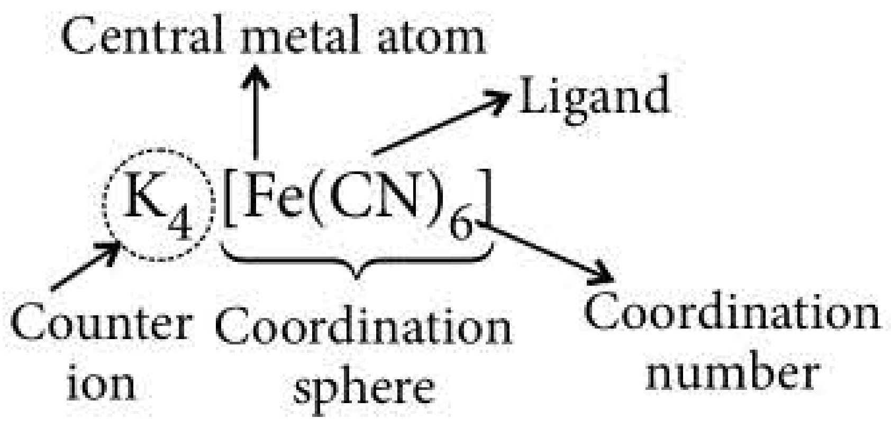
COORDINATION COMPOUNDS

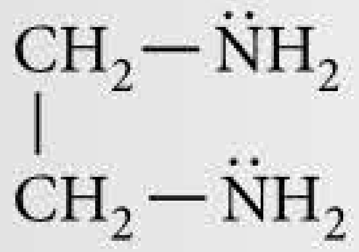
- A coordination compound contains a central metal atom or ion surrounded by a number of oppositely charged ions or neutral molecules, called ligands.



Types of Ligands

Monodentate
Only one donor atom is present, *e.g.*, NH_3, H_2O, CN^-, NO_2^-, CO

Bidentate
Two donor atoms are present, *e.g.*, ethylenediamine (*en*)

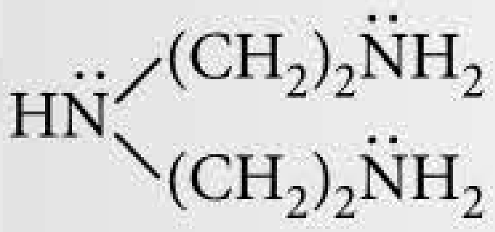


$$\begin{array}{l} CH_2-\ddot{N}H_2 \\ | \\ CH_2-\ddot{N}H_2 \end{array}$$

oxalato (*ox*)

$$\begin{array}{l} COO^- \\ | \\ COO^- \end{array}$$

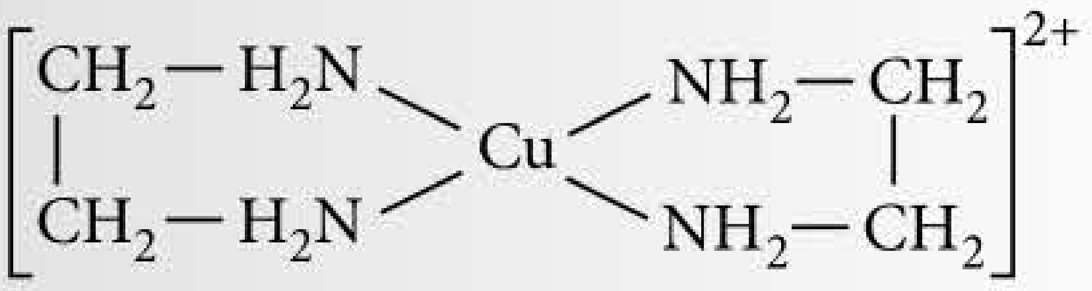
Tridentate
Three donor atoms are present, *e.g.*,



Diethylenetriamine (*dien*)

Polydentate
Tetradentate : Triethylenetetraamine (*trien*)
Pentadentate : Ethylenediaminetriacetate ion
Hexadentate : Ethylenediaminetetraacetate ion (EDTA)

Chelating ligands
A bidentate or a polydentate ligand is known as chelating ligand if on coordination it results in the formation of a closed or cyclic ring structure. The complex thus formed are called chelates.

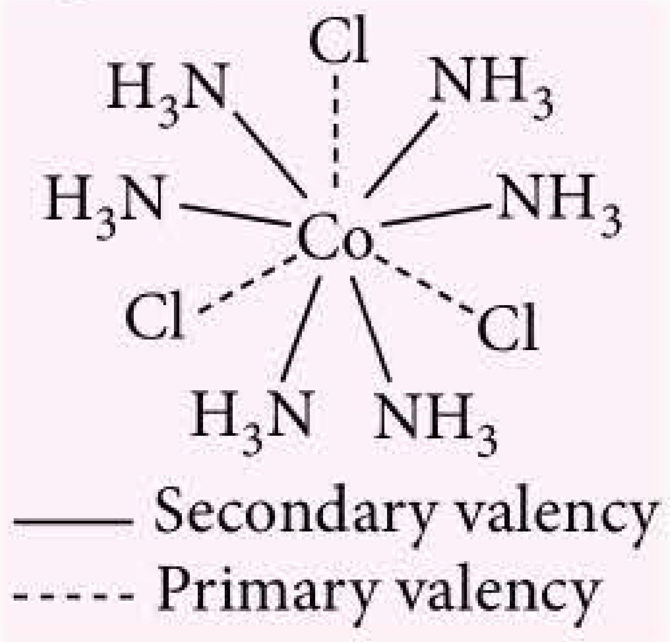


EAN RULE

EAN = Z – O.N + 2(C.N)
Z = Atomic number of central metal atom
O.N. = Oxidation number of central metal atom
C.N. = Coordination number of central metal atom

WERNER'S THEORY

- Metal possesses two types of valencies, *i.e.*, primary valency (ionisable) and secondary valency (non-ionisable).
- Primary valency corresponds to the oxidation state of the central metal and secondary valency represents the coordination number of the metal.
- Primary valencies are satisfied by negative ions, while secondary valencies may be satisfied by neutral or negative ions.



- Negative ion can satisfy both primary and secondary valencies at the same time.

NOMENCLATURE OF COORDINATION COMPOUNDS

Rules for nomenclature :

- Positive ion is named first followed by negative ion.
- Negative ligands are named by adding suffix – o.
- Positive ligands are named by adding suffix – ium.
- Neutral ligands are named as such without adding any suffix or prefix.
- Ligands are named in alphabetical order.
- Name of the ligands is written first followed by name of metal with its oxidation number mentioned in roman numerals in simple parenthesis.
- Number of the polysyllabic ligands *i.e.*, ligands which have numbers in their name, is indicated by prefixes bis, tris, tetrakis, etc.
- When both cation and anion are complex ions, the metal in negative complex is named by adding suffix -ate.

Ligand	Name in complexes	Ligand	Name in complexes
Azide (N_3^-)	Azido	Oxalate ($C_2O_4^{2-}$)	Oxalato
Bromide (Br^-)	Bromido	Oxide (O^{2-})	Oxo
Chloride (Cl^-)	Chlorido	Ammonia (NH_3)	Ammine
Cyanide (CN^-)	Cyano	Carbon monoxide (CO)	Carbonyl
Fluoride (F^-)	Fluorido	Ethylene-diamine (*en*)	Ethylene-diamine
Hydroxide (OH^-)	Hydroxo	Pyridine (C_5H_5N)	Pyridine
Carbonate (CO_3^{2-})	Carbonato	Water (H_2O)	Aqua

Few examples illustrate the nomenclature :

- $[Pt(NH_3)_6]Cl_4$ – Hexaammineplatinum(IV) chloride
- $[Cu(en)_2]SO_4$ – *bis*(ethane-1,2-diamine)copper(II) sulphate
- $K_4[Fe(CN)_6]$ – Potassium hexacyanoferrate(II)
- $[Pt(NH_3)_4Cl_2][PtCl_4]$ – Tetraamminedichlorido-platinum(IV) tetrachloridoplatinate(II)

Isomerism in Coordination Compounds

Stereoisomerism

Structural Isomerism

Ionisation isomerism

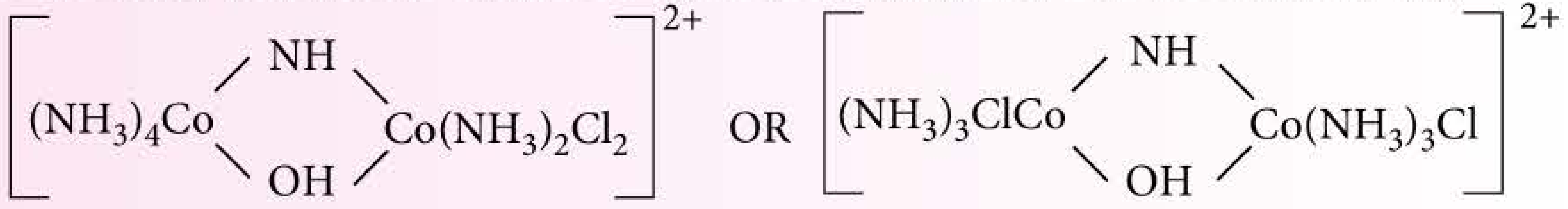
- Isomerism arises in the compounds which have same molecular formula but give different ions in solution, *e.g.*, $[Co(NH_3)_5Br]SO_4$, $[Co(NH_3)_5SO_4]Br$.

Linkage isomerism

- Occurs in the complex compounds which contain ambidentate ligand. *e.g.*, $[Co(NH_3)_5NO_2]Cl_2$ or $[Co(NH_3)_5ONO]Cl_2$

Coordination (position) isomerism

- Exhibited by polynuclear complexes by interchanging the position of ligands. *e.g.*,



Hydrate or solvate isomerism

- Isomerism arises when different number of water molecules are present inside and outside the coordination sphere, *e.g.*, $CrCl_3{\cdot}6H_2O$ exists in three isomeric forms.
  $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]H_2O.Cl_2$, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

Polymerisation isomerism

- Isomerism arises in the compounds which have same stoichiometric composition but different molecular composition.
  $[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_4]$ $[PtCl_4]$

Coordination isomerism

- Isomerism arises when both complex cation and complex anion are present.
  $[Pt(NH_3)_4]$ $[CuCl_4]$ and $[PtCl_4]$ $[Cu(NH_3)_4]$

Stereoisomerism

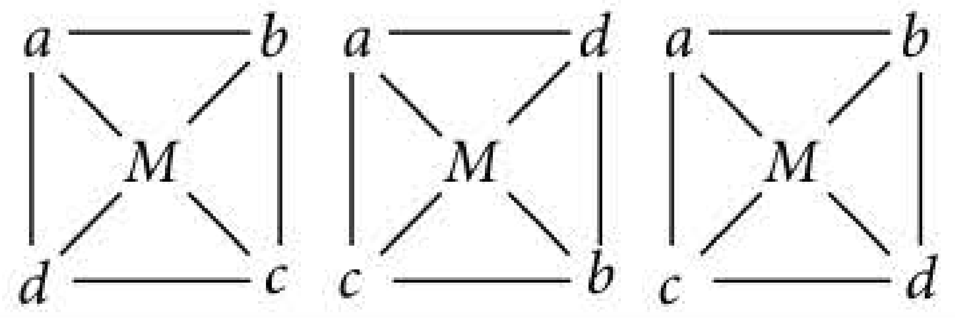
Geometrical

Tetrahedral Complex
Geometrical isomerism is not possible

Square planar complex

Structure	No. of isomers
$Mabcd$	3
$Mabc_2$	2 (*cis-trans*)
Ma_2b_2	2 (*cis-trans*)
$M(ab)_2$	2 (*cis-trans*)

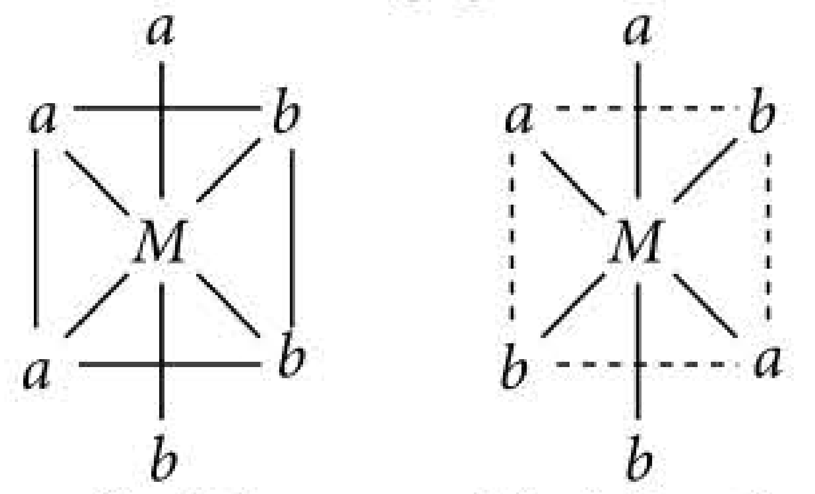
Isomers of *Mabcd* :



Octahedral complex

Ma_2b_4	2 (*cis-trans*)
$M(aa)_2b_2$	2 (*cis-trans*)
$M(aa)_2bc$	2 (*cis-trans*)
Ma_3b_3	2 (*fac/mer*)

Isomers of Ma_3b_3:



Facial or '*fac*'　　*Meridional* or '*mer*'

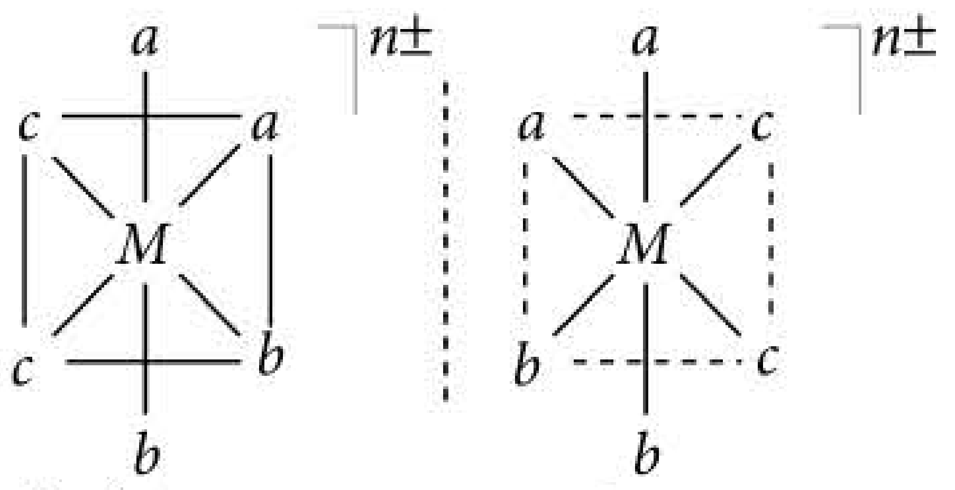
Optical

Tetrahedral complexes : Optical isomerism is possible but no isomer has been isolated.

Square planar complexes : Optical isomerism is not possible.

Octahedral complexes :
Octahedral complexes like $Ma_2b_2c_2$, $Mabcdef$, $[M(AA)_3]^{n\pm}$, $[M(AA)_2a_2]^{n\pm}$ $[M(AA)_2ab]$and $[M(AB)_3]$ show optical isomerism.

Isomers of $[Ma_2b_2c_2]^{n\pm}$:



cis-d-isomer　　*cis-l*-isomer

**AA* and *AB* are bidentate ligands.

BONDING IN COORDINATION COMPOUNDS

- For explaining the nature of bonding and different properties of coordination compounds such as colour, geometry and magnetic properties, some theories has been developed.

Valence Bond Theory (VBT)

- The central atom uses its number of empty *s*-, *p*- and *d*-atomic orbitals which is equal to its coordination number.
- These empty orbitals hybridise together to form hybrid orbitals.
- The non-bonding electrons of the metal occupy the inner orbitals.
- The *d*-orbitals participating in the process of hybridization in octahedral complexes may either be $(n-1)d^2sp^3$, inner or low spin complexes or nsp^3d^2 outer or high spin complexes.

Coordination number	Type of hybridization	Geometry	Examples
2	sp	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3 dsp^2	Tetrahedral Square planar	$[Ni(CO)_4]$, $[NiX_4]^{2-}$, $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$ (where $X = Cl^-, Br^-, I^-$) $[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$ $[Ni(NH_3)_4]^{2+}$
5	sp^3d	Trigonal bipyramidal	$[Fe(CO)_5]$, $[SbF_5]^{2-}$
6	d^2sp^3 or sp^3d^2	Octahedral	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$ $[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$

Differences between inner orbital and outer orbital complexes :

S.N.	Inner orbital octahedral complexes or low spin complexes	Outer orbital octahedral complexes or high spin complexes
1.	The complexes are formed by strong ligands and showing d^2sp^3-hybridisation.	The complexes are formed by weak ligands and showing sp^3d^2-hybridisation.
2.	These complexes generally possess less number of unpaired electrons *i.e.*, they show either low or no magnetic moment.	These complexes generally possess greater number of unpaired electrons *i.e.*, they show high magnetic moment.
3.	These are less reactive *i.e.*, more stable. Substitution reactions are difficult to occur.	These are reactive *i.e.*, less stable. Substitution reactions are easy to occur.

Crystal Field Theory (CFT)

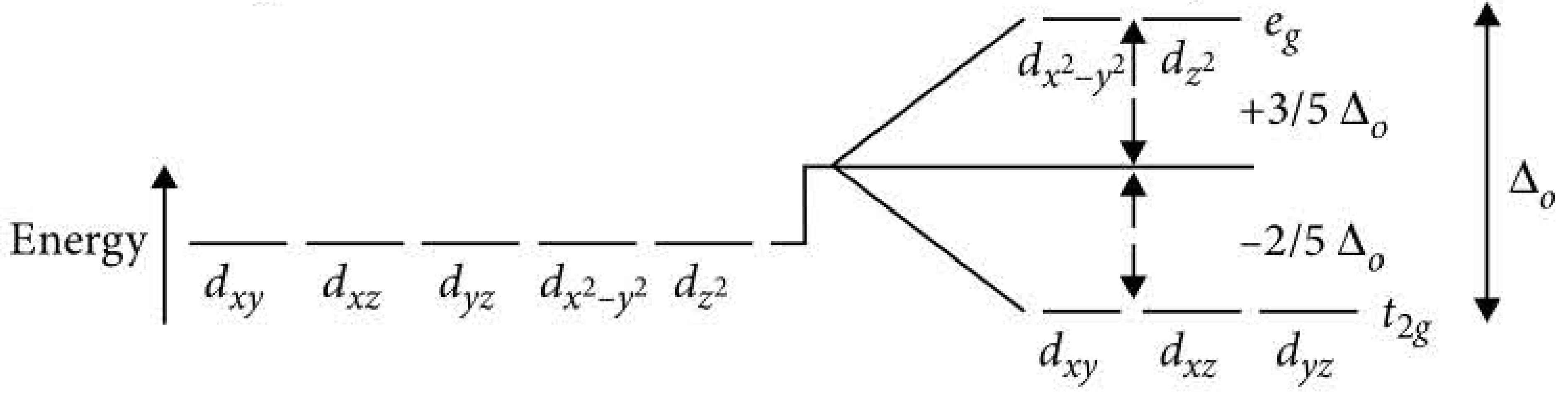
- According to crystal field theory, the bonding in complexes is purely electrostatic.
- The complex is regarded as a combination of a central metal ion surrounded by ligands which act as point charges or point dipoles.
- Interaction between positively charged central metal ion or atom and the negatively charged ligands are of two types.
  - The attractive forces arise due to the positive metal ion and the negatively charged ligands or the negative end of a polar neutral molecules.
  - The repulsive forces arise between the lone pairs on the ligands and electrons in the *d*-orbitals of the metal or atom.
- In a free transition metal or ion, there are five *d*-orbitals which are designated as d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}. The five *d*-orbitals are split into two sets, depending on the nature of their orientation in space. This splitting known as crystal field splitting.
- The splitting is different in different structures with different coordination numbers. The crystal field splitting (Δ_o) depends upon the nature of the ligands. The ligands which cause only a small degree of crystal field splitting are called weak field ligands while those which cause a large degree of splitting are called strong field ligands.

← Strong Weak →

$CO > CN^- > NO_2^- > en > NH_3 \approx Py > EDTA > H_2O > ox > OH^- > F^- > NO_3^- > Cl^- > SCN^- > Br^- > I^-$

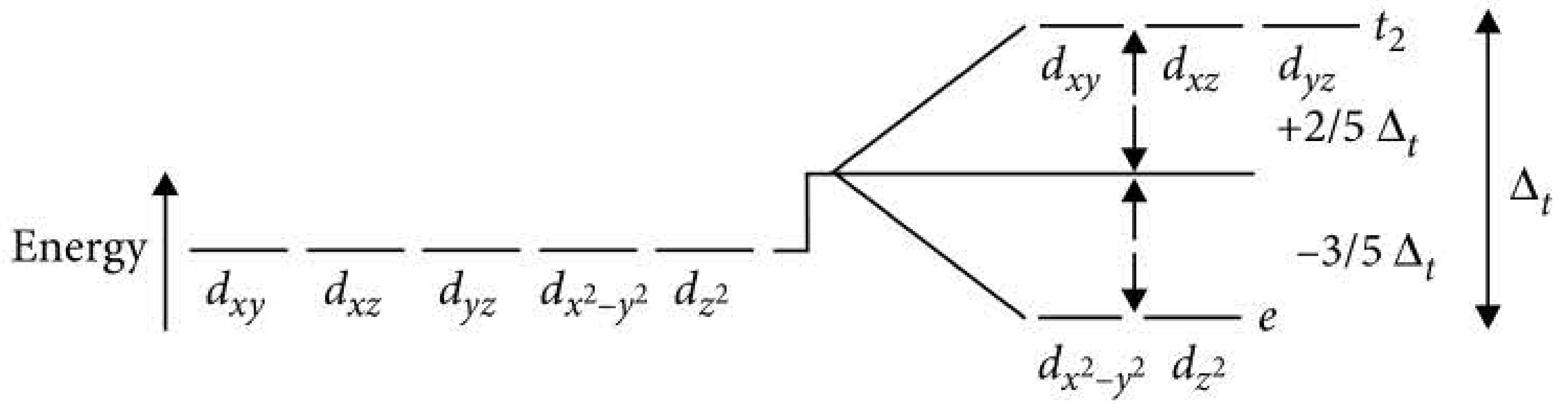
Relative ligand field strengths

- In octahedral complexes, e_g orbitals are of higher energy than that of t_{2g} orbitals.



Splitting of *d*-orbitals in an octahedral complex

- In tetrahedral complexes, *e* orbitals are of lower energy than t_2 orbitals.



Splitting of *d*-orbitals in a tetrahedral complex

Splitting in tetrahedral complexes (Δ_t) is considerably less than in octahedral complexes (Δ_o) *i.e.*, $\Delta_t \approx 4/9\ \Delta_o$

Calculation of CFSE

- In an octahedral complex, each electron occupying t_{2g} orbital results in lowering of energy by $-0.40\ \Delta_o$ (or -4 Dq). Similarly, each electron occupying e_g orbital results in increase of energy by $+0.60\ \Delta_o$ (or $+6$ Dq). Thus, CFSE $= (-0.4x + 0.6y)\ \Delta_o$

  where, x = number of electrons occupying t_{2g} orbitals and y = number of electrons occupying e_g orbitals. Negative value of CFSE indicates net lowering in energy, *i.e.*, gain in stability.

Calculation of CFSE Values for d^1 to d^{10} Configurations

Metal ion configuration	Low spin state (strong field ligand)	CFSE (Δ_o/Dq)	High spin state (weak field ligand)	CFSE (Δ_o/Dq)
d^1	$t_{2g}^1\ e_g^0$	$-0.4 \times 1 = -0.4\ \Delta_o$ or -4 Dq	$t_{2g}^1\ e_g^0$	$-0.4 \times 1 = -0.4\ \Delta_o$ or -4 Dq
d^2	$t_{2g}^2\ e_g^0$	$-0.4 \times 2 = -0.8\ \Delta_o$ or -8 Dq	$t_{2g}^2\ e_g^0$	$-0.4 \times 2 = -0.8\ \Delta_o$ or -8 Dq
d^3	$t_{2g}^3\ e_g^0$	$-0.4 \times 3 = -1.2\ \Delta_o$ or -12 Dq	$t_{2g}^3\ e_g^0$	$-0.4 \times 3 = -1.2\ \Delta_o$ or -12 Dq
d^4	$t_{2g}^4\ e_g^0$	$-0.4 \times 4 = -1.6\ \Delta_o$ or -16 Dq	$t_{2g}^3\ e_g^1$	$-0.4 \times 3 + 0.6 = -0.6\ \Delta_o$ or -6 Dq
d^5	$t_{2g}^5\ e_g^0$	$-0.4 \times 5 = -2.0\ \Delta_o$ or -20 Dq	$t_{2g}^3\ e_g^2$	$-0.4 \times 3 + 2 \times 0.6 = 0.0\ \Delta_o$ or 0 Dq
d^6	$t_{2g}^6\ e_g^0$	$-0.4 \times 6 = -2.4\ \Delta_o$ or -24 Dq	$t_{2g}^4\ e_g^2$	$-0.4 \times 4 + 2 \times 0.6 = -0.4\ \Delta_o$ or -4 Dq
d^7	$t_{2g}^6\ e_g^1$	$-0.4 \times 6 + 0.6 = -1.8\ \Delta_o$ or -18 Dq	$t_{2g}^5\ e_g^2$	$-0.4 \times 5 + 2 \times 0.6 = -0.8\ \Delta_o$ or -8 Dq
d^8	$t_{2g}^6\ e_g^2$	$-0.4 \times 6 + 2 \times 0.6 = -1.2\ \Delta_o$ or -12 Dq	$t_{2g}^6\ e_g^2$	$-0.4 \times 6 + 2 \times 0.6 = -1.2\ \Delta_o$ or -12 Dq
d^9	$t_{2g}^6\ e_g^3$	$-0.4 \times 6 + 3 \times 0.6 = -0.6\ \Delta_o$ or -6 Dq	$t_{2g}^6\ e_g^3$	$-0.4 \times 6 + 3 \times 0.6 = -0.6\ \Delta_o$ or -6 Dq
d^{10}	$t_{2g}^6\ e_g^4$	$-0.4 \times 6 + 4 \times 0.6 = 0.0\ \Delta_o$ or 0 Dq	$t_{2g}^6\ e_g^4$	$-0.4 \times 6 + 4 \times 0.6 = 0.0\ \Delta_o$ or 0 Dq

Similarly, for tetrahedral complex CFSE $= (-0.6\ x + 0.4\ y)\ \Delta_t$

- The actual configuration adopted by the complex is decided by the relative values of Δ_o and P, where P represents the energy required for electron pairing in a single orbital.
- If Δ_o is less than $P(\Delta_o < P)$, we have weak field, the fourth electron will enter one of the e_g orbitals giving the configuration, $t_{2g}^3\ e_g^1$. It will be high spin complex.
- If Δ_o is more than $P(\Delta_o > P)$, we have strong field and the pairing will occur in the t_{2g} orbitals with e_g orbitals remaining unoccupied giving the configuration, $t_{2g}{}^4$. It will be low spin complex.

STABILITY OF COORDINATION COMPOUNDS

- Consider the following reaction

  $M + 4L \rightleftharpoons ML_4$ ...(i)

  The equilibrium constant for the reaction is called the stability constant and is represented by β_4.

  $$\beta_4 = \frac{[ML_4]}{[M][L]^4}$$

  Larger the stability constant, higher is the proportion of ML_4 that exists in solution.

$$M + L \rightleftharpoons ML\ ; \qquad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2\ ; \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \rightleftharpoons ML_3\ ; \qquad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$ML_3 + L \rightleftharpoons ML_4\ ; \qquad K_4 = \frac{[ML_4]}{[ML_3][L]}$$

K_1, K_2 etc. referred to as stepwise stability constants. Overall stability constant, $\beta_4 = K_1 \times K_2 \times K_3 \times K_4$,

or, $$\beta_4 = \frac{[ML_4]}{[M][L]^4}$$

The instability constant or the dissociation constant of coordination compounds is defined as the reciprocal of the formation constant (stability constant).

ORGANOMETALLIC COMPOUNDS

Organometallic compounds :
Compounds in which metal is directly attached to carbon, are called organometallic compounds.

Sigma bonded compounds

Metal carbon bond is sigma bond. *e.g.,* $R - Mg - X$, R_2Zn, $(CH_3)_4Sn$, $(C_2H_5)_4Pb$ etc.

π-bonded compounds

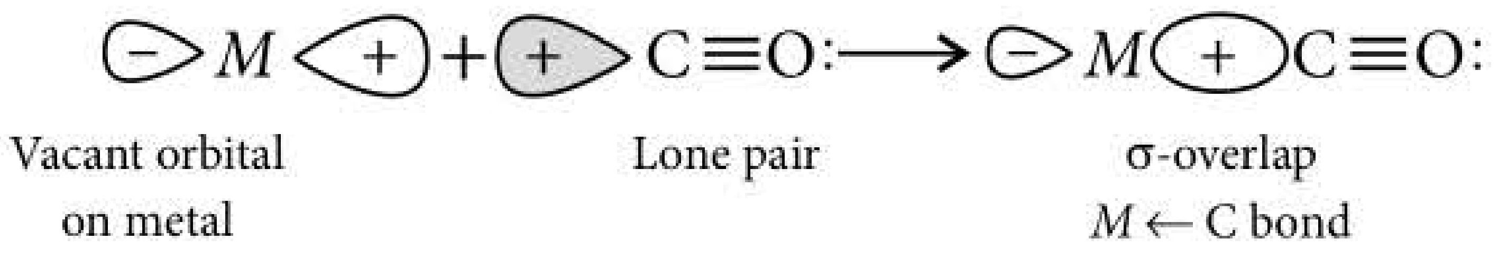
Metal and ligands form a bond that involve π-electrons of ligands. *e.g.,* ferrocene, zeise's salt, etc.

σ and π bonded compounds

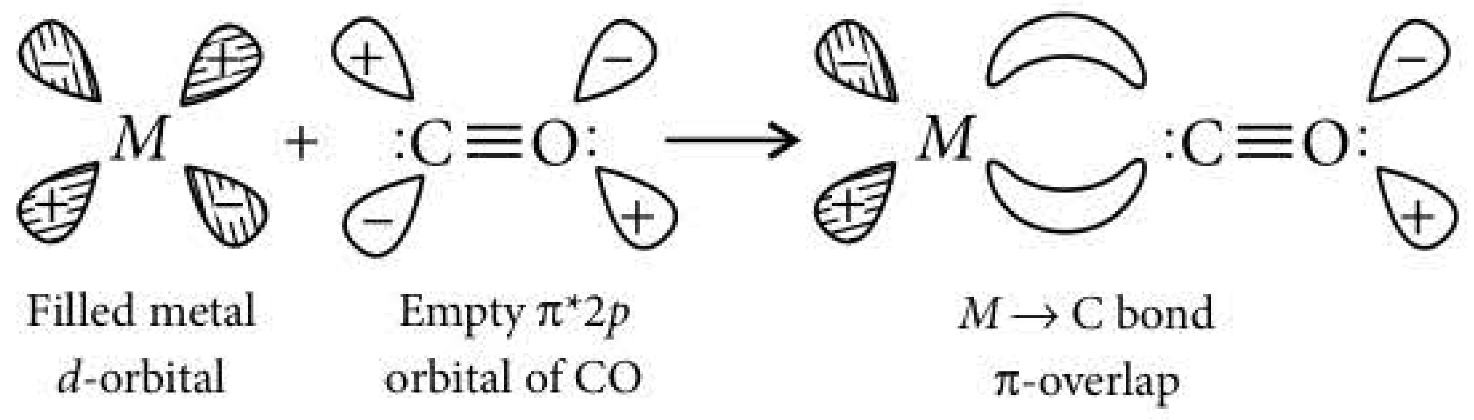
These compound possess both σ -and π- bonding between *M* and ligands. *e.g.,* $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ etc.

BONDING OF METAL CARBONYLS

- In a metal carbonyl, the metal-carbon bond possesses both the σ- and π-character. A σ-bond between metal and carbon atoms is formed when a vacant hybrid orbital of the metal atom overlaps with an orbital on C atom of carbon monoxide containing a lone pair of electrons.



Formation of π-bond is caused when a filled orbital of the metal atom overlaps with a vacant antibonding π* orbital of C atom of carbon monoxide. This overlap is also called back donation of electrons by metal atom to carbon *i.e.*, synergic bonding.



The π-overlap is perpendicular to the nodal plane of σ-bond.

IMPORTANCE OF COORDINATION COMPOUNDS

- In both qualitative and quantitative methods of analysis.
- In metallurgical operations.
- In photography.
- **In electroplating :** Metal complexes release metal slowly and thus give a uniform coating *i.e.*, electroplating of the metal on the desired object.
- **In biological processes :** Coordination compounds are essential in storage and transport of oxygen as electron transfer agents, acts as catalysts and are used in photosynthesis.
- **In medicinal field :** The complex of Ca with EDTA is used for treatment of lead poisoning. *Cis*-platin is used as an antitumor agent.

INFOSHOTS

Some Recent Developments in Coordination Chemistry

Catalysts of the type $(R_3Q)_2MX_2$ (R is an alkyl, aryl, or phenoxy group ; Q is P, As, or Sb ; M is Ni, Pd, or Pt, X is a halogen or halogenoid are recently developed. In the presence of such a substance, polyunsaturated compounds, especially esters of long chain fatty acids are hydrogenated until one double bond remains. The hydrogenation is preceded by *cis-trans* rearrangement of the double bond and migration of the double bonds along the carbon chain ocours for a conjugated system. Another research project has shown that certain bacteria can utilize the nitrogen from *d*-$[Co(en)_3]Cl_3$ but that *l*-$[Co(en)_3]Cl_3$ inhibits their growth.