# Co-ordination Compounds & D Block

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By
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# Co-ordination Chemistry

Solutions containing two (or) more simple stable compounds in molecular proportions when allowed to evaporate, crystals of new substances are obtained

$$KCl + MgCl_2 + 6H_2O \longrightarrow KCl.MgCl_2.6H_2O$$

carnalite

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O$$

$$CuSO_4 + 4NH_3 \longrightarrow CuSO_4.4NH_3$$

# IUPAC Nomenclature for Co-ordination Compounds

1) Positive part is named first and is followed by the negative part.

2). For complex ion, name the ligands in alphabetical order regardless of their charge followed by metal.

3). When more number of ligands of the same kind are present , prefixes like di, tri, tetra, penta and hexa are used.

An exception occurs when the name of the ligand includes a number (di, tri etc).

To avoid confusion in such cases bis, tris and tetrakis are used instead of di, tri and tetra and the name of the ligand is placed in brackets.

# Nomenclature

- In complexes, the complex ion is enclosed by square brackets. Groups are named in order metal - coordinated groups in order; negative ligands, neutral ligands; positive ligands (and alphabetically according to the first symbol with in each group).

- Complex containing two or more metal atoms- polynuclear :

For more than two or more bridging ligands of the same kind, di-$\mu$, tri-$\mu$ are used

  - Bridging groups are listed alphabetically with the other groups unless the symmetry of the molecule allows a simpler name.
  - If a bridging group bridges more than two metal atoms it is shown as $\mu_3$, $\mu_4$, $\mu_5$ or $\mu_6$ to indicate how many atoms it is bonded to.

- Complete metal name is name of the metal, followed by-*ate* if the complex is an anion, followed by the oxidation number of the metal, indicated by roman numerals in parenthesis.

# Nomenclature : Latin Name of Element

- When there is a latin name for the metal, it is used to name the anion (except for Hg).

| English name | Latin name | Anion name |
|---|---|---|
| Copper | Cuprum | Cuprate |
| Gold | Aurum | Aurate |
| Iron | Ferrum | Ferrate |
| Lead | Plumbum | Plumbate |
| Silver | Argentum | Argentate |
| Tin | Stannum | Stannate |

| | |
|---|---|
| Dichloridobis(ethane-1,2-diamine)cobalt(III) | $[CoCl_2(en)_2]^+$ |
| $[Pt(NH_3)_2Cl(NO_2)]$ | diamminechloridonitrito-n-ptatinum(II) |
| $Hg[Co(SCN)_4]$ | mercurytetrathiocyanatocobaltate(III) |

# Bonding in Co-ordination Compounds

## Factors governing complex formation by Transition metals

- possess greater positive charge that attract the negatively charged ligands to form stable complexes.
- have vacant-d-orbitals that can accept lone pair of electrons donated by the ligands to form complex.

## Effective Atomic Number

- Co-ordinate bond formed between metal ion and ligand.
- Number of bond formed depends upon number of vacant orbitals
- Total electrons gained by central metal is called its effective atomic number
- Metal ion often obtain EAN of next inert gas ( exception exist).

**Example :**

Fe $\Rightarrow$ atomic number is 26

and forming a complex, $[Fe(CN)_6]^{4-}$

the number of electrons lost = 2

the number of electrons gained = 12 $\Rightarrow$ EAN = 36

# Isomerism in Coordination Compounds

- It is necessary to produce a symmetrical structure irrespective of the number of electrons involved.

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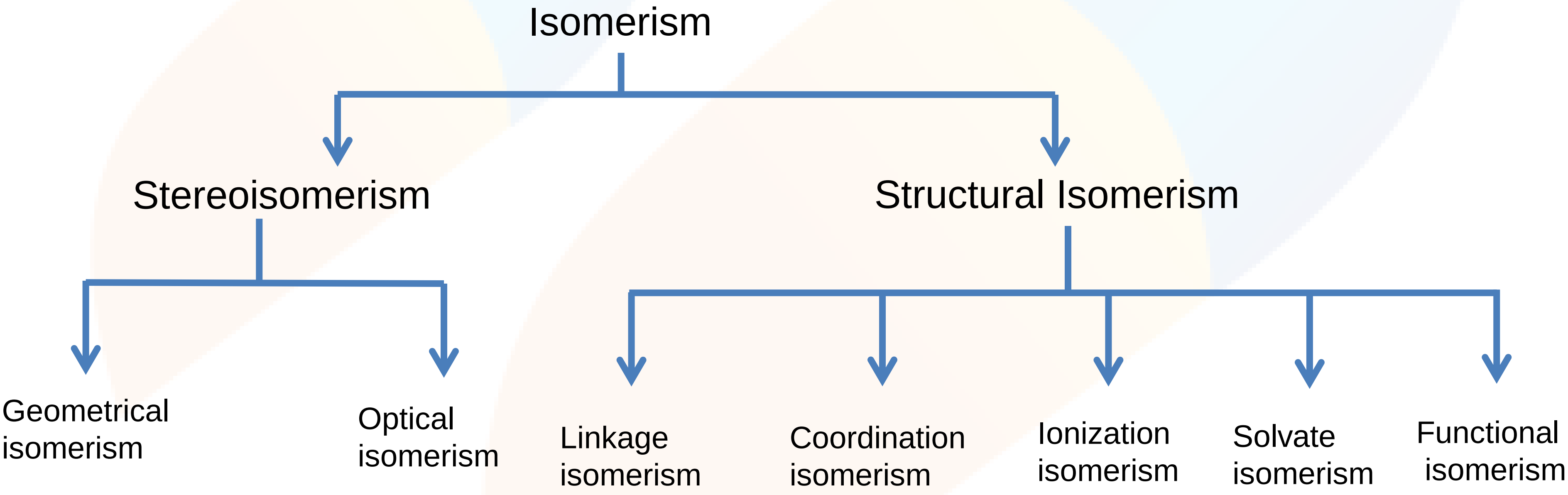
## Isomerism in Coordination Compounds

compounds with same chemical formula but different structural arrangements are called **isomers.**



- Isomerism
  - Stereoisomerism
    - Geometrical isomerism
    - Optical isomerism
  - Structural Isomerism
    - Linkage isomerism
    - Coordination isomerism
    - Ionization isomerism
    - Solvate isomerism
    - Functional isomerism

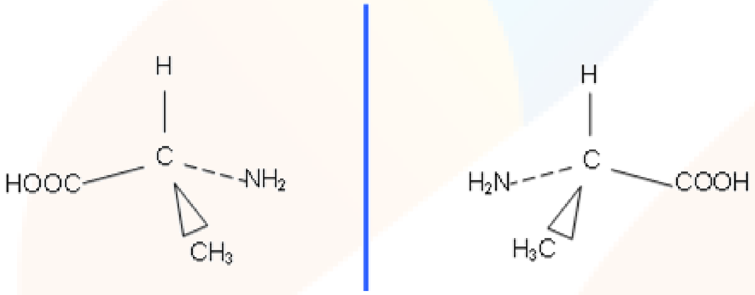
# Stereo-Isomerism

**Stereo-Isomerism** have same chemical formula and chemical bonds but they have different spatial arrangement.

Optical isomerism are mirror image but non- superimposable to each other called as enantiomers.

The molecules or ions that cannot be superimposed are called chiral

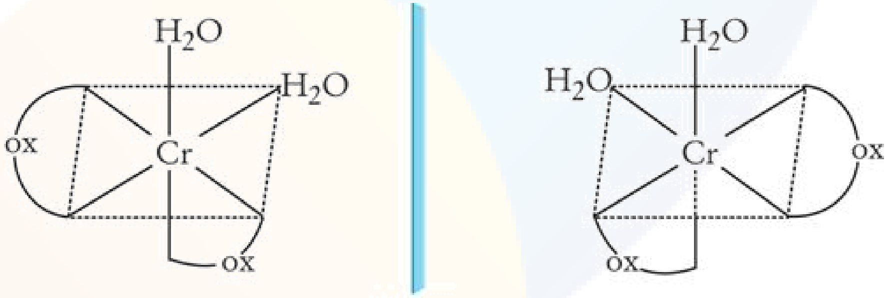
The two forms are called dextro (d)[rotate the plane polarise light clockwise] and laevo (l)[rotate the plane polarise light anticlockwise]



d-alanine

l-alanine

**Optical isomerism alanine**



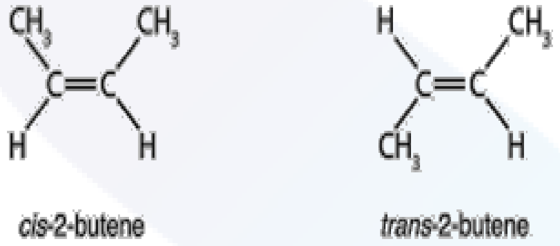
d-form

l-form

**Optical isomerism of $[Cr(H_2O)_2(ox)_2]$**

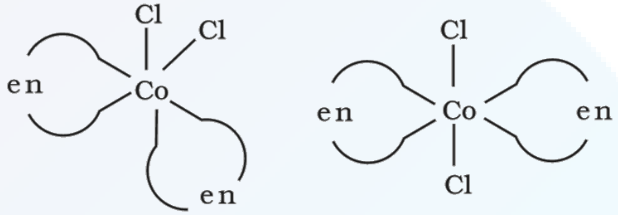
# Geometric Isomerism

Isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands.

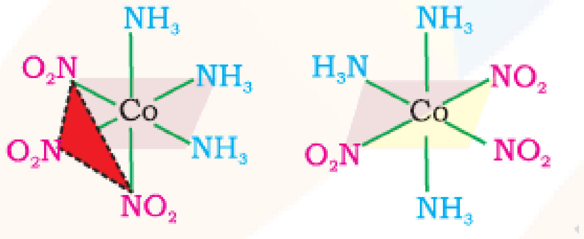


*cis*-2-butene *trans*-2-butene

**Geometrical isomers (cis and trans) of 2-butene**

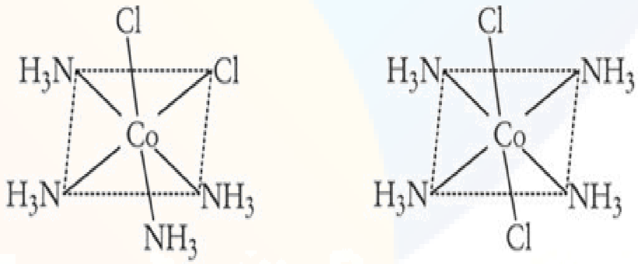


**Geometrical isomers (cis and trans) of $[CoCl_2(en)_2]$**



*fac–* *mer–*

**The facial (fac) and meridional (mer) isomers of $[Co(NH_3)_3(NO_2)_3]$**



**Geometrical isomers (cis and trans) of $[Co(NH_3)_4Cl_2]^+$**

# Structural Isomerism 2

## Linkage isomerism

Linkage isomerism in a coordination compound containing ambidentate ligand.

$[Co(NH_3)_5(NO_2)]Cl_2$

Nitrate ligand is bound through oxygen (-ONO) and by nitrogen ($-NO_2$)

## Coordination Isomerism

Isomerism aries from the interchange of ligand between cationic and anionic entities of different metal ions present in a complex.

$[Co(NH_3)_6][Cr(CN)_6]$ ⇨ $NH_3$ ligands are bound to $Co^{3+}$ and the $CN^-$ ligands to $Cr^{3+}$.

$[Cr(NH_3)_6][Co(CN)_6]$ ⇨ $NH_3$ ligands are bound to $Cr^{3+}$ and the $CN^-$ ligands to $Co^{3+}$.

# Structural Isomerism 3

## Ionization isomerism

isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.

$[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

## Solvate Isomerism

form of isomerism is known as ‘hydrate isomerism’ in case where water is involved as a solvent. This is similar to ionisation isomerism.

Aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

# Valence Bond Theory

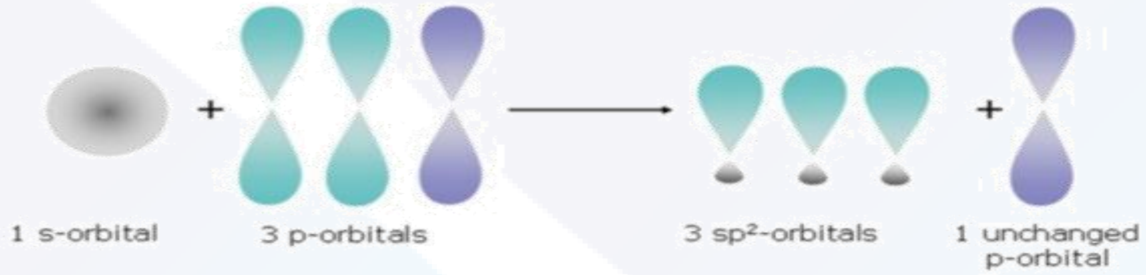
## Valence Bond Theory

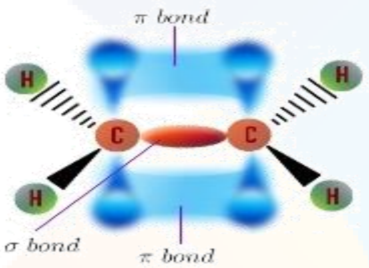
The valence-bond approach considers the overlap of the atomic orbitals (AO) of the participation atoms to form a chemical bond. Due to the overlapping, electrons are localized in the bond region.

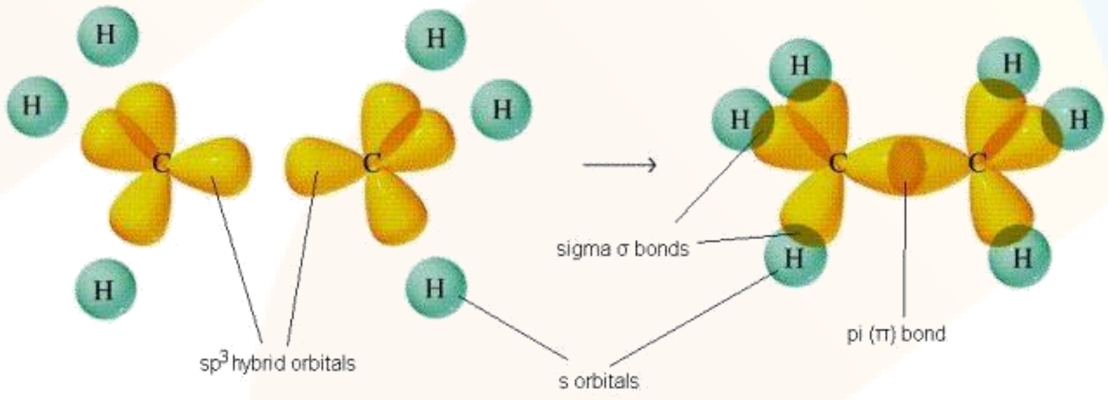
| Coordination Number | Types of hybridisation | Geometry |
|---|---|---|
| 2 | $sp$ | Linear |
| 4 | $sp^3$ | Tetrahedral |
| 4 | $dsp^2$ | Square Planar |
| 6 | $d^2sp^3$ | Octahedral |
| 6 | $sp^3d^2$ | Octahedral |

# Orbital Overlapping

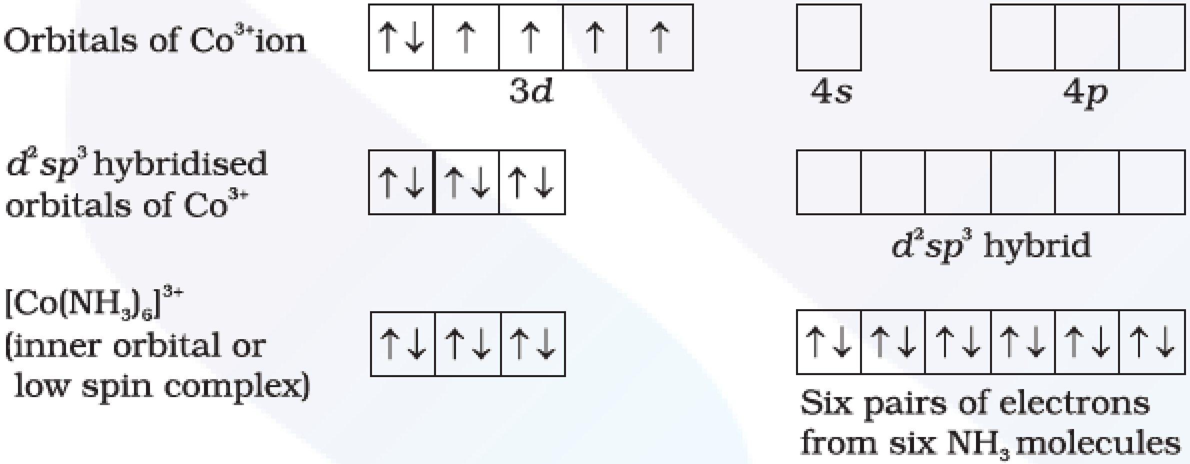
Atomic orbitals overlap and form  hybrid atomic orbital







# Limitations of Valence Bond Theory



cobalt ion is in +3 oxidation state

Electronic configuration $3d^6$

Diamagnetic

## Limitations of Valence Bond Theory

- ➢ It involves a number of assumptions.
- ➢ It does not give quantitative interpretation of magnetic data.
- ➢ It does not explain the colour exhibited by coordination compounds.
- ➢ It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds
- ➢ It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
- ➢ It does not distinguish between weak and strong ligands

# Crystal Field Theory

CFT is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interaction between the metal ion and the ligand.

## CFT octahedral coordination entities

six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal d- orbitals and the electrons (or negative charges) of the ligands.

**$d_{x^2-y^2}$ and $d_{z^2}$** orbital are in between the axis

**$d_{xy}$ , $d_{xz}$ , $d_{yz}$** orbitals on the axis

the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, $t_2g$ set and two orbitals of higher energy, eg set

The splitting of degenerate level due to the presence of ligands in definite geometry is termed as **crystal field splitting** and energy separation is denoted by $\Delta_{0.}$

# Crystal Field Splitting in Octahedral Coordination Entities

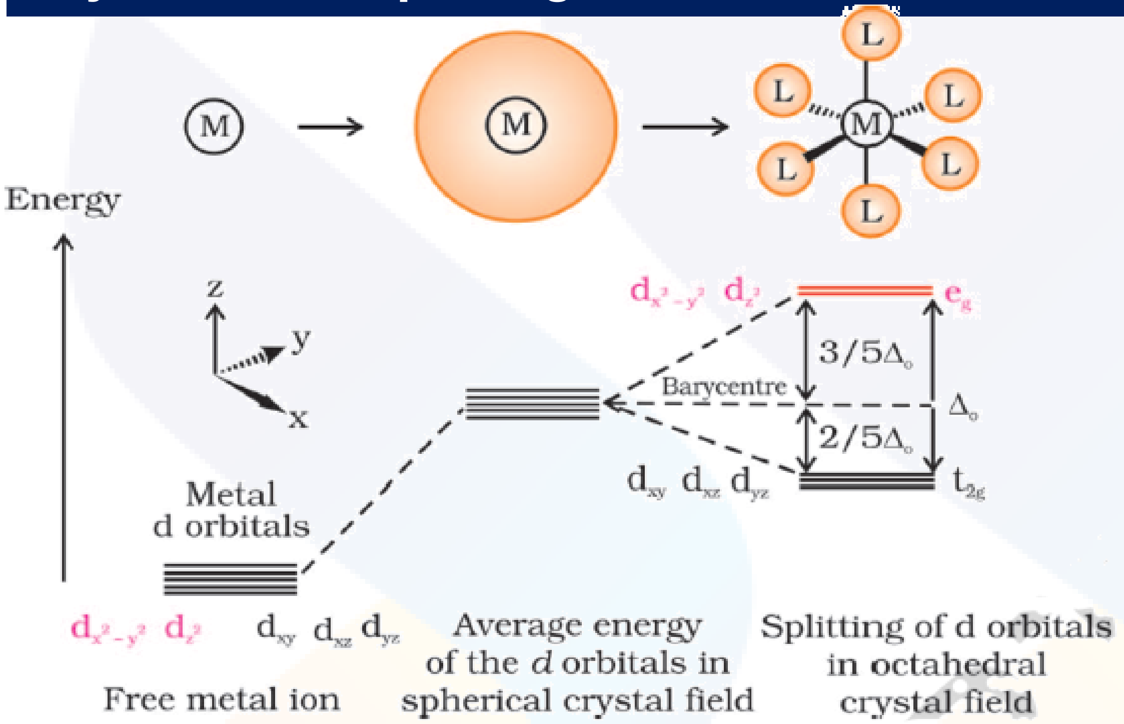


**Fig : d orbital splitting in an octahedral crystal field**

**Electron filling take place by hund's rule**

**$\Delta_0$ > P pairing take place , low spin complex, strong field ligand**

**$\Delta_0$ < P pairing will not take place ,high spin complex, weak field ligand**

ligands can be arranged in a series in the order of increasing field strength series is termed as **spectrochemical series.**

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$

$d^4$ to $d^7$ coordination entities are more stable for strong field as compared to weak field cases.

# Crystal Field Splitting in Tetrahedral Coordination Entities

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting

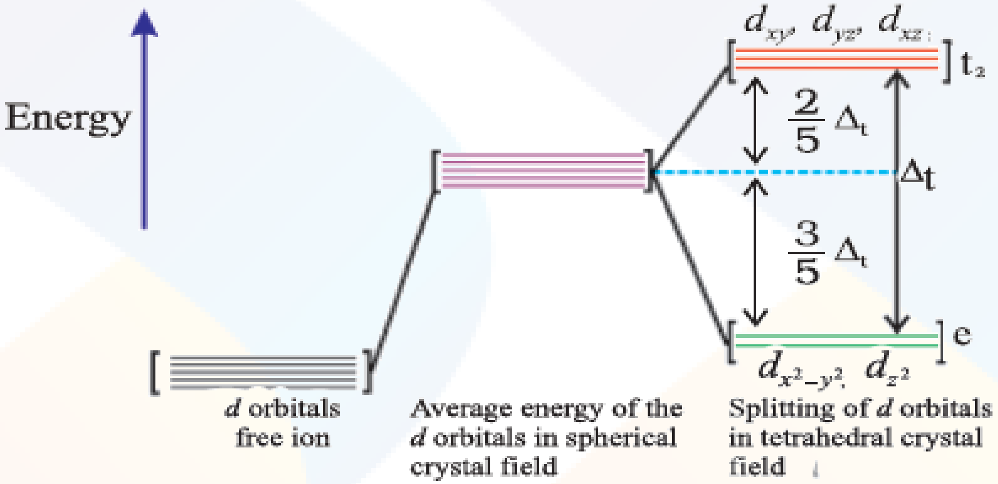


**Fig : d-orbital splitting in a tetrahedral crystal field**

Low spin configurations are rarely observed

# Colour in Coordination Compounds

White light as it passes through the sample , so the light that emerges is no longer white.

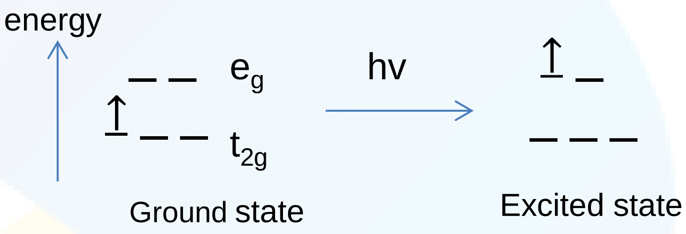
The colour of complex is complementary to that which is absorbed.

Green light is absorbed by the complex, it appears red.

the complex $[Ti(H_2O)_6]^{3+}$, which is violet in colour

$Ti^{3+}$ is a $3d^1$ system

$t_{2g}^1$ electronic configuration



If light corresponding to the energy of blue-green region is absorbed by the complex, it would excite the electron from t2g level to the eg level

Electron can jump from $t_{2g}$ to $e_g$ level.

The crystal field theory attributes the colour of the coordination compounds to d-d transition of the electron.

the complex appears violet in colour

# Colour in Coordination Compounds 2

| Coordination Entity | Wavelength of Light Absorbed (nm) | Colour of Light Absorbed | Colour of Coordination Entity |
|---|---|---|---|
| $[CoCl(NH_3)_5]^{2+}$ | 535 | Yellow 🟨 | Violet 🟪 |
| $[Co(NH_3)_5(H_2O)]^{3+}$ | 500 | Blue Green 🟩 | Red 🟥 |
| $[Co(NH_3)_6]^{3+}$ | 475 | Blue 🟦 | Yellow Orange 🟧 |
| $[Co(CN)_6]^{3-}$ | 310 | Ultraviolet ⬜ | Pale Yellow 🟨 |
| $[Cu(H_2O)_4]^{2+}$ | 600 | Red 🟥 | Blue 🟦 |
| $[Ti(H_2O)_6]^{3+}$ | 498 | Blue Green 🟩 | Purple 🟪 |

# $[Ni(H_2O)_6]^{2+}$ and Limitation of CFT

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

Ethane-1,2-diamine(en) is progressively added in the molar ratios **en:Ni**, 1:1, 2:1, 3:1, the following series of reactions and their associated colour changes occur:

$Ni(H_2O)_6]^{2+}$ (aq) + en (aq) = $[Ni(H_2O)_4(en)]^{2+}$(aq) + $2H_2O$

Green pale blue

$[Ni(H_2O)_4(en)]^{2+}$(aq) + en (aq) = $[Ni(H_2O)_2(en)_2]^{2+}$(aq) + $2H_2O$

blue / purple

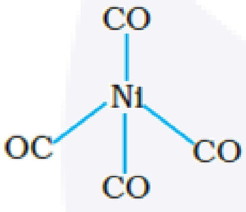
$[Ni(H_2O)_2(en)_2]^{2+}$(aq) + en (aq) = $[Ni(en)_3]^{2+}$(aq) + $2H_2O$

violet

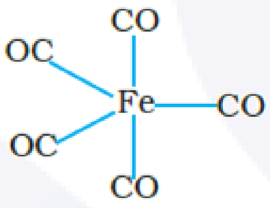
## Limitations of Crystal Field Theory

- from the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. The anionic ligands actually are found at the low end of the spectrochemical series.
- it does not take into account the covalent character of bonding between the ligand and the central atom.

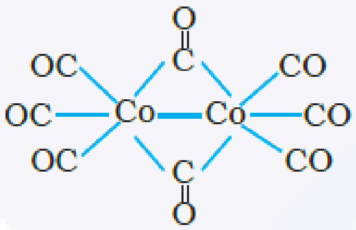
# Bonding in Metal Carbonyls



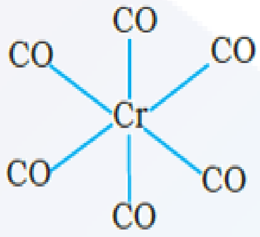
$Ni(CO)_4$
Tetrahedral



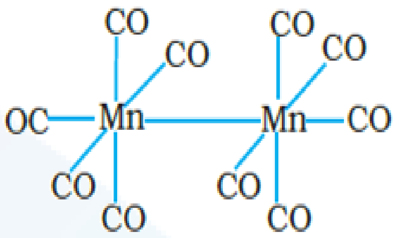
$Fe(CO)_5$
Trigonal bipyramidal



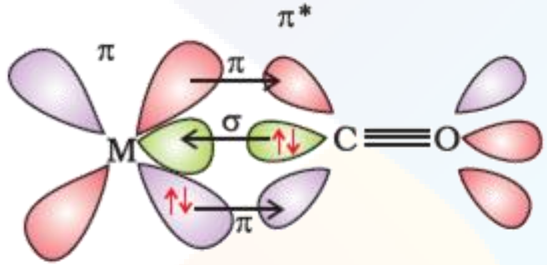
$[Co_2(CO)_8]$



$Cr(CO)_6$ Octahedral



$[Mn_2(CO)_{10}]$



Synergic bonding

The M–C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant anti-bonding π* orbital of carbon monoxide.

The metal to ligand bonding creates a **synergic effect** which strengthens the bond between CO and the metal.

## Stability of Coordination Compounds :

The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium.

Equilibrium constant for the association, quantitatively expresses the stability.

# Interstitial compounds and non stoichiometric compounds

## 12. Interstitial compounds and non stoichiometric compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. e.g. TiC, WC, TiH, ScH

They are usually non stoichiometric and are neither typically ionic nor covalent, for example, $Fe_{0.93}O$, $Ni_{0.98}O$ , $VH_{0.56}$ and $TiH_{1.7}$

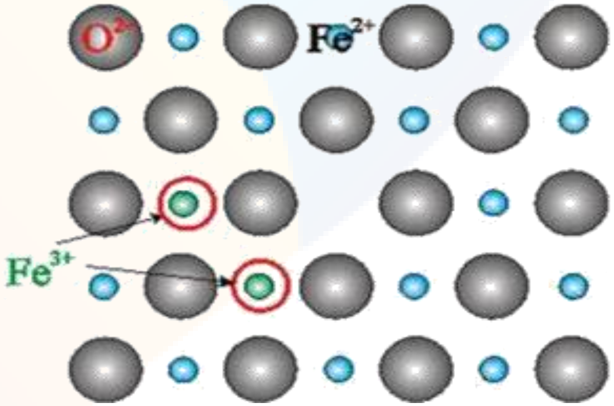
The principal physical and chemical characteristics of these compounds are as follows:

(i) They have high melting points, higher than those of pure metals.

(ii) They are very hard, some borides approach diamond in hardness.

(iii) They retain metallic conductivity.

(iv) They are chemically inert



**Non-stoichiometric compounds $Fe_xO$**

# Alloy and Complex Formation

## 13.Alloy formation

Condition for alloys formation : similar size of atoms.

**e.g.** (Ni-Cr) alloy

(M-Hg) amalgam

(copper-tin) bronze

## 14. Complex formation

Forms complexes because of

a) smaller sizes of the metal ions

b) availability of *d* orbitals for bond formation

c) their high ionic charges

$$Co^{3+} + 6(NH_3) \longrightarrow [Co(NH_3)_6]^{3+}$$

$$Fe^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-}$$

# Potassium Permanganate

## Compound of Mn

Potassium permanganate ($KMnO_4$)

### Preparation of $KMnO_4$

**Raw material used :** pyrolusite

$$MnO_2 + KOH + O_2 \longrightarrow K_2MnO_4$$

**Colour pink purple**

This $K_2MnO_4$ can be separated by electrolysis, $O_3$ treatment.

**Electrolysis**

$$K_2MnO_4 \longrightarrow 2K^+ + MnO_4^{2-}$$

$$MnO_4^{2-} \longrightarrow MnO_4^- + \text{electron}$$

$$K_2MnO_4 + Cl_2 \longrightarrow KMnO_4 + KCl$$

$$K_2MnO_4 + O_3 \longrightarrow KMnO_4$$

In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

# Properties of Potassium Permanganate($KMnO_4$)

$$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$$

**Acidic condition :**

$$KMnO_4 + H_2SO_4 \longrightarrow Mn^{2+} + K_2SO_4$$

$KMnO_4 \xrightarrow{H^+}$

Oxidising agent

$Fe^{2+} \longrightarrow Fe^{3+}$

$I^- \longrightarrow I_2$

$SO_3^{2-} \longrightarrow SO_4^{2-}$

$SO_2 \longrightarrow H_2SO_4$

$C_2O_4^{2-} \longrightarrow CO_2$

$S^{2-} \longrightarrow S$

$NO_2^- \longrightarrow NO_3^-$

| | |
|---|---|
| Acidic medium | +7 to +2 |
| Basic medium | +7 to +4 |
| Neutral medium | +7 to +6. |

# $KMnO_4$ in Neutral and Basic Medium

**Neutral conditions:**

$$KMnO_4+H_2O \longrightarrow MnO_2+KOH+[O]$$

Whenever $H_2S$ comes with oxidising agent it gives S

$$KMnO4 + H2O \longrightarrow$$

$$MnSO_4 \longrightarrow MnO_2$$

$$H_2S \longrightarrow S$$

$$I^- \longrightarrow IO_3^- \text{ (iodate ion)}$$

$$S_2O_3^{2-} \longrightarrow SO_4^{2-}$$

**Basic medium:**

$$KMnO_4+KOH \longrightarrow K_2MnO_4+H_2O+[O]$$

$$KMnO_4 + OH^- \longrightarrow$$

$$KI \longrightarrow KIO_3$$

$$CH_2{=}CH_2 \longrightarrow \begin{matrix} CH2\text{-}OH \\ | \\ CH2\text{-}OH \end{matrix}$$

$KMnO_4$ in basic medium oxidise ethene

**Order of oxidising agent :** $O_3 > KMnO_4 > K_2CrO_7$

# Potassium dichromate ($K_2CrO_7$)

## 2. Potassium dichromate ($K_2CrO_7$)

### Preparation

$$FeOCrO_3 + NaOH + O_2 \longrightarrow Na_2CrO_4 + Fe_2O_3$$

chromite ore basic medium

$$4FeCrO_3 + 8\ Na_2CO_3 + 7\ O_2 \longrightarrow 8Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$$

yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7 . 2H_2O$ can be crystallised.

$$2Na_2CrO_4 + 2\ HSO_4 \longrightarrow Na_2Cr_2O_7 + 2\ Na_2SO_4 + H_2O$$

Sodium dichromate is more soluble than potassium dichromate.

$$Na_2Cr_2O_7 + 2\ KCl \longrightarrow K_2Cr_2O_7 + 2\ NaCl$$

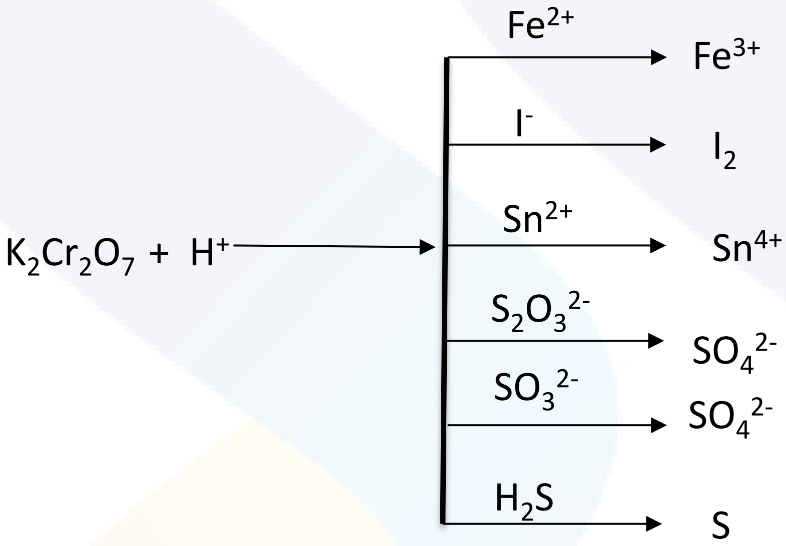
Orange crystals of potassium dichromate crystallise out

We can’t use KOH instead of NaOH because ($K_2SO_4$ & $K_2Cr_2O_7$) are highly miscible to each other and difficult to separate.

# Properties of Dichromate

**Acidic condition :**

$Cr_2O_7^{2-} + 14\,H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$



$K_2Cr_2O_7 + H^+ \longrightarrow$

$Fe^{2+} \longrightarrow Fe^{3+}$

$I^- \longrightarrow I_2$

$Sn^{2+} \longrightarrow Sn^{4+}$

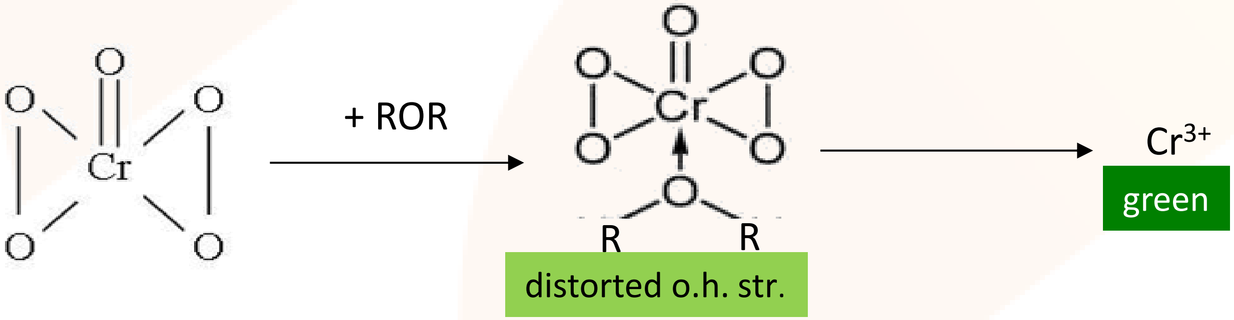
$S_2O_3^{2-} \longrightarrow SO_4^{2-}$

$SO_3^{2-} \longrightarrow SO_4^{2-}$

$H_2S \longrightarrow S$

$K_2Cr_2O_7 + H_2O_2 + H^+ \longrightarrow CrO_5 + K_2SO_4 + H_2O$

$CrO_5$ is blue in etheral layer(distorted octahedral geometry) but still unstable it decomposes to $Cr^{3+}$(green colour).



+ ROR

distorted o.h. str.

$Cr^{3+}$

green