Module-2:

Metal Complexes and Organometallics

Inorganic complexes - structure, bonding and application;

Organometallics - introduction, stability, structure and applications of metal carbonyls, ferrocene

Metals in biology: haemoglobin and chlorophyll- structure and property).

Inorganic Complexes: Structure, Bonding and Applications

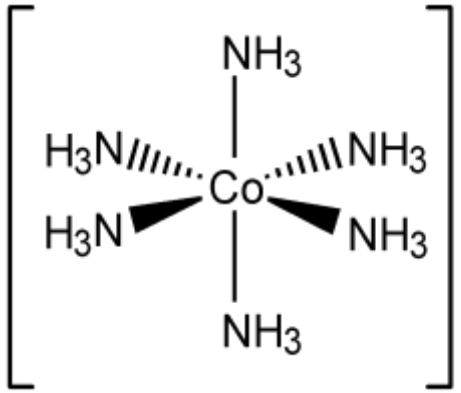
Double Salts and Coordination Compounds

❖ **Double Salt:**

Mohr's salt: $Fe(SO)_4\,(NH_4)_2SO_4.6H_2O$

In water: NH_4^+, SO_4^{2-}, Fe^{3+}

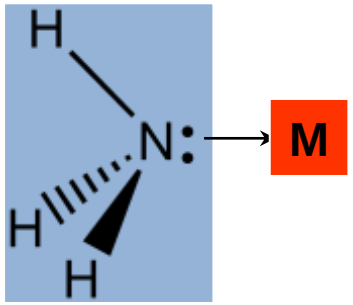
A double salt dissociates in water completely into simple ions



$3Cl^-$

(counter ion)

ligand (coordination sphere)



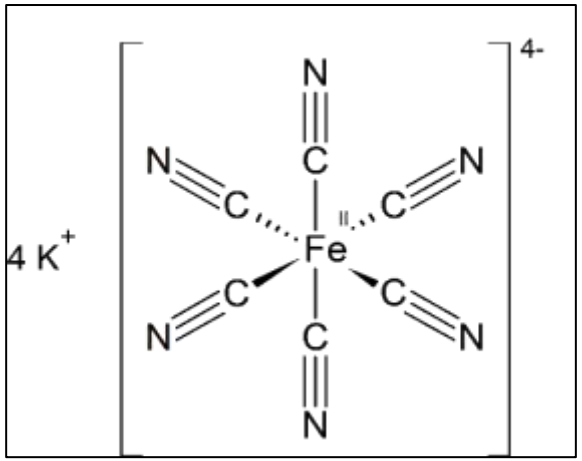
N forms a coordinate covalent bond to the metal

❖ **Co-ordination Compounds:**

$K_4[Fe(CN)_6]$

A coordination complex dissociates in water with at least one complex ion.

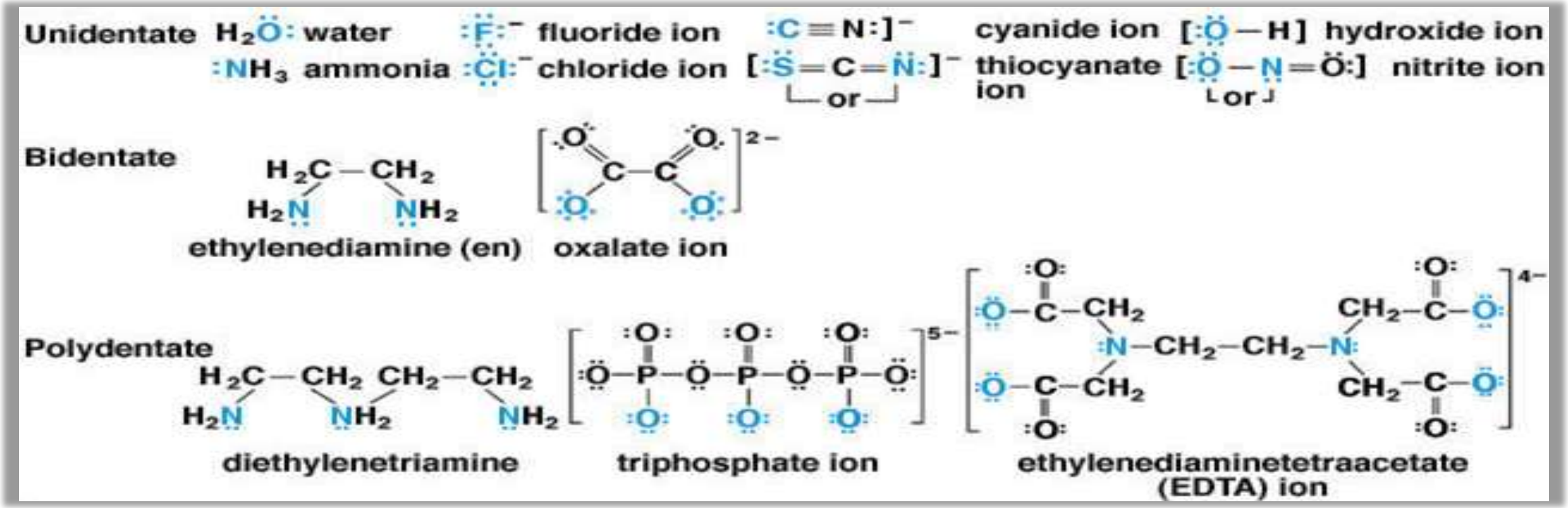
$Fe(CN)_2 + 4KCN \longrightarrow Fe(CN)_2.4KCN$



$4K^+ + [Fe(CN)_6]^{4-}$

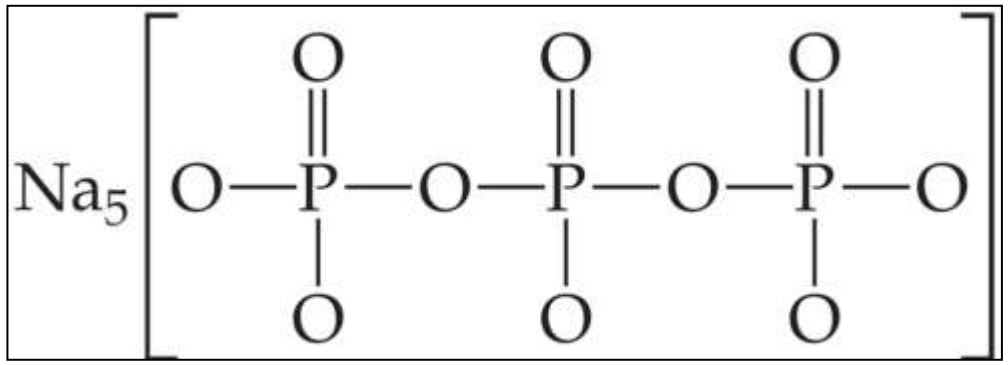
Ligands

- **Molecule or ion having a lone electron pair that can be used to form a bond to a metal ion (Lewis base).**
- **coordinate covalent bond**: metal-ligand bond
- **monodentate** : one bond to metal ion
- **bidentate** : two bond to metal ion
- **polydentate** : more than two bonds to a metal ion possible

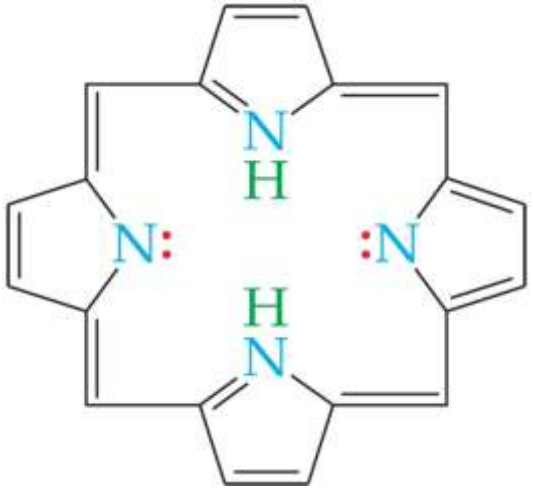


Chelating Agents

- Bind to metal ions and removing them from solution.
- Phosphates are used to tie up Ca^{2+} and Mg^{2+} in hard water to prevent them from interfering with detergents.



- Important biomolecules like heme and chlorophyll are porphyrins



Werner Coordination Theory

Werner's Theory: Alfred Werner, Swiss chemist put forward **a theory to explain the formation of complex compounds**.

- He studied the following metal complexes
- $CoCl_3$ forms four different compounds with NH_3.
- When these four compounds are treated with excess $AgNO_3(aq)$, different mol of $AgCl(s)$ precipitated per mole of complex.

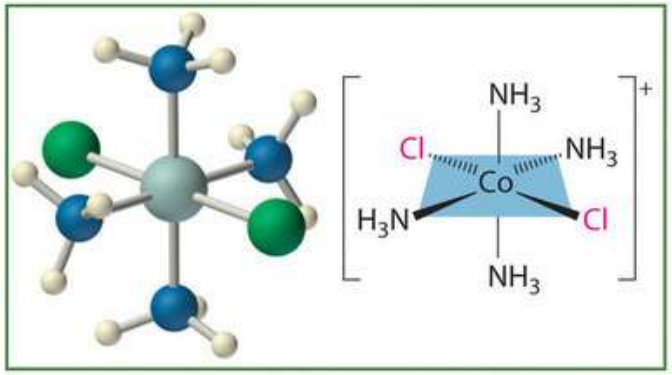
Ex. $CoCl_3.6NH_3$ + excess $AgNO_3 \longrightarrow 3AgCl(s)\downarrow$

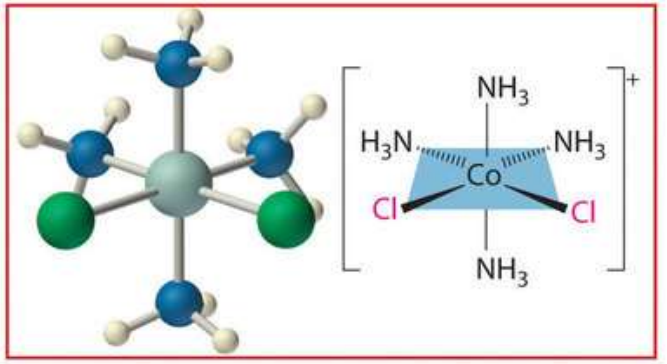
$CoCl_3.5NH_3$ + excess $AgNO_3 \longrightarrow 2AgCl(s)\downarrow$

$CoCl_3.4NH_3$ + excess $AgNO_3 \longrightarrow 1AgCl(s)\downarrow$

TABLE 23.3 Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$CoCl_3 \cdot 6\,NH_3$	Orange	4	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5\,NH_3$	Purple	3	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4\,NH_3$	Green	2	1	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4\,NH_3$	Violet	2	1	*cis*-$[Co(NH_3)_4Cl_2]Cl$





Werner Coordination Theory

Werner's Theory: According to Werner (father of Co-ordination chemistry) transition metals possess two types of valencies.

a) Primary valency (Ionisable valency)

b) Secondary valency (non ionisable valency)

Primary Valency (Ionisable Valency)

i) It is referred to as oxidation state.

ii) It is satisfied by only anions.

iii) It is represented by dotted lines while writing the structure of complex.

Secondary valency (Non-Ionisable valency)

i) It is satisfied by anions or neutral molecules or rarely with cations. The groups satisfying secondary valencies are called ligands.

ii) The number of secondary valencies is equal to coordination number.

iii) It is represented by thick lines while writing the structure of the complex.

In some complexes the same groups satisfies both primary and secondary valencies.

The ligands are directed in space around the central metal atom in different ways. This leads to a definite geometry to the molecule.

Werner studied the following metal complexes:

- $CoCl_3$ forms four different compounds with NH_3.

$CoCl_3.6NH_3$ (1:6 mol ratio) (Yellow) $\xrightarrow{AgNO_3\ (excess)}$ 3AgCl (ppt)

$CoCl_3.5NH_3$ (Lavender) $\xrightarrow{AgNO_3\ (excess)}$ 2AgCl (ppt)

One Cl does not react

$CoCl_3.4NH_3$ (Green) $\xrightarrow{AgNO_3\ (excess)}$ 1AgCl (ppt)

$CoCl_3.4NH_3$ (Violet) $\xrightarrow{AgNO_3\ (excess)}$ 1AgCl (ppt)

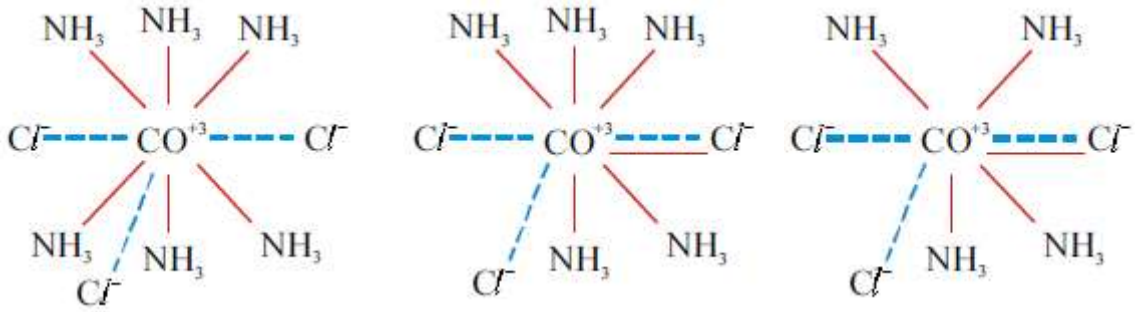
Defects in Werner's Theory

This theory does not relate the electronic configuration of metal with the formation of the complex.

It is known now that the metal tries to acquire the nearest inert gas configuration during the formation of complex

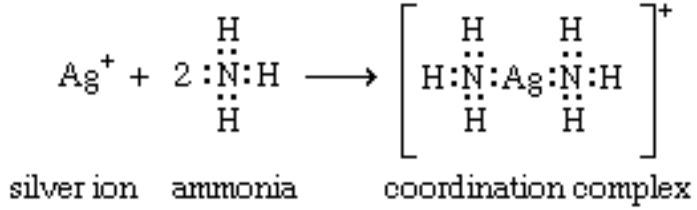
This theory does not explain the reason for the colour of the complex

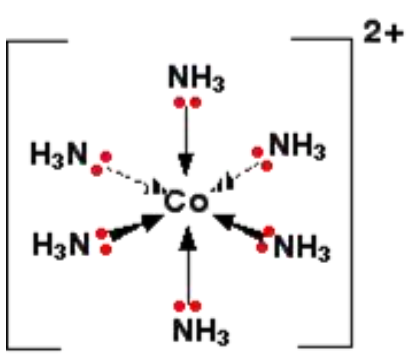
This theory does not explain the magnetic behaviour of complexes.



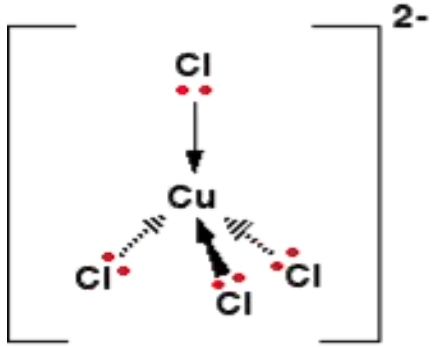
Lewis Acid Base Theory - Gilbert N. Lewis, 1920s

- **Lewis Acid/Base reactions: Base: electron pair donor; Acid: electron pair acceptor**
- **Ligands: Lewis bases ;**
- **Metals: Lewis acids ; Coordinate covalent bonds**
- **Metal Complexes - Formation of a complex was described as an acid - base reaction according to Lewis**





$[Co(NH_3)_6]^{2+}$



$[CuCl_4]^{2-}$

Sidgwick's Rule

- **Effective atomic number (EAN)** concept was introduced by Sidgwick to explain the stability of complexes
- **Effective atomic number (EAN) rule** is based on the octet theory of Lewis and this is the first attempt to account for the bonding in complexes.

- **EAN** = The sum of the e^- on the central atom (**Lewis acid**) ± No of e^- gained or lost in ion formation + e^- donated by the ligands (**Lewis base**) = Atomic No. of next higher inert gas

$[Ni(CO)_4]$ – 28 – 0 + 8 = 36

$[V(CO)_6]^-$ – 23 + 1 + 12 = 36

Valence Bond Theory (Linus Pauling, 1931)

Valence bond theory predicts that the bonding in a metal complex arises from overlap of **filled ligand orbitals** and **vacant metal orbitals**.

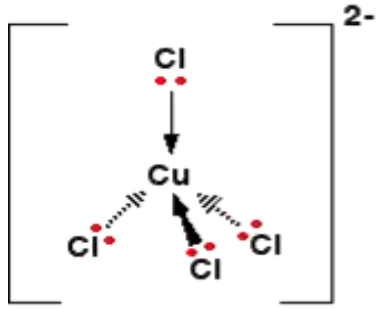
The central metal atom or ion makes available a number of empty s, p and d atomic orbitals equal to its coordination number. These vacant orbitals hybridise together to form hybrid orbitals. These hybrid orbitals are vacant, equivalent in energy and have definite geometry. The most common hybridizations in complex are given.

Coordination number	Hybridisation	Geometry	Examples
2	sp	Linear	$[CuCl_2]^-$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$[Ni(CO)_4]$, $[NiCl_4]^{2-}$
4	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$
5	dsp^3 ($d_{x^2-y^2}$ orbital is involved)	Trigonal bipyramidal	$Fe(CO)_5$
6	d^2sp^3 (d_{z^2} and $d_{x^2-y^2}$ orbitals of inner shell are involved)	Octahedral	$[Ti(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{2-}$, $[Fe(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$ (Inner orbital complexes)
6	sp^3d^2 (d_{z^2} and $d_{x^2-y^2}$ orbitals of the outer shell are involved)	Octahedral	$[FeF_6]^{4-}$, $[CoF_6]^{4-}$, $[Fe(H_2O)_6]^{2+}$ (Outer orbital complexes)

Coordination Number	Shape	Examples
2	Linear	$[CuCl_2]^-$, $[Ag(NH_3)_2]^+$, $[AuCl_2]^-$
4	Square planar	$[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$
4	Tetrahedral	$[Cu(CN)_4]^{3-}$, $[Zn(NH_3)_4]^{2+}$, $[CdCl_4]^{2-}$, $[MnCl_4]^{2-}$
6	Octahedral	$[Ti(H_2O)_6]^{3+}$, $[V(CN)_6]^{4-}$, $[Cr(NH_3)_4CL_2]^+$, $[Mn(H_2O)_6]^{2+}$, $[FeCl_6]^{3-}$, $[Co(en)_3]^{3+}$

Tetrahedral geometry

Tetrahedral copper complex $[CuCl_4]^{2-}$



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

	3d	4s	4p
Cu ground state $3d^{10}4s^1$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑	
Cu^{2+} - $3d^9 4s^0$	↑↓ ↑↓ ↑↓ ↑↓ ↑		
$[CuCl_4]^{2-}$	↑↓ ↑↓ ↑↓ ↑↓ ↑	↑↓	↑↓ ↑↓ ↑↓

4 e^- pairs by Cl^- ions

The spin only magnetic moment of the complex can be calculated by the formula

$$\mu_s = \sqrt{n(n+2)}\ BM$$

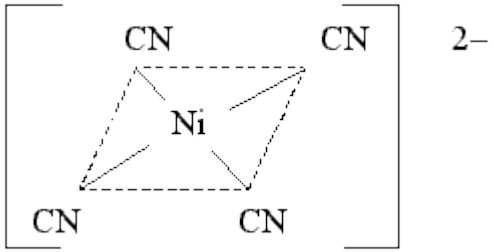
(n = number of unpaired electrons)

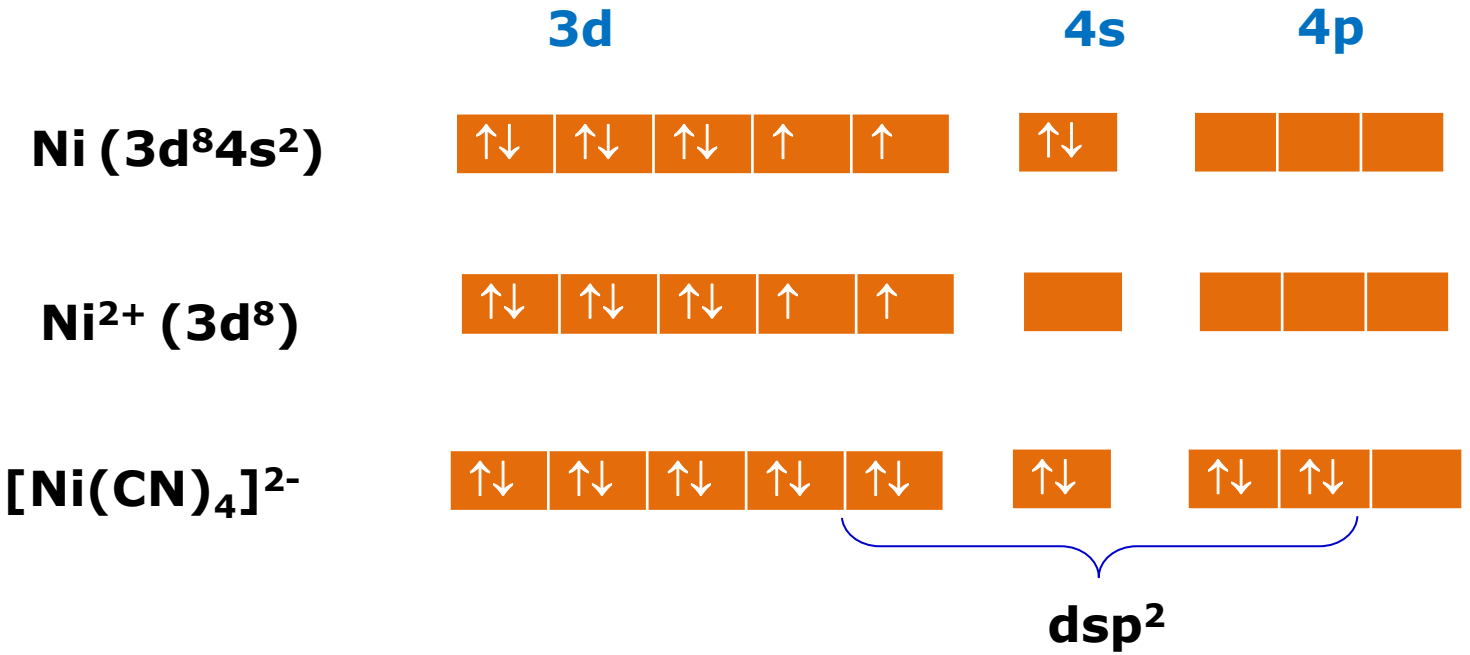
One unpaired electrons - paramagnetic and attracted by magnets

$$\mu = \sqrt{n\,(n+2)}$$
$$\mu = \sqrt{3} = 1.732\ BM$$

Square Planar Geometry

Square planar nickel complex $[Ni(CN)_4]^{2-}$





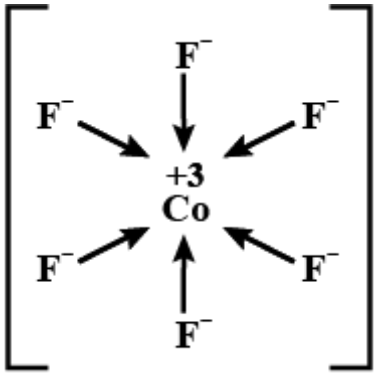
All paired electrons – diamagnetic - weakly repelled by magnets

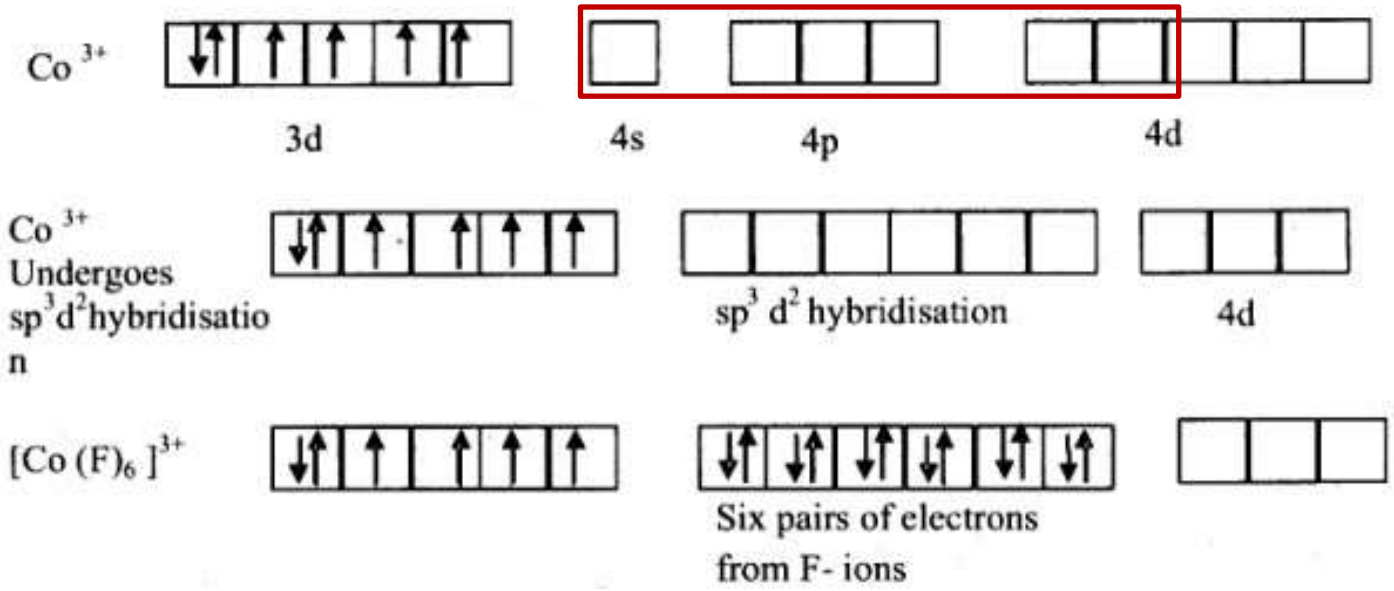
$[NiCl_4]^{2-}$ = Hybridization, Geometry & Magnetic property ???

Octahedral sp^3d^2 Geometry

Gives $[CoF_6]^{3-}$ four unpaired electrons, which makes it paramagnetic and is called a *high-spin complex*.

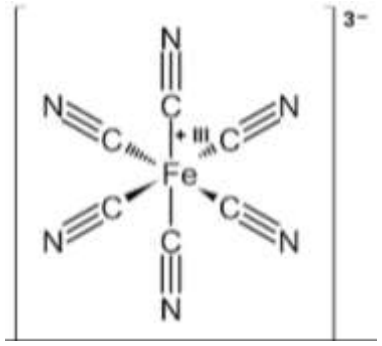
Ground state Co= $(3d^74s^2)$



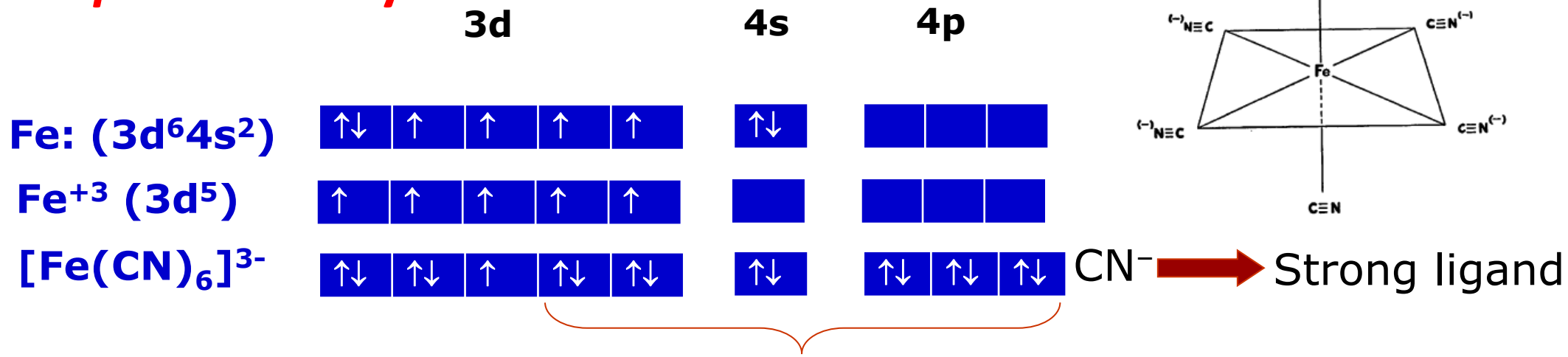


$[Co(CN)_6]^{3-}$ = Hybridization, Geometry & Magnetic property???

Octahedral d^2sp^3 Geometry



$[Fe(CN)_6]^{3-}$



Limitations of VBT

- It gives only the qualitative explanations for complexes.
- It does not explain the detailed magnetic properties of complexes.
- This thoery does not explain the spectral properties of coordination compounds.
- It does not explain the thermodynamic and kinetic stabilities of different coordination compounds.
- It does not distinguish between weak and strong ligands.
- It does not make exact predictions regarding terahedral or square planar coordinations entities with co-ordination number is 4.

Bonding in Coordination Compounds

- Many of the properties of metal complexes are dictated by their electronic structures.

Crystal field theory (CFT): ***Electronic structure can be explained by an ionic model that attributes formal charges on to the metals and ligands.***

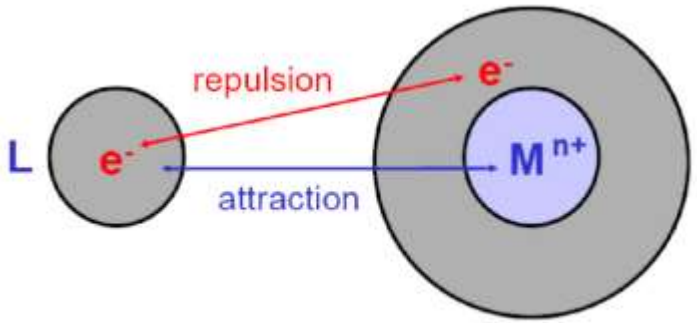
This forms basis of crystal field theory (CFT), which is considered as the core concept in inorganic chemistry.

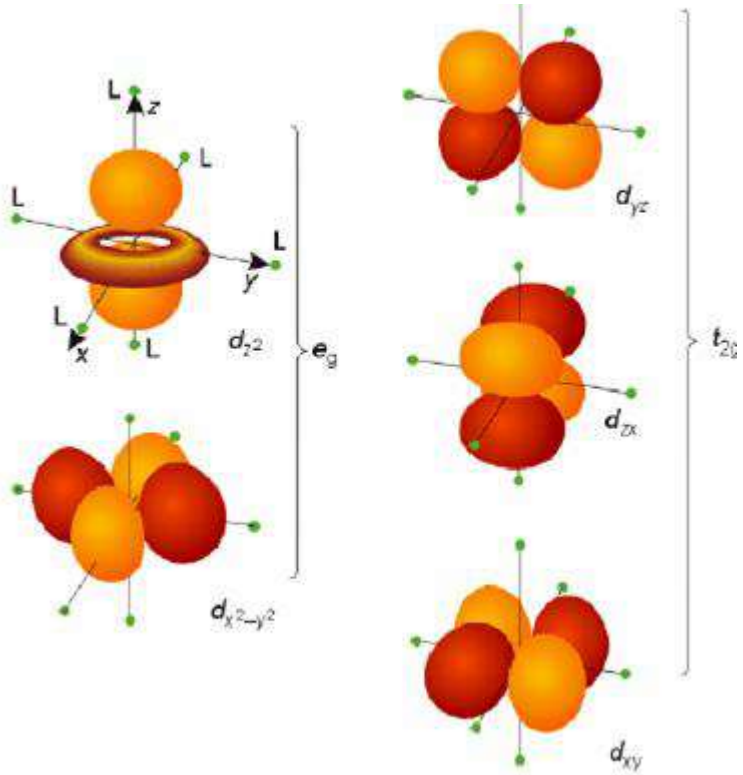
- *Consider,* ***bonding in a complex*** *to be an* ***electrostatic attraction*** *between a* ***positively charged nucleus and the electrons of the ligands.***
  - **Electrons on metal atom repel electrons on ligands.**
  - **Focus particularly on the *d*-electrons on the metal ion.**

- *Ligand field theory (**LFT**) and the molecular orbital theory (**MOT**) are considered sophisticated models as compared to **CFT**.*
- ***LFT explains complexes, wherein, the interactions are covalent.***

Crystal field theory (CFT)

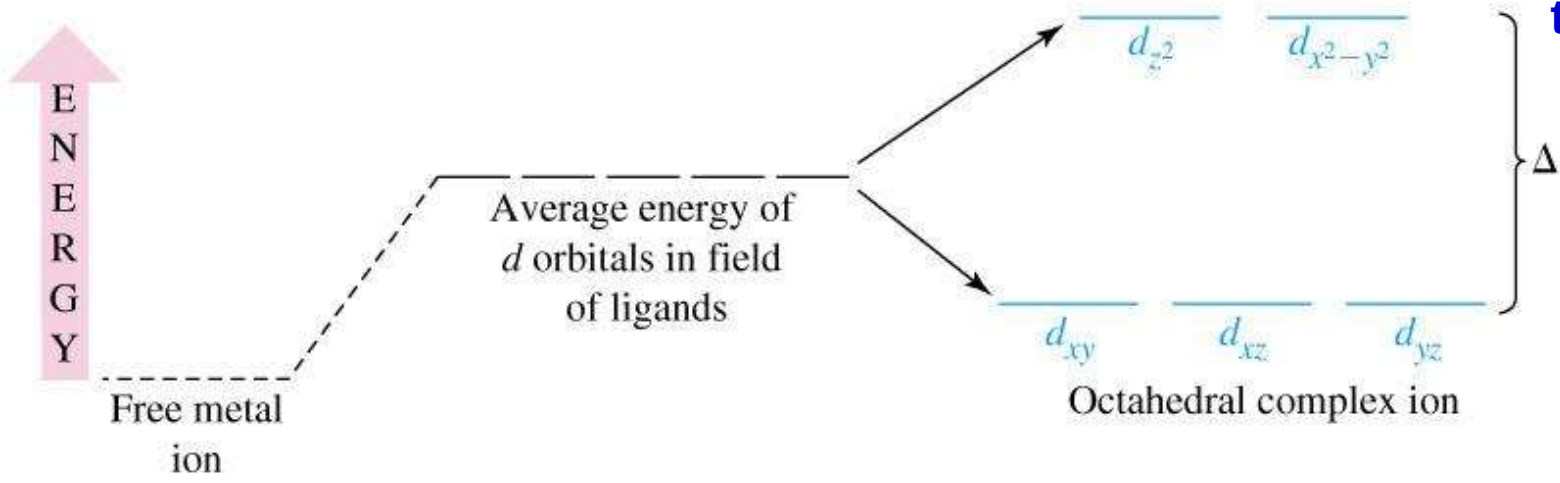
- ***Interaction between the metal ion and the ligands are purely electrostatic (ionic)***
- ***Ligands are considered as point charges***
- ***Ion-ion interaction, if the ligand is negatively charged, and ion-dipole interaction, if the ligand is neutral***
- ***Electrons on the metal are under repulsive from those on the ligands***
- ***Electrons on metal occupy those d-orbitals, farthest away from the direction of approach of ligands.***





- ***Interaction between electrons of the metal ion and those of ligands are entirely repulsive. This is responsible for splitting of d orbitals.***
- ***CFT does not consider the overlapping between metal and ligand orbitals.***
- ***The d-orbitals lose their degeneracy due to the approach of ligands during the formation of complex***

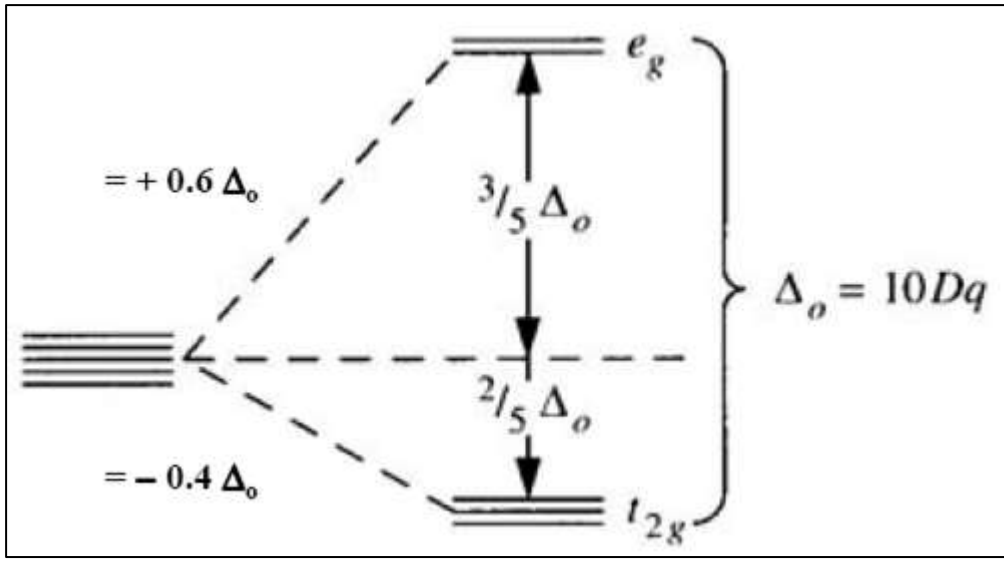
Octahedral Complex and *d*-Orbital Energies



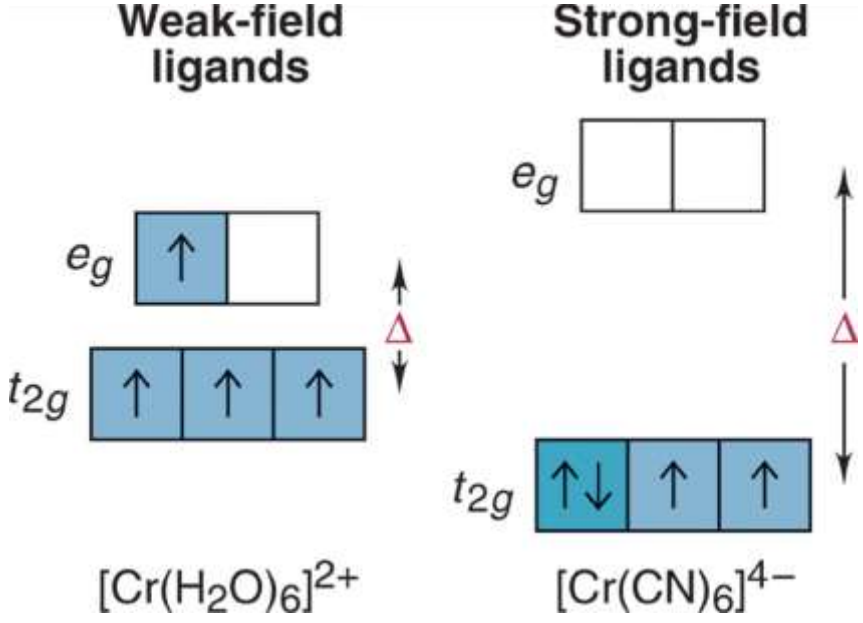
Oriented along the axes

Oriented in between the co-ordinate axes

- For the Octahedral point group, the $d_{x^2-y^2}$, d_{z^2} orbitals belong to the e_g representation and d_{xy}, d_{xz}, d_{yz} belong to the t_{2g} representation.
- The extent to these two sets of orbitals are split is denoted by Δ_o or **10 Dq.**
- As the **barycenter** must be conserved on going from a spherical field to an octahedral field, the t_{2g} set must be stabilized as much as the e_g set is destabilized.



- For **d^1-d^3** systems: Hund's rule predicts that the electrons will not pair and occupy the t_{2g} set.
- For **d^4-d^7** systems (2 possibilities): Either pairing the electrons in t_{2g} set (low spin or strong field) or electrons in e_g set, higher in energy, but do not pair (high spin or weak field).
- **Pairing energy (P) and $e_g - t_{2g}$ splitting (Δ_o or 10 Dq)**



Δ_o vs Pairing Energy (P)

- **If CFSE is very large, pairing occurs**

  i.e. CFSE>P
- **If CFSE is smaller, No pairing occurs**

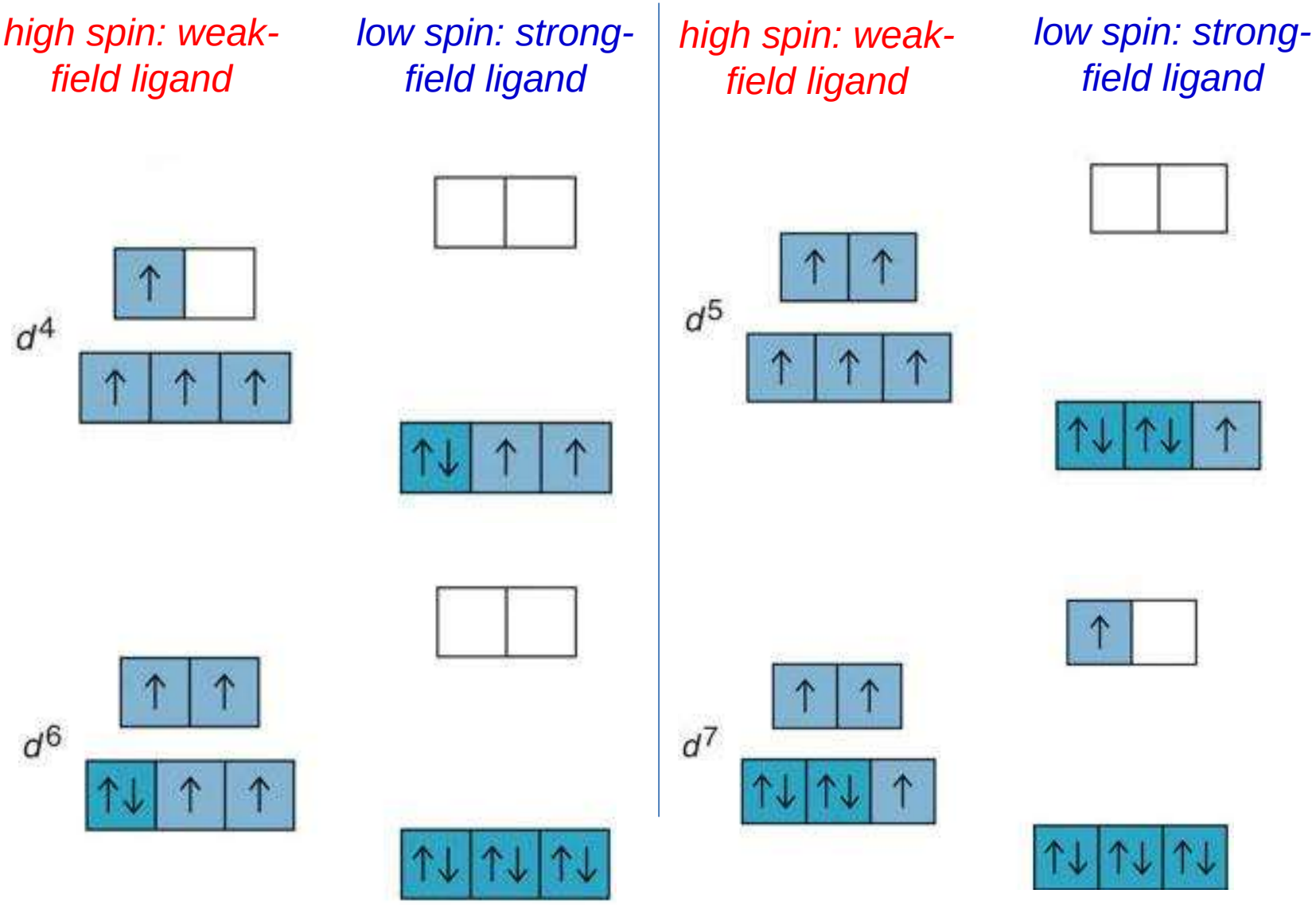
  i.e. CFSE < P

Orbital occupancy for high- and low-spin complexes of d^4 through d^7 metal ions

For d^4 ions, two possible patterns of electron distribution.

1) If $\Delta_0 < p$, the fourth electron enters one of the e_g orbital giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_0 < p$ are known as weak field ligands and form high spin complexes.

2) If $\Delta_0 > p$, it becomes more energetically favourable for fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as strong field ligands and form low spin complex.



CFSE and electronic arrangements in octahedral complexes

Number of d electrons	Arrangement in weak ligand field				Arrangement in strong ligand field			
	t_{2g}	e_g	CFSE Δ_o	Spin only magnetic moment μ_s(D)	t_{2g}	e_g	CFSE Δ_o	Spin only magnetic moment μ_s(D)
d^1	↑		−0.4	1.73	↑		−0.4	1.73
d^2	↑ ↑		−0.8	2.83	↑ ↑		−0.8	2.83
d^3	↑ ↑ ↑		−1.2	3.87	↑ ↑ ↑		−1.2	3.87
d^4	↑ ↑ ↑	↑	−1.2 +0.6 = −0.6	4.90	↑↓ ↑ ↑		−1.6	2.83
d^5	↑ ↑ ↑	↑ ↑	−1.2 +1.2 = −0.0	5.92	↑↓ ↑↓ ↑		−2.0	1.73
d^6	↑↓ ↑ ↑	↑ ↑	−1.6 +1.2 = −0.4	4.90	↑↓ ↑↓ ↑↓		−2.4	0.00
d^7	↑↓ ↑↓ ↑	↑ ↑	−2.0 +1.2 = −0.8	3.87	↑↓ ↑↓ ↑↓	↑	−2.4 +0.6 = −1.8	1.73
d^8	↑↓ ↑↓ ↑↓	↑ ↑	−2.4 +1.2 = −1.2	2.83	↑↓ ↑↓ ↑↓	↑ ↑	−2.4 +1.2 = −1.2	2.83
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	−2.4 +1.8 = −0.6	1.73	↑↓ ↑↓ ↑↓	↑↓ ↑	−2.4 +1.8 = −0.6	1.73
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	−2.4 +2.4 = 0.0	0.00	↑↓ ↑↓ ↑↓	↑↓ ↑↓	−2.4 +2.4 = 0.0	0.00

Δ_o is dependent on:

- *Nature of the ligands*
- *The charge on the metal ion*
- *Whether the metal is a 3d, 4d, or 5d element*

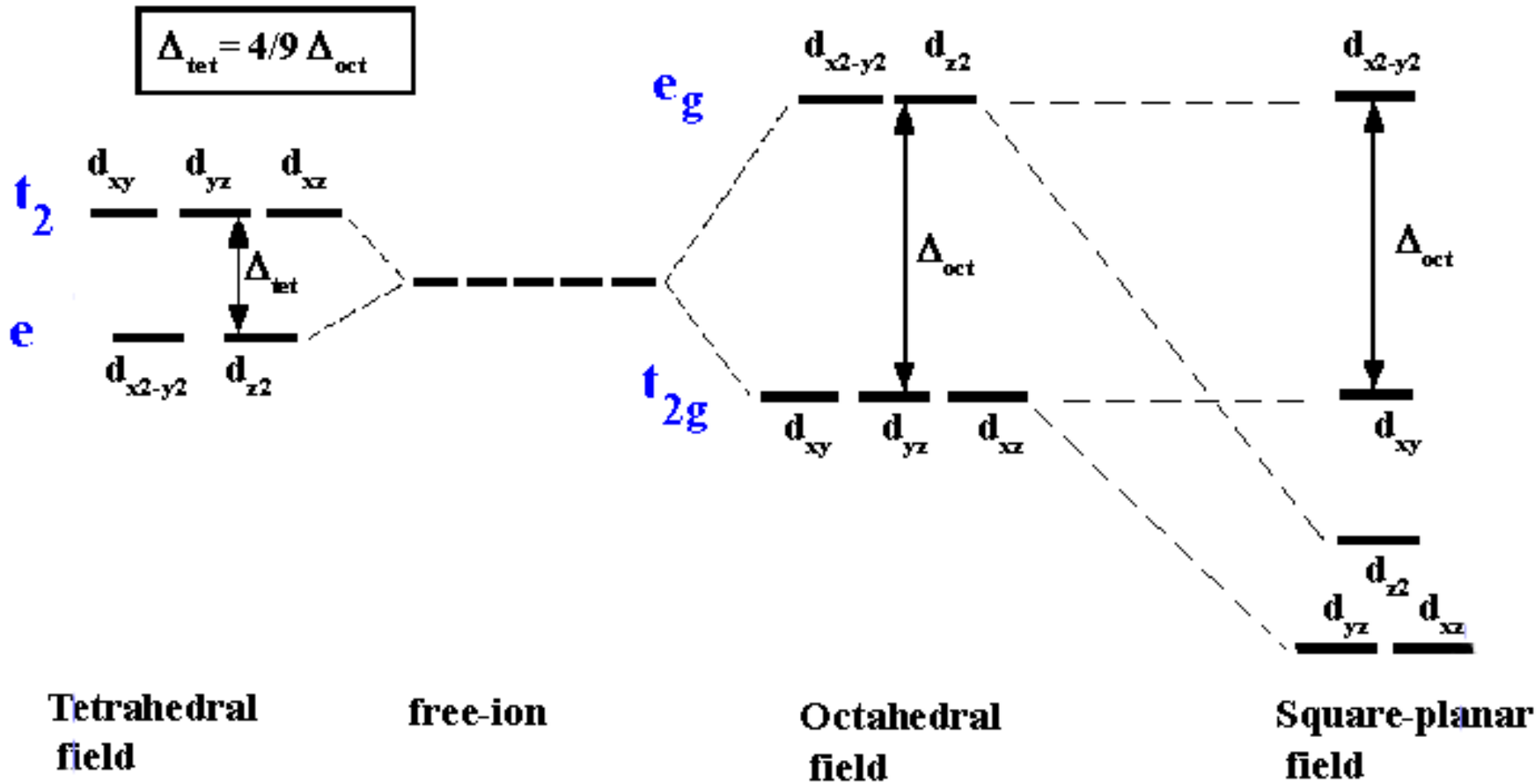
$[Co(NH_3)_6]^{3+} > [Co(NH_3)_6]^{2+}$

27 Co $[Co(NH_3)_6]^{3+}$ = 23,000 cm^{-1} (3d)

45 Rh $[Rh(NH_3)_6]^{3+}$ = 34,000 cm^{-1} (4d)

77 Ir $[Ir(NH_3)_6]^{3+}$ = 41,000 cm^{-1} (5d)

Crystal field d orbital splitting diagrams for common stereochemistries.



Spectrochemical Series

- For a given ligand, the color depends on the oxidation state of the metal ion.

$I^- < Cl^- < F^- < OH^- < H_2O < SCN^- < NH_3 < en < NO_2^- < CN^- < CO$

WEAKER FIELD → STRONGER FIELD

SMALLER Δ → LARGER Δ

LONGER λ → SHORTER λ

Coordination entity	Wave length of light absorbed(nm)	Colour of light absorbed	Colour of coordination entity (transmitted)
$[Co(CN)_6]^{3-}$	310	Violet	Pale yellow
$[Co(H_2O)_6]^{3+}$	475	Blue	Yellow orange
$[Co(H_2O)(NH_3)_5]^{3+}$	500	Blue green	Red
$[Ti(H_2O)_6]^{3+}$	510	Blue green	Purple
$[CoCl(NH_3)_5]^{3+}$	53.5	Yellow	Violet
$[Cu(H_2O)_6]^{3+}$	600	Red	Blue

- For a given metal ion, the color depends on the ligand.

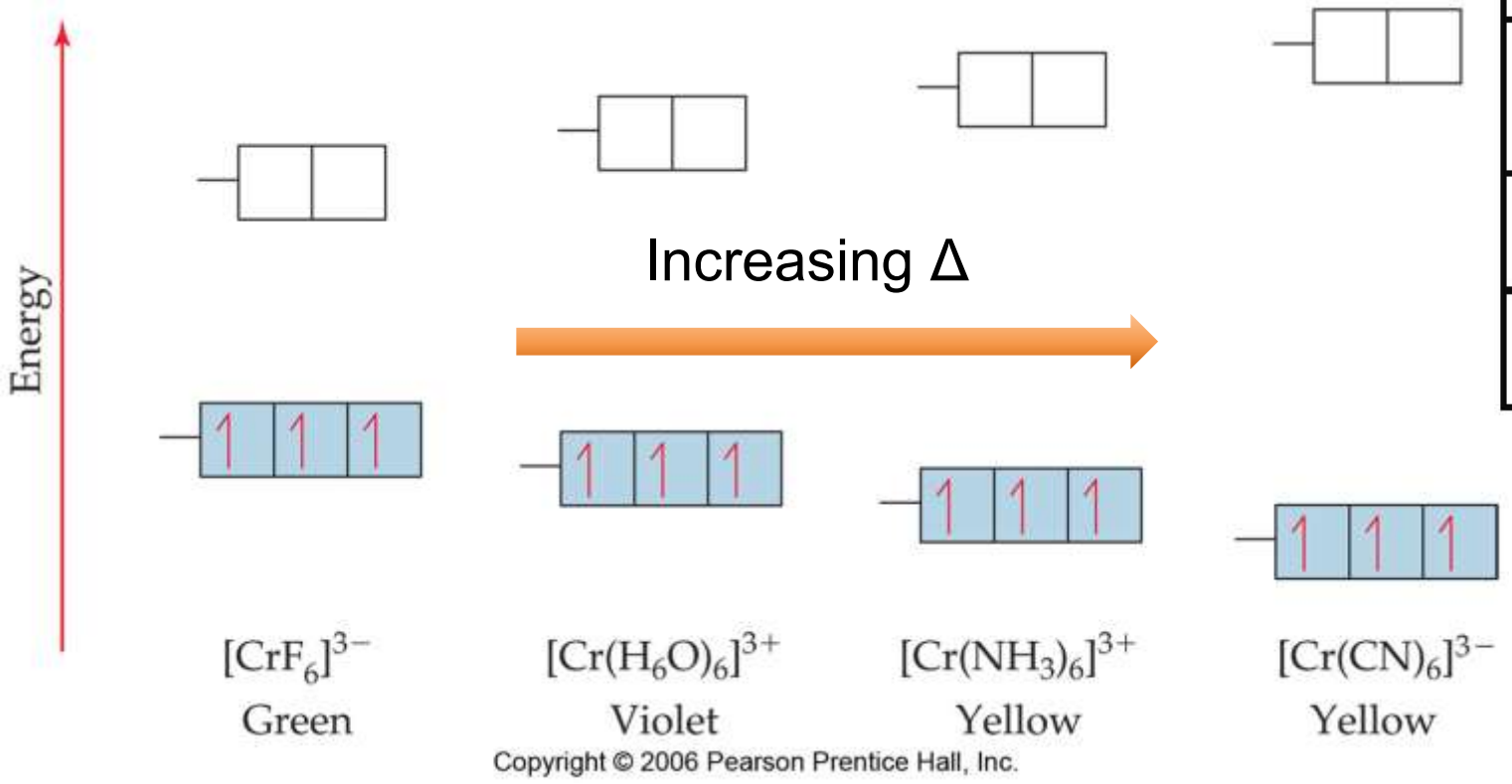
- Complexes of cobalt (III) show the shift in color due to the ligand.
- (a) CN^-, (b) NO_2^-, (c) phen, (d) en, (e) NH_3, (f) gly, (g) H_2O, (h) ox^{2-}, (i) CO_3^{2-}

Spectrochemical series (strength of ligand interaction)

Effect of ligand on splitting energy

Increasing Δ

$Cl^- < F^- < H_2O < NH_3 < en < NO_2^- < CN^-$



	$[Co(H_2O)_6]^{3+}$	$[Co(NH_3)_6]^{3+}$	$[Co(CN)_6]^{3+}$
Δ_o value	small	Intermediate	Large
Excitation energy(ΔE)	small	Intermediate	Large
Absorption wavelength (λ)	large	Intermediate	small
Colour absorbed	Orange	Blue	Violet
Colour transmitted	Blue	Yellow orange	Yellow

Low spin – color variations shown with increasing CFSE **($Cr^{3+} = 24 - 3 - 18 = d^3$)**

Merits of crystal Field Theory

- Predict most favorable geometry of a complex
- Accounts for four coordinated complexes (tetrahedral and square planar)
- Explains the ligands forming outer / inner orbital complexes (high spin / low spin)
- Interprets magnetic properties taking in to consideration the orbital contributions also
- Interprets color of transition metal complexes
- Explains spectral properties of many transition metal complexes

Some Limitations of CFT…

- This theory **only considers the *d*-orbitals** of a central atom. The ***s* and *p* orbits are not taken into account** in this study.
- The theory **fails to explain the behaviour of certain metals**, which exhibit large splitting while others exhibit minor splitting. For example, the theory provides no explanation for why H_2O is a stronger ligand than OH^-.
- The theory **excludes the possibility of *π* bonding**. This is a significant disadvantage because it is found in many complexes.
- **The orbits of the ligands have no significance** in the theory. As a result, it cannot explain any properties of ligand orbitals or their interactions with metal orbitals.

Applications of Coordination Compounds

- Coordination compounds are of great importance.
- Play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine.

- **Catalysis**
- **Extraction of metal ions**
- **Analytical chemistry (development of numerous analytical methods)**
- **Hardness estimation**
- **Biological importance**
- **Medicinal application**
- **Industrial application**

Extraction / Purification of metal

Extraction

- Processes of metals, like those of **silver and gold**, make use of complex formation.
- These noble metals are extracted from their ore by the formation of cyanide complexes - dicyanoargentite(I) - $[Ag(CN)_2]^-$ and dicyanoaurate (I) - $[Au(CN)_2]^-$ in the presence of oxygen and water, from which the metallic forms can be separated by the addition of zinc.

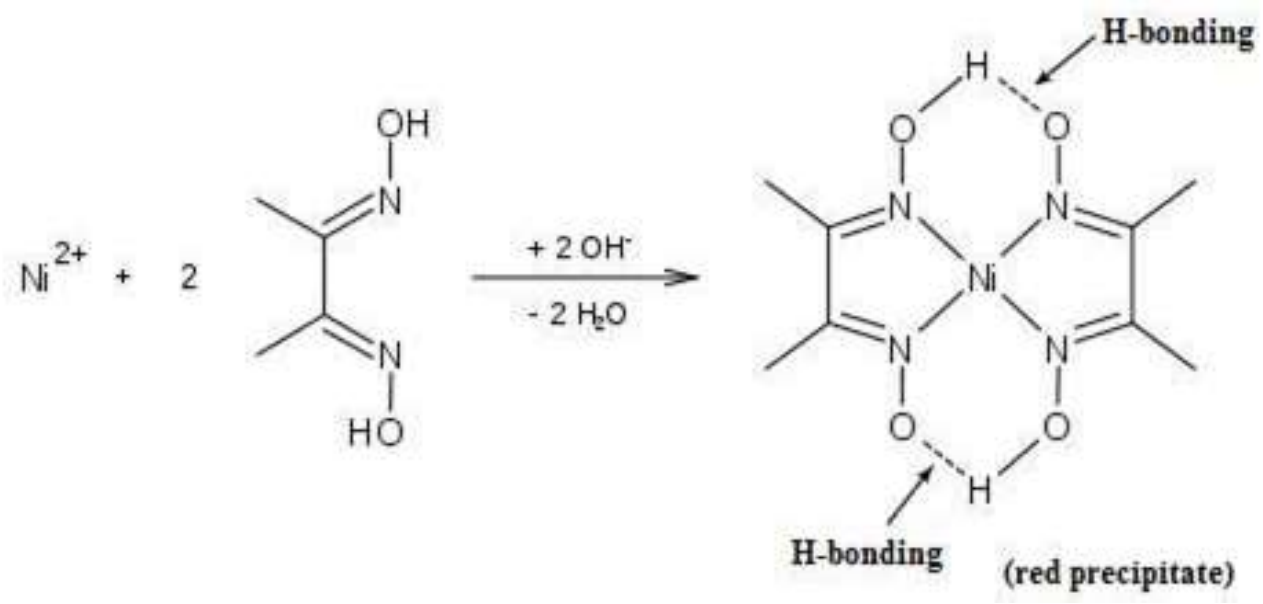
- $Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$
- $2\ Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$

- **Purification of metals** can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to **$[Ni(CO)_4]$,** which is decomposed to yield pure nickel.

Detection of Complex formation

- Formation of Precipitate

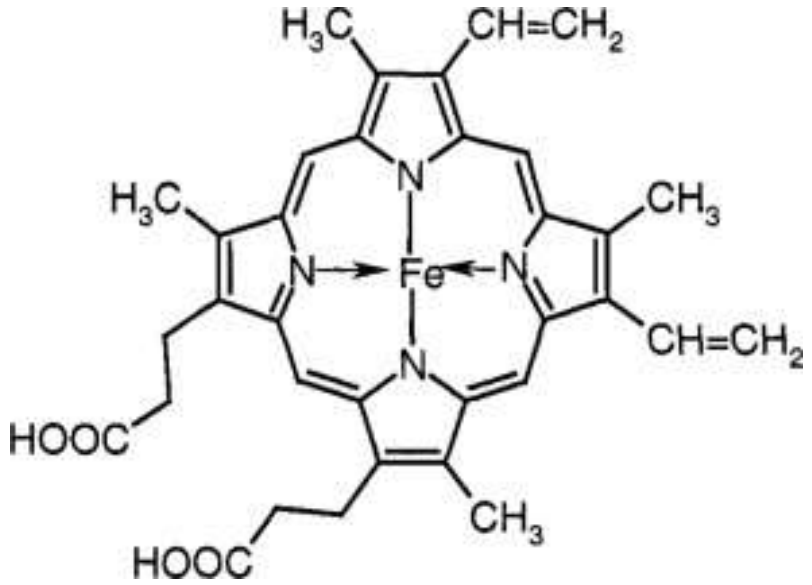
$$Ni^{2+} + 2\ HDMG \longrightarrow [Ni(DMG)_2] + 2H^+$$



- Ni^{2+} and Pd^{2+} form insoluble colored precipitates with dimethyglyoxime

Biological Importance

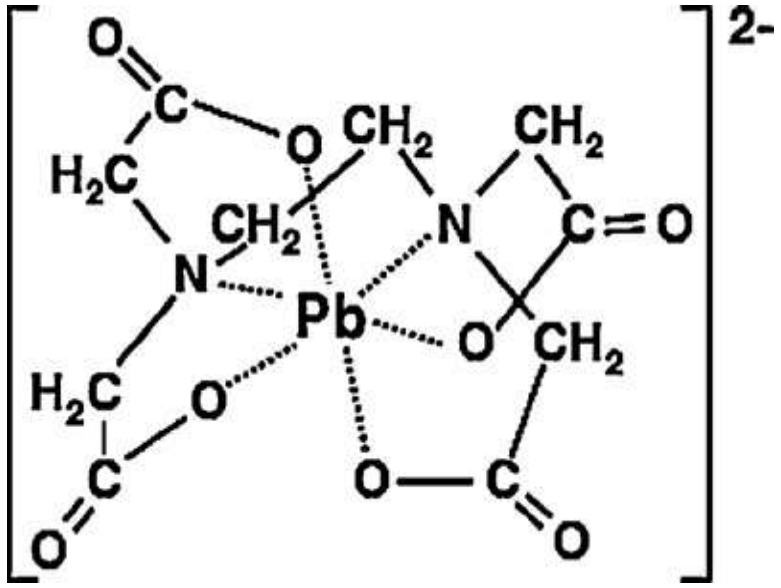
- Pigment responsible for photosynthesis, **chlorophyll**, is a coordination compound of Magnesium.
- **Haemoglobin,** the red pigment of blood which acts as oxygen carrier is a coordination compound of Iron.
- **Vitamin B12**, cyanocobalamine, the anti-pernicious anaemia factor, is a **coordination compound of Cobalt**.



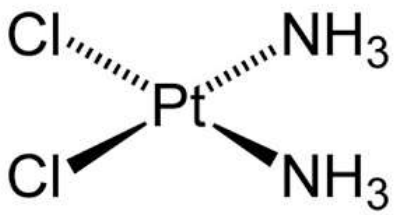
Heme B: Heme B is a porphyrin (four linked pyrrole rings) that readily binds iron, as shown. This is an example of a biomolecule that contains non-protein ligands for a transition metal.

- Other compounds of biological importance with coordinated metal ions are the enzymes like, **carboxypeptidase A** and **carbonic anhydrase** (catalysts of biological systems)
- ***Metalloprotein with the metal ion cofactor have many diverse functions including transport, storage, and signal transduction.***

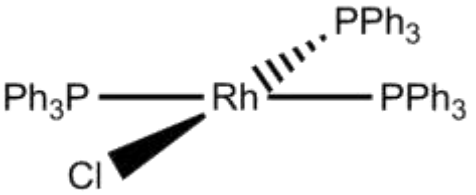
Medicinal Application



- *To treat problems caused by the presence of metals in toxic proportions in plant/animal systems, chelate therapy is used.*
- **Excess of Copper and Iron** are removed by the chelating ligands ***D–penicillamine*** **and** ***Desferrioxime B*** *via* ***formation of the coordination compounds*****.**
- **EDTA** is used in the **treatment of lead poisoning.**
- **Coordination compound of platinum *effectively inhibit the growth of tumours*. i.e. *Cisplatin* - cis $[PtCl_2(NH_3)_2]$, and related compounds.**



Industrial applications



- Coordination compounds are used as ***catalysts*** for many industrial processes. Ex. **Rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst - *hydrogenation of alkenes***.

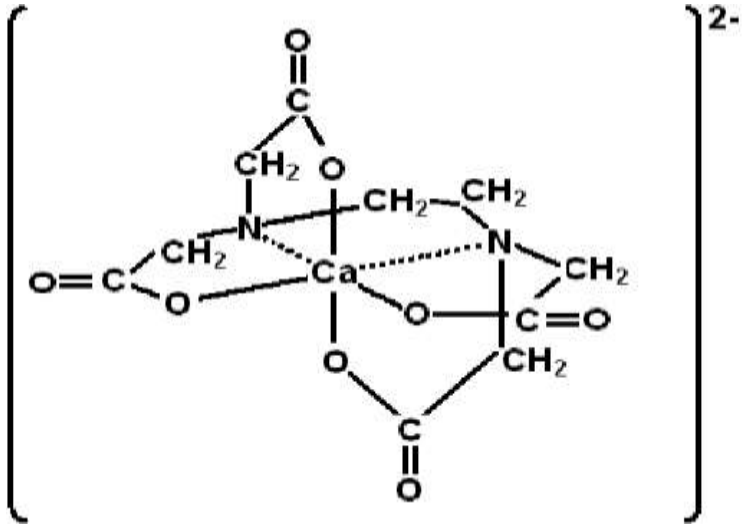
- Articles can be **electroplated with silver and gold** much more smoothly and evenly *from solutions of the complexes*, **$[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$** *than from a solution of simple metal ions*.

- In black and white photography, the developed film is fixed by washing with **Hypo solution which dissolves the non decomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$** .

- **Prussian blue** – Mixture of **Hexacyano Fe(II) and Fe(III) - $Fe_4[Fe(CN)_6]_3$ inks, blueprinting, cosmetics, paints (commercial coloring agents)**

Hardness of water

- Hardness of water is estimated by titration with the sodium salt of **EDTA**.
- During titration, the calcium and magnesium ions in hard water form the stable complexes, Calcium EDTA and Magnesium EDTA.
- Hardness of water is estimated by simple titration with Na_2EDTA.
- The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.



Representative Metal Complexes in Catalysis

- **Zeise's Salt** : $K[Pt(C_2H_4)Cl_3]$
- **Magnus Green Salt** : $[Pt(NH_3)_4][PtCl_4]$
- **Edman's Salt** : $K[Co(NH_3)_2(NO_2)_4$
- **Reinecke's Salt** : $NH_4[Cr(NH_3)_2(NCS)_4]$
- **Vaska's Complex** : $[Ir(CO)(PPh_3)2Cl]$
- **Wilkinson's Catalyst** : $[Rh(PPh_3)_3Cl]$