichromate. (phen=1,10-phenanthroline)

- (a) $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{3+}$
- (b) $[\text{Fe}(\text{phen})_3]^{3+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$
- (c) $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$
- (d) $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$

Ans. $[\text{Fe}(\text{phen})_3]^{2+} \xrightarrow{\text{Oxidising agent}} [\text{Fe}(\text{phen})_3]^{3+} + e$

In presence of dichromate the colour changes from red to blue.

Correct option is (a).

Q. The W–W bond order in $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-Cl})(\text{CO})_2]_2$ is

- (a) three
- (b) two
- (c) one
- (d) zero

Ans.

Total valence electron (A) = $(6 + 5 + 3 + 4) \times 2 = 36$

$B = n \times 18 - A = 2 \times 18 - 36 = 0$

Therefore, the number of M–M bond = $\frac{B}{2} = 0$.

Correct option is (d).

Q. $[\text{MnO}_4]^-$ is deep purple in colour whereas $[\text{ReO}_4]^-$ is colourless. This is due to greater energy required for

- (a) d–d transitions in the Re compound compared to the Mn compound
- (b) d–d transitions in the Mn compound compared to the Re compound
- (c) charge transfer from O to Re compared to O to Mn
- (d) charge transfer from O to Mn compared to O to Re

Ans. The colour arises due to LMCT. The difference in colour is due to the difference in position of central metal ion, Mn is 3d block element (lower energy) and Re is 5d block element (higher energy).

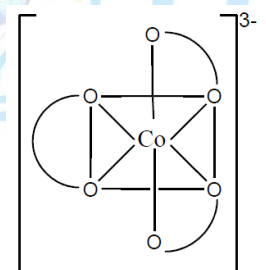
Correct option is (c).

Q. Among the following complexes

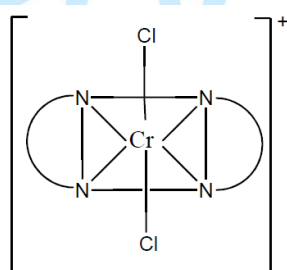
A. $[\text{Co}(\text{ox})_3]^{3-}$, B. $\text{trans}-[\text{CoCl}_2(\text{en})_2]^+$, C. $[\text{Cr}(\text{EDTA})]^-$ the chiral one(s) is/are,

- (a) A and B
- (b) C and B
- (c) C only
- (d) A and C

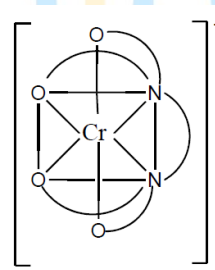
Ans.



(A) No plane of symmetry
Optically Active



(B) Plane of symmetry
Optically Inactive



(C) No plane of symmetry
Optically Active

Correct

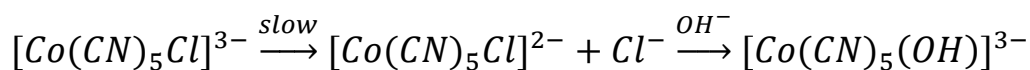
option is (d).

Q. The correct statement about the substitution reaction of $[\text{Co}(\text{CN})_5\text{Cl}]^{3-}$ with OH^- to give $[\text{Co}(\text{CN})_5(\text{OH})]^{3-}$ is,

- (a) it obeys first order kinetics
- (b) its rate is proportional to the concentration of both the reactants
- (c) it follows the SN^1_{CB} mechanism
- (d) its rate is dependent only on the concentration of $[\text{OH}]^-$

Ans. $[\text{Co}(\text{CN})_5\text{Cl}]^{3-} + \text{OH}^- \rightarrow [\text{Co}(\text{CN})_5(\text{OH})]^{3-} + \text{Cl}^-$

Reaction passes through a dissociative way as well the rate depends only upon the substrate



Correct option is (a).

Q. Choose the correct statements about Tanabe-Sugano diagrams:

- A. E/B is plotted against Δ_o/B .
- B. The zero energy is taken as that of the lowest term.
- C. Terms of the same symmetry cross each other.
- D. Two terms of the same symmetry upon increase of ligand field strength bend apart from each other.

Correct answer is

- a. A and B b. A and C c. A, B and D d. A, B, C and D

Correct option is (c).

NET JUNE 2016

Q. $[\text{Ni}^{\text{II}}\text{L}_6]^{n+ \text{ or } n-}$ shows absorption bands at 8500, 15400, and 26000 cm^{-1} whereas $[\text{Ni}^{\text{II}}\text{L}'_6]^{n+ \text{ or } n-}$, at 10750, 17500 and 28200 cm^{-1} . L and L' are respectively

- (a) OH^- and N_3^- (b) Cl^- and I^-
(c) NCS^- and RCO_2^- (d) H_2O and NH_3

Ans. For the first complex, the absorption bands are at low energy level i.e., ligand is weak field and the later is strong field.

Correct option is (d).

Q. The number of microstates present in ^3F term is

- (a) 3 (b) 21 (c) 9 (d) 28

Ans. As we know , microstate is calculated as $(2S + 1)(2L + 1)$.

Now for 'F', $L = 3$

Hence total no. of microstates are 21

Correct option is (b)



Q. Complex $[\text{Cr}(\text{bipyridyl})_3]^{3+}$ shows red phosphorescence due to transition

- (a) ${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$ (b) ${}^4\text{T}_{1g} \leftarrow {}^4\text{A}_{2g}$ (c) ${}^4\text{T}_{2g} \leftarrow {}^2\text{E}_g$ (d) ${}^2\text{E}_g \leftarrow {}^4\text{A}_{2g}$

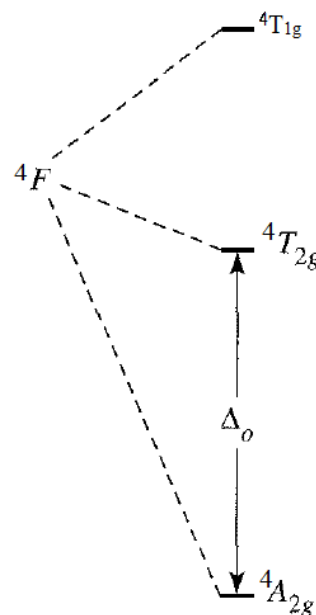
Ans.

$[\text{Cr}(\text{bipyridyl})_3]^{3+} \Rightarrow d^3 \equiv {}^4\text{F}$ (Ground state term)

Phosphorescence is a spin-forbidden transition and also occurs when electron comes from excited state to ground.

Hence, ${}^4\text{T}_{2g} \leftarrow {}^2\text{E}_g$ is responsible for the transition.

Correct option is (c).



d³ electronic configuration

Q. The complex that shows orbital contribution to the magnetic moment, is

- (a) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (b) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ (c) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (d) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$

Ans. When t_{2g} sets of orbital is unequally filled up, it shows orbital contribution.

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+} \rightarrow t_{2g}^6 e_g^3 \rightarrow$ No contribution

$[\text{Ni}(\text{H}_2\text{O})_6]^{2+} \rightarrow t_{2g}^6 e_g^2 \rightarrow$ No contribution

$[\text{Co}(\text{H}_2\text{O})_6]^{2+} \rightarrow t_{2g}^5 e_g^2 \rightarrow$ Orbital contribution

$[\text{Cr}(\text{H}_2\text{O})_6]^{2+} \rightarrow t_{2g}^3 e_g^1 \rightarrow$ No contribution

Correct option is (c).

Q. A 100 mL solution of $2.5 \times 10^{-3} \text{M}$ in Bi(III) and Cu(II) each, is photometrically titrated at 745 nm with 0.1M EDTA solution. Identify correct statements for this titration

- (A) Total volume of EDTA solution used is 5 mL
- (B) 3 mL of EDTA is required to complex Bi(III) and 2 mL for Cu(II)
- (C) 2.5 mL of EDTA is used for each metal ion
- (D) First break in titration curve is for Cu(II)

Correct statements are

- (a) A and B (b) A and C (c) A, B and C (d) B, C and D

Ans. Milimoles of each ion are 0.25 in solution.

On titrating with 0.1M EDTA each ion will take 2.5 ml of EDTA

So total used EDTA is $2.5 + 2.5 = 5$

Correct option is (b).

Q. The room temperature magnetic moment (μ_{eff} in BM) for a monomeric Cu(II) complex is greater than 1.73. This may be explained using the expression:

- (a) $\mu_{\text{eff}} = \mu_s \left(1 - \frac{\alpha\lambda}{\Delta}\right)$ (b) $\mu_{\text{eff}} = \sqrt{n(n+2)}$
 (c) $\mu_{\text{eff}} = \sqrt{4s(s+1) + L(L+1)}$ (d) $\mu_{\text{eff}} = \sqrt{g(j+1)}$

Ans. Cu(II) is a $3d^9 (t_{2g}^6 e_g^3)$ electronic system where in ground state the t_{2g} level equally filled up but upon pursuing energy, at excited state, the t_{2g} levels are becomes unequally filled up ($t_{2g}^5 e_g^4$) i.e., the μ_{eff} is been calculated by $\mu_{\text{eff}} = \mu_s \left(1 - \frac{\alpha\lambda}{\Delta}\right)$.

Correct option is (a).

NET DEC 2016

Q. In the hydrolysis of $\text{trans}[\text{Co}(\text{en})_2\text{Cl}(\text{A})]^+$, if the leaving group is chloride, the formation of *cis*-product is the least, when A is

- (a) NO_2^- (b) NCS^- (c) Cl^- (d) OH^-

Ans. The π -donor ligands such as Cl^- , Br^- , I^- , N-bonded NCS^- etc. stabilises the TBP intermediate and favour the stereochemical change. The trans-form has tendency to isomer $\text{A} = \text{NO}_2^- < \text{Cl}^- < \text{NCS}^- < \text{OH}^-$

Correct option is (a)

Q. The nephelauxetic parameter β is highest for

- (a) Br^- (b) Cl^- (c) CN^- (d) F^-

Ans. The series of Nephelauxetic parameter is



Correct option is (d).

Q. The ${}^2\text{E}_g \leftarrow {}^4\text{A}_{2g}$ transition in the electronic spectrum of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ occurs nearly at

- (a) 650 nm (b) 450 nm (c) 350 nm (d) 200 nm

Ans. The ${}^2\text{E}_g \leftarrow {}^4\text{A}_{2g}$ transition in the electronic spectrum of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ occurs nearly at 650nm.

Correct option is (a).

Q. For $[\text{Ce}(\text{NO}_3)_4(\text{OPPh}_3)_2]$, from the following

- A. Its aqueous solution is yellow-orange in color
- B. Coordination number of Ce is ten
- C. It shows metal to ligand charge transfer
- D. It is diamagnetic in nature

The correct answer is

- (a) A and B (b) A and C (c) A, B and D (d) B, C and D

Ans. $[\text{Ce}(\text{NO}_3)_4(\text{OPPh}_3)_2] \Rightarrow \text{Ce}^{4+} \equiv 4f^0$ i.e., no f-f transition.

No unpaired electrons i.e., diamagnetic.

Colour is due to LMCT and coordination no = 10.

Correct option is (C).

Q. Consider the following statements for $[\text{FeO}_4]^{4-}$.

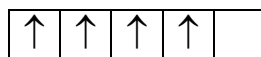
- A. It is paramagnetic
- B. It has T_d symmetry
- C. Adopts distorted square planar geometry
- D. Shows approximately D_{2d} symmetry

The correct answer is

- (a) A, B and C (b) A, C and D (c) A and D (d) A and B

Ans.

$[\text{FeO}_4]^{4-} \Rightarrow \text{Fe}^{+4} \equiv 3d^4 \equiv$



Jahn- Teller distorted away from the tetrahedral towards a flattered structure.

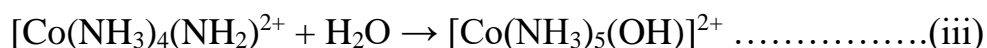
It is paramagnetic as $n = 4$, $\pi = \sqrt{24}BM$.

Correct option is (c).

Q. For OH^- catalysed S_{N}^1 conjugate base mechanism of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$, the species obtained in the first step of the reaction is/are

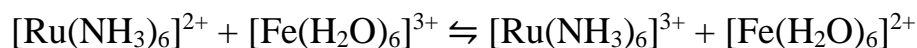
- (a) $[\text{Co}(\text{NH}_3)_5(\text{OH})]^{2+} + \text{Cl}^-$ (b) $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+ + \text{H}_2\text{O}$
 (c) $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)^{2+} + \text{Cl}^-$ (d) $[\text{Co}(\text{NH}_3)_5\text{Cl}(\text{OH})]^+$ only

Ans.



Correct option is (b)

Q. In the following redox reaction with an equilibrium constant $K = 2.0 \times 10^8$,



the self exchange rates for oxidant and reductant are $5.0 \text{ M}^{-1}\text{s}^{-1}$ and $4.0 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$, respectively. The approximate rate constant ($\text{M}^{-1}\text{s}^{-1}$) for the reaction is

- (a) 3.16×10^6 (b) 2.0×10^6 (c) 6.32×10^6 (d) 3.16×10^4

Ans. We know,

$$k_{12} = (k_{11}k_{12}f)^{1/2} = (5 \times 4 \times 10^3 \times 2 \times 10^8 \times 1.0)^{1/2} = 2.0 \times 10^6$$

Correct option is (b)

NET JUNE 2017

Q. CdS, HgS and BiI₃, are coloured due to

- (a) $L \rightarrow M$ charge transfer transitions
- (b) $d \rightarrow d$ electronic transitions
- (c) $M \rightarrow L$ charge transfer transitions
- (d) combination of $L \rightarrow M$ charge transfer and $d \rightarrow d$ electronic transitions

Ans.

CdS, HgS and BiI₃, are coloured due to LMCT as the metal ions are strong oxidizing agent and ligands are reducing one. No $d \rightarrow d$ electronic transitions takes place.

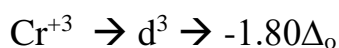
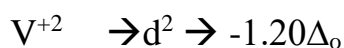
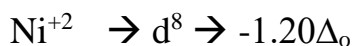
Correct option is (a).

Q. The relative rates of water exchange for the hydrated complexes of (1) Ni²⁺, (2) V²⁺ and (3) Cr³⁺ ions follows the trend

- (a) (1) > (2) > (3)
- (b) (1) < (2) < (3)
- (c) (1) > (2) < (3)
- (d) (1) < (2) > (3)

Ans.

CFSE of the metal ions in Oh field is



Higher the charge density higher will be the enthalpy of hydration. [See curve of Variation of hydration energy with respect to no of d electrons].

Correct option is (a).

Q. A copper(II) complex having distorted octahedral geometry shows an absorption band at 625 nm. Given spin-orbit coupling of the complex as -625 cm^{-1} , the μ_{eff} (in B.M.) is

- (a) 1.73 (b) 1.81 (c) 1.63 (d) 1.93

Ans. $\mu_{eff} = \mu_s \left(1 - \frac{\alpha\lambda}{\Delta}\right)$

$$\Delta = \frac{1}{\lambda} = \frac{1}{625 \times 10^{-7}}$$

For $\text{Cu}^{+2} \rightarrow 2D \rightarrow \alpha=2, \lambda=-625 \text{ cm}^{-1}$.

$$\begin{aligned}\mu_{eff} &= 1.73 \left(1 - \frac{2 \times (-625)}{10^7} \times 625\right) = 1.73 \left(1 + \frac{2 \times 625 \times 625}{10^7}\right) \\ &= 1.73 \times 1.078\end{aligned}$$

$$\boxed{\mu_{eff} = 1.864}$$

Correct option is (b).

Q. Consider the following statements for octahedral complexes, (a) $[\text{CrF}_6]^{3-}$, (b) $[\text{Cr}(\text{ox})_3]^{3-}$ and (c) $[\text{Cr}(\text{en})_3]^{3+}$:

- A. their $d \rightarrow d$ transitions are at $14900, 17500, \text{ and } 21800 \text{ cm}^{-1}$, respectively
 B. their spin-only magnetic moments are same
 C. two of them have optical isomers
 D. all of them show Jahn-Teller distortion

The correct statements are

- (a) A, B, and C (b) A, C, and D (c) B, C, and D (d) B and D

Ans. As per spectrochemical series $\text{F}^- < \text{ox}^{2-} < \text{en}$.

All complex have same number of odd electrons as well as same spin only magnetic moment.

Correct option is (a).

Q. The μ_{eff} of $[\text{Fe}(\text{S}_2\text{CNEt}_2)_3]$ changes with temperature with the involvement of two electronic states. The states are

- (a) low spin $^2T_{2g}$ and high-spin $^6A_{1g}$ (b) low spin $^1A_{1g}$ and high-spin $^3T_{2g}$
 (c) low spin 2E_g and high-spin $^6A_{1g}$. (d) low spin $^2T_{2g}$ and high-spin $^4T_{1g}$.

Ans. In $[\text{Fe}(\text{S}_2\text{CNEt}_2)_3]$ the metal is Fe^{3+}

Fe^{+3} (Lsp) : $t_{2g}^5 e_g^2$ ($^2T_{2g}$)

Fe^{+3} (Hsp) : $t_{2g}^3 e_g^2$ ($^6A_{1g}$)

Correct option is (a).

Q. Match the items in the three columns.

Complex (column 1)	Color (column 2)	Absorption max (λ_{max} , nm) (column 3)
A. $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2$	I. Blue	X. 675
B. $[\text{Ni}(\text{NH}_3)_6](\text{NO}_3)_2$	II. Green	Y. 565
C. $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$	III. Violet	Z. 615

The correct answer is

- (a) A-II-X; B-I-Z; C-III-Y (b) A-I-X; B-II-Y; C-III-Z
 (c) A-III-Y; B-I-Z; C-II-X (d) A-I-X; B-II-Z; C-III-Y

Ans. The Δ_o value increases when moving from $\text{H}_2\text{O} < \text{NH}_3 < \text{en}$.

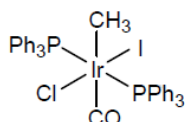
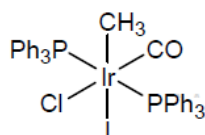
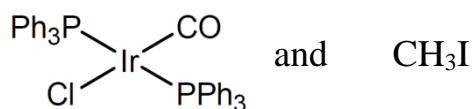
Thus, order for energy absorption is $675(\text{A}) < 615(\text{B}) < 565(\text{C})$.

Complementary colour, Blue \rightarrow Orange, Green \rightarrow Red, Violet \rightarrow Yellow.

Thus the order of energy is yellow $>$ orange $>$ red.

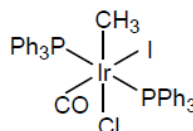
Correct option is (a).

Q. Identify the product in the reaction between going at room temperature *via* S_N^2 mechanism



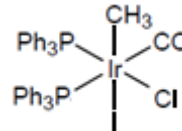
(a)

(c)



(b)

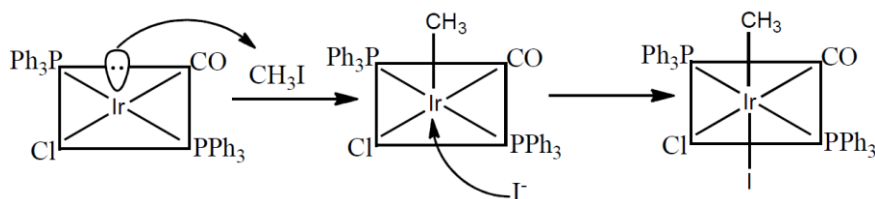
(d)



Ans.

Mechanism:

Correct option is (a).



NET DEC 2017

Q. For the following complexes, the increasing order of magnetic moment (spin only value) is

- A. $[\text{TiF}_6]^{3-}$ B. $[\text{CrF}_6]^{3-}$ C. $[\text{MnF}_6]^{3-}$ D. $[\text{CoF}_6]^{3-}$
- (a) $D < A < B < C$ (b) $C < A < D < B$
- (c) $B \approx A < D < C$ (d) $A < B < C \approx D$

Ans.

$$[\text{TiF}_6]^{3-} \Rightarrow \text{Ti}^{3+} \Rightarrow 3d^1 \Rightarrow t_{2g}^1 e_g^0 \Rightarrow n=1$$

$$[\text{CrF}_6]^{3-} \Rightarrow \text{Cr}^{3+} \Rightarrow 3d^3 \Rightarrow t_{2g}^3 e_g^0 \Rightarrow n=3$$

$$[\text{MnF}_6]^{3-} \Rightarrow \text{Mn}^{3+} \Rightarrow 3d^4 \Rightarrow t_{2g}^3 e_g^1 \Rightarrow n=4$$

$$[\text{CoF}_6]^{3-} \Rightarrow \text{Co}^{3+} \Rightarrow 3d^6 \Rightarrow t_{2g}^4 e_g^2 \Rightarrow n=4$$

Correct option is (d)

Q. In trigonal prismatic ligand field, the most stabilized d orbital is

- (a) d_z^2 (b) d_{xy} (c) d_{xz} (d) d_{yz}

Ans.

In trigonal prismatic ligand field, the energy splitting of d orbitals are

$$d_{yz} = d_{xy} > d_z^2 > d_x^2 - y^2 = d_{xy}$$

Correct option is (b).

Q. The most **unstable** complex on the basis of electro-neutrality principle among the following is

- (a) $[\text{Al}(\text{OH}_2)_6]^{3+}$ (b) $[\text{Al}(\text{NH}_3)_6]^{3+}$ (c) $[\text{AlF}_6]^{3-}$ (d) $[\text{Al}(\text{NCCH}_3)_6]^{3+}$

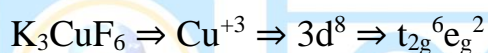
Ans. In case of $[\text{Al}(\text{NH}_3)_6]^{3+}$, N is sp^3 hybridized i.e., least stable.

Correct option is (b)

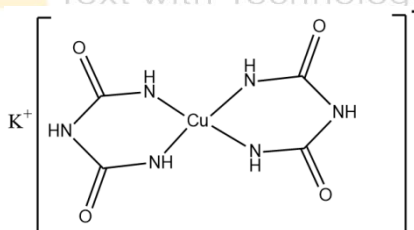
Q. The geometry around Cu and its spin state for K_3CuF_6 and KCuL_2 , [$\text{H}_2\text{L} = \text{H}_2\text{NCONHCONH}_2$], respectively are:

- (a) (octahedral, high-spin) and (square planar, low-spin)
 (b) (octahedral, low-spin) and (square planar, low-spin)
 (c) (trigonal prismatic, high-spin) and (tetrahedral, high-spin)
 (d) (trigonal prismatic, low-spin) and (tetrahedral, high-spin)

Ans.



Hence square planar complex



Correct option is (a).

Q. The total degeneration of the ground state term of Co^{II} (high spin) in octahedral geometry is

- (a) 18 (b) 12 (c) 28 (d) 9

Ans. $\text{Co}^{2+} (\text{Hsp}) \rightarrow t_{2g}^5 e_g^2$

Hence $S = 3/2$ and $L = 3$

Therefore, degeneracy $= (2S+1)(2L+1) = 4 \times 7 = 28$

Correct option is (c).

Q. High spin Complex of 3d metal ion **M** has a magnetic moment of 2.9 B.M. in octahedral coordination environment and 4.1 B.M. in tetrahedral environment. The **M** ion is

- (a) Co^{III} (b) Ni^{II} (c) Cu^{II} (d) Co^{II}

Ans.

$\text{Ni}^{+2} (3d^8) \Rightarrow 3d^8 \Rightarrow t_{2g}^6 e_g^2, n=2, \mu = 2.9 \text{ BM}$

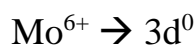
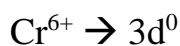
$\text{Ni}^{+2} (\text{Td}) \Rightarrow 3d^8 \Rightarrow t_2^4 e^4, n=2, \mu = 4.1 \text{ BM}$

High value (4.1 BM) is due to orbital contribution because t_2 is electronically degenerate.

Q. For electronic spectra of K_2CrO_4 (A) and K_2MoO_4 (B) the correct combination is

- (a) Transition is $d-d$ and λ_{max} for $A < B$
- (b) Transition is LMCT and λ_{max} for $A < B$
- (c) Transition is LMCT and λ_{max} for $A > B$
- (d) Transition is MLCT and λ_{max} for $A > B$

Ans.



In both Cr^{+6} and Mo^{6+} ions, there is no d electrons, therefore, there is no $d-d$ transition, since in both the ions oxidation state is very high there is LMCT in both the case.

Correct option is (c).

Q. Identify the pair of molecules which are isoelectronic as well as isostructural from the following

$[\text{Pd}(\text{PPh}_3)_4]$ (A), $[\text{V}(\text{CO})_6]$ (B), $[\text{Cr}(\text{CO})_6]$ (C), $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ (D), $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{NO})]$ (E), $\text{Ni}(\text{CO})_4$ (F)

Ans.

$[\text{Pd}(\text{PPh}_3)_4]$ and $\text{Ni}(\text{CO})_4$ are iso-electronic as per 18e- rule and square planar.

Correct option is (b).

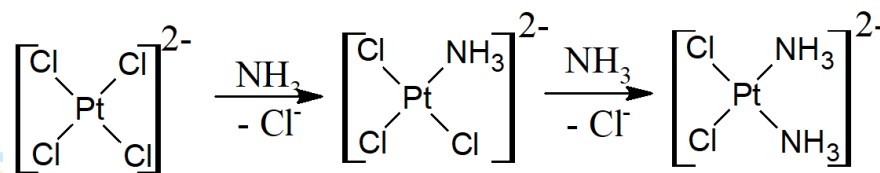
Q. Choose the correct set of statements for *cis*-platin.

- (A) It can be prepared from $K_2[PtCl_4]$
- (B) It can be prepared from $[Pt(NH_3)_4]Cl_2$
- (C) In its preparation, the observed *trans* effect for Cl^- is greater than that of NH_3
- (D) In blood it stays in equilibrium with *cis*- $[Pt(NH_3)_2Cl(H_2O)]^+$
- (E) In DNA strand, it binds to two adjacent cytosine bases

The correct set is

- (a) A, C and D (b) A, C, D and E (c) B, C and D (d) B, C, D and E

Ans.



Trans effect:

$Cl^- > NH_3$

In blood it stays in equilibrium with *cis*- $[Pt(NH_3)_2Cl(H_2O)]^+$

In DNA strand, *cis*-platin binds to two adjacent guanine bases.

Correct option is (a).