Werner's Co-ordination Theory:

The formation of simple compounds like $CoCl_3 \cdot NH_3$ etc. can be explain from the concept of electronic theory of valency but there is no plausible explanation to explain the formation of those compounds where simple compounds are bound together such as $CoCl_3 \cdot 6NH_3$.

Alfred Werner made a systematic investigation on cobalt amine complexes. Those complexes are

a. $CoCl_3 \cdot 6NH_3$ (Luteo cobaltic chloride).

b. $CoCl_3 \cdot 5NH_3 \cdot H_2O$ (Roseo cobaltic chloride)

c. $CoCl_3 \cdot 5NH_3$ (Purpureo cobaltic chloride).

d. $CoCl_3 \cdot 4NH_3$ (violeo cobaltic chloride)

e. $CoCl_3 \cdot 3NH_3$.

Some observations on these compounds were as follows—

I. When Luteo cobaltic chloride was treated with H_2SO_4, all the Cl are removed as HCl but the NH_3 molecules remain unchanged and form $Co_2(SO_4)_3 \cdot 12NH_3$

II. When the aqueous sol^n of Luteo cobaltic chloride is treated with $AgNO_3$ sol^n, then all the Cl atoms are precipitated as AgCl but NH_3 molecule remain unchanged.

III. Roseo cobaltic chloride looses the water only at 100°C or above and forms perpureo cobaltic chloride.

iv. Purpureo Cobaltic chloride and Violeocobaltic chloride loose only two and one Cl atom respectively on the treatment with H_2SO_4. This indicates there are only two and one Cl atoms respectively having ionic character.

v. On boiling with conc. HCl or NaOH, no any change was observed.

vi. Luteo cobaltic chloride on boiling with very much reactive reagent such as Na_2O_2, the compound was broken.

vii. Roseo cobaltic Chloride gives 3 mole AgCl per 1 mole on treatment with $AgNO_3$ solⁿ.

The reactions are summerised below —

$$2COCl_3 \cdot 6NH_3 \xrightarrow{H_2SO_4} CO_2(SO_4)_3 \cdot 12NH_3 + 6HCl$$

$$CoCl_3 \cdot 6NH_3 \xrightarrow[(aq.)]{AgNO_3} Co(NO_3)_3 \cdot 6NH_3 + 3AgCl$$

*** $CoCl_3 \cdot 5NH_3 \xrightarrow{AgNO_3} Co(NO_3)_2Cl \cdot 5NH_3 + 2AgCl$

$$CoCl_3 \cdot 4NH_3 \xrightarrow{AgNO_3} Co(NO_3)Cl_2 \cdot 4NH_3 + AgCl$$

$$CoCl_3 \cdot 3NH_3 \xrightarrow{AgNO_3} \text{No change.}$$

*** $CoCl_3 \cdot 5NH_3 \cdot H_2O \xrightarrow{AgNO_3} Co(NO_3)_3 \cdot 5NH_3 \cdot H_2O + 3AgCl.$

From these observations Werner proposed some postulates which is known as Werner's co-ordination theory. The postulates are —

1. Each metal ion has two types of valencies —

a. Primary valency, which corresponds to the oxidation state of metal ion also known as ionic or principal or ionisable valency.

b. Secondary valency which corresponds to the coordination number of central metal atom or ion, which is known as non-ionisable valency.

II. Primary valencies are satisfied by negatively charged ions whereas the secondary valencies are satisfied by negative ions or neutral molecules or cations. Sometimes an anion may have to satisfy both the valencies of the metal.

III. Each metal ion has the fixed number of secondary valency. The fulfilment of secondary is very essential.

IV. The secondary valencies are directed in space around the central metal ion in definite geometrical shape.

The above observations can be explained with the help of werner's theory. In case of 1st & 2nd compounds, they give 3 moles of AgCl per mole on treatment with $AgNO_3$ solutions ie, all the three Cl atoms in each compounds are bound to Co^{3+} by primary valency. So these are ionised.

But in 3rd, 4th and 5th compounds 1, 2 & 3 Cl atom respectively go to fill up the secondary valency as well as primary valency. So, when per mole of these compounds are treated with $AgNO_3$ solⁿ, we get 2, 1 & 0 mole of AgCl respectively.

Werner used third bracket to include the ligands bound with the metal ion by secondary valency. The ligands bound to the metal ion by primary valency are shown outside the bracket. According to this conversion the above compounds can be written as follows—

a. $[Co(NH_3)_6]Cl_3$ ⇒ Luteo cobaltic Chloride (orange-yellow)

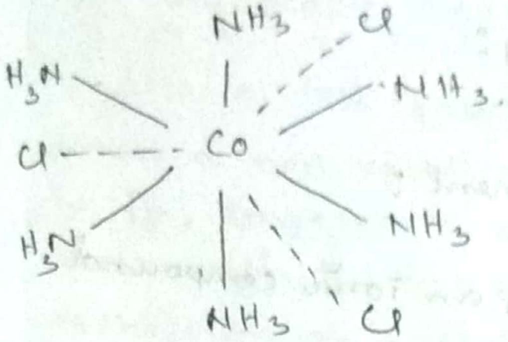
b. $[Co(NH_3)_5(H_2O)]Cl_3$ ⇒ Roseo cobaltic Chloride (Pink)

c. $[Co(NH_3)_5Cl]Cl_2$ ⇒ Purpureo cobaltic Chloride (violet).

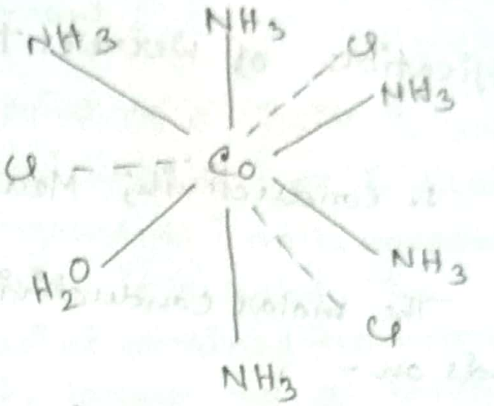
d. $[Co(NH_3)_4Cl_2]Cl$ ⇒ Violeo cobaltic Chloride (violet)

e. $[Co(NH_3)_3Cl_3]$ ⇒ Blue-green.

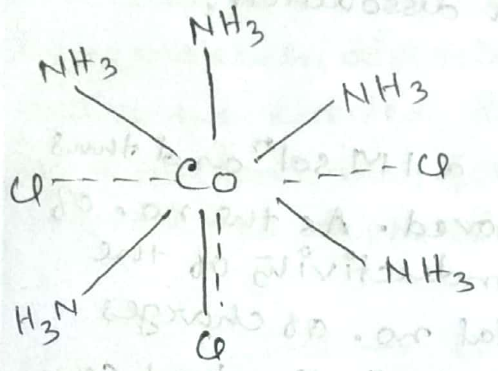
These gives 4, 4, 3, 2 & 0 ions in the solⁿ. $[Co(NH_3)_3Cl_3]$ behaves as a non-electrolyte. The structure of the compounds are —



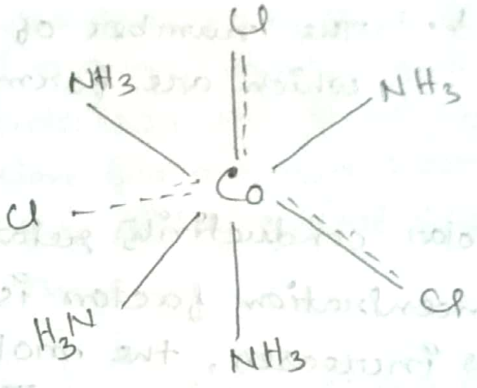
Luteo cobaltic chloride



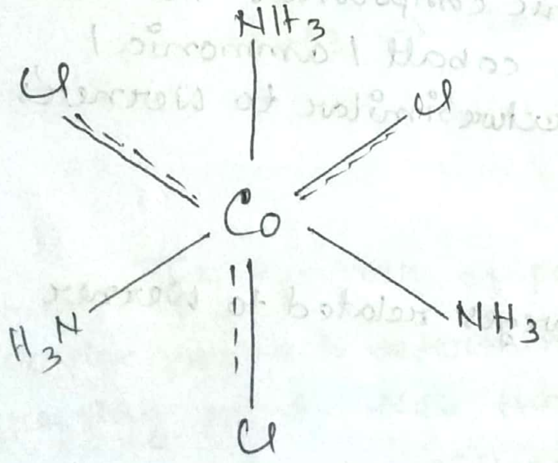
Roseo cobaltic chloride



Purpureo cobaltic chloride



Violeo cobaltic chloride



$[Co(NH_3)_3Cl_3]$

Here dotted lines indicate the primary valency and solid lines indicate the secondary valencies.

Verification of Werner's theory:

1. Conductivity Measurement:

The molar conductivity of an ionic compound depends on –

a. The concentration of solute

b. The number of charges on the species which are formed on dissolution.

Molar conductivity relates to a 1M sol^{n} and thus the concentration factor is removed. As the no. of charges increases, the molar conductivity of the complexes also increases. The total no. of charges on the species formed when the complex is dissolved, can be deducted by comparison of its molar conductivity with that of known simple ionic compound. The molar conductivity measurement of cobalt / ammonia / chlorine complexes suggest structure similar to Werner's theory.

Table: Number of charges related to Werner structures:

	Charges	Primary Valency Ionisable chlorines	Secondary Valency
$[Co(NH_3)_6]^{3+}, 3Cl^-$	6	3	$6NH_3 = 6$
$[Co(NH_3)_5Cl]^{2+}, 2Cl^-$	4	2	$5NH_3 + 1Cl^- = 6$
$[Co(NH_3)_4Cl_2]^{+}. Cl^-$	2	1	$4NH_3 + 2Cl^- = 6$

2. Cryoscopic Measurement :

The freezing point of a liquid is lowered when a non volatile chemical substance is dissolved in it. Cryoscopic measurements involve measuring how much the freezing point is lowered. The depression of freezing point obtained depends on the no. of particles present. Larger no. of ions cause a greater amount of depression in freezing point. Cryoscopic measurements can be used to find if a molecule dissociates & how many ions are formed. If a molecule dissociates into two ions it will give twice the expected depression for a single particle. If three ions are formed this will give three times the expected depression. Thus -

$LiCl \rightarrow Li^+ + Cl^-$	(2 particles)	(2 charges)
$MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$	(3 ")	(4 ")
$LaCl_3 \rightarrow La^{3+} + 3Cl^-$	(4 ")	(6 ")

The number of particles formed from a complex molecule determines the size of the depression of freezing point. Note that the number of particles formed may be different from the total no. of charges which can be obtained from conductivity measurements. The two types of information can be used togather to establish the structure.

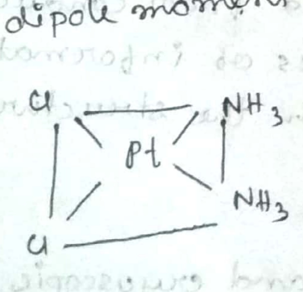
Molar conductivities and cryoscopic measurements for chromium (III) complexes involving ammonia molecules and chloride ions, for example, helps in demarcating the co-ordination sphere from ionisation sphere.

Table : Elucidation of structure on the basis of molar conductivity and cryoscopic measurements.

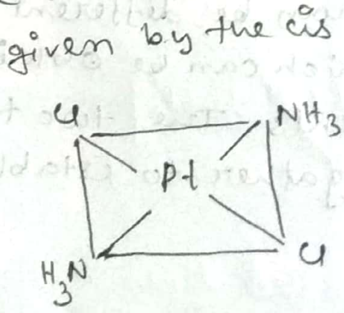
Compound	Molar conductivity	Cryoscopic Measurements	Structure.
$CrCl_3 \cdot 6NH_3$	6 charges	4 particles	$[Cr(NH_3)_6]^{3+} + 3Cl^-$
$CrCl_3 \cdot 5NH_3$	4 charges	3 "	$[Cr(NH_3)_5Cl]^{2+} + 2Cl^-$
$CrCl_3 \cdot 4NH_3$	2 charges	2 "	$[Cr(NH_3)_4Cl_2]^+ + Cl^-$
$CrCl_3 \cdot 3NH_3$	0 charges.	1 "	$[Cr(NH_3)_3Cl_3]$

3. Dipole moment Measurement

Dipole moment measurement may also give structural information but only for non-ionic complexes. For example, the complex $[Pt(NH_3)_2Cl_2]$ is square planar and can exist as cis or trans forms. The dipole moment from the various metal-ligand bonds cancel out in the trans forms. However, a finite dipole moment is given by the cis forms.



Cis



trans.

Valence Bond Theory (VBT)

This theory was developed by Pauling.

Assumption of VBT

1. The bond between metal & ligand is covalent & is formed by overlapping of metal hybrid orbitals and ligand orbitals.

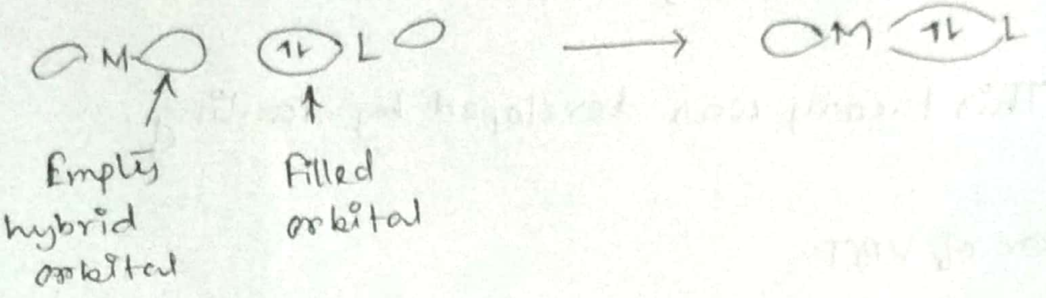
2. The central metal ion makes available a number of empty orbitals (e.g; s, p, d, f) which are equal to its co-ordination number.

3. The vacant orbitals of central metal ion undergo hybridisation as hybrid orbitals f m stronger and better overlapping than unhybridized orbitals. In hybridisation, all and any the vacant half filled and fulfilled orbitals can participate but they must not have more difference in their energies.

4. In VBT, the role of 'd' orbitals in hybridisation was given more importance as transition metal atom have vacant 'd' orbitals of suitable energies. In hybridisation both (n-1)d and nd orbitals can participate. Complexes in which (n-1)d orbitals are involved are called inner orbital complexes and complexes in which nd orbitals are involved are called outer orbital complexes.

5. Usually octahedral inner orbital complexes are more stable than those of octahedral outer orbital complexes.

6. There after the empty hybrid orbital of metal ion overlap with filled orbital of ligands to form covalent co-ordinate bond.



7. Magnetic moment and coordination number of central metal ion are important for deciding the geometry hybridisation, inner/outer nature of complex. The knowledge of magnetic moment gives idea about number of unpaired electrons ($\mu = \sqrt{n(n+2)}$)

8. According to Pauling ligands may be classified into two classes.

a. Strong ligands : They have tendency to pair up electrons of metal ion e.g. CO, CN^- etc.

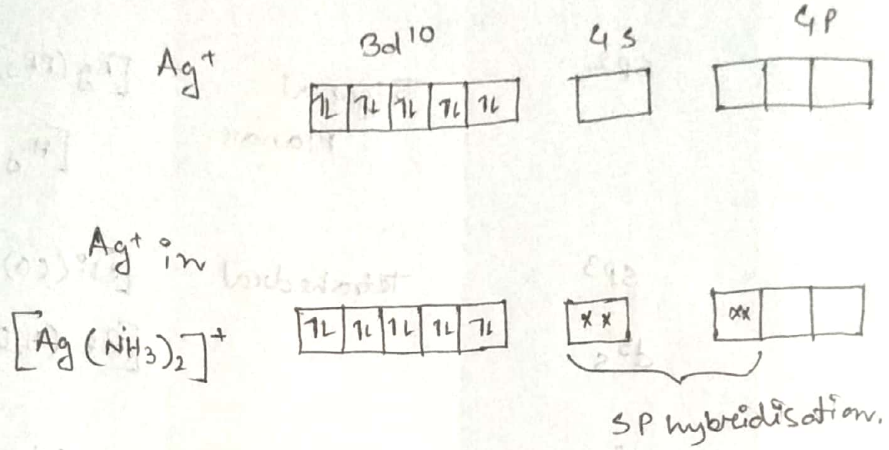
b. Weak ligands : They donot have tendency to pair up the electrons of metal ion e.g. F^-, Cl^-, Br^-, H_2O etc.

Table: Hybrid orbitals for common co-ordination chemistry

Co-ordination Number	Hybridisation	Geometry	Examples
2	sp	Linear	$Ag(NH_3)_2^+$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal Planar	$[Ag(PR_3)_3]^+$, $[HgI_3]^-$
4	sp^3	Tetrahedral	$[Ni(CO)_4]$, $[Zn(NH_3)_4]^{2+}$ $[Be(H_2O)_4]^{2+}$
	d^3s	Tetrahedral	MnO_4^-
	dsp^2	Square Planar	$[Ni(CN)_4]^{2-}$, $[Ni(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$
5	dsp^3	Trigonal Bipyramid	$[Fe(CO)_5]$, $[CuCl_5]^{3-}$
	sp^3d $(ns, np, nd_{x^2-y^2})$	Square Pyramidal	$[VO(AcAc)_2]$
6	d^2sp^3	Octahedral	$[Co(NH_3)_6]^{3+}$ $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$
	sp^3d^2	Octahedral	$[CoF_6]^{3-}$, $[FeF_6]^{3-}$, $[Co(H_2O)_6]^{2+}$

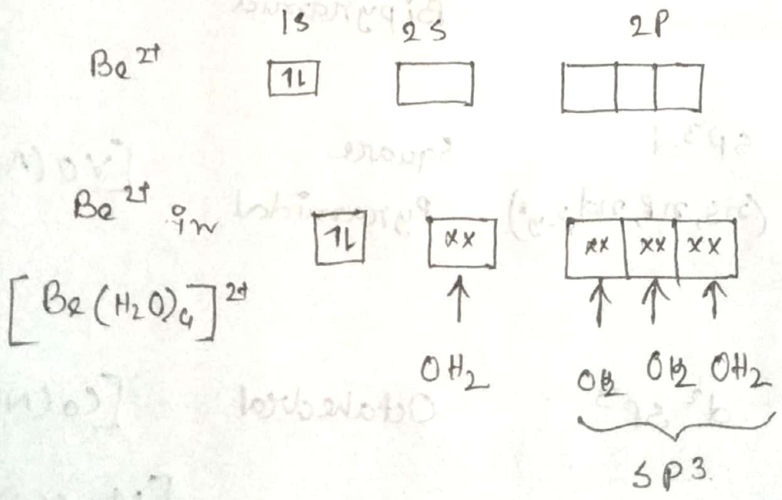
Illustration →

1. $[Ag(NH_3)_2]^+$:



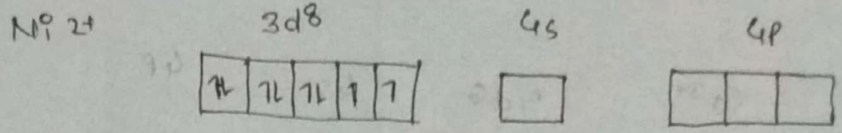
No unpaired electron. Linear & Diamagnetic

II. $[Be(H_2O)_4]^{2+}$:

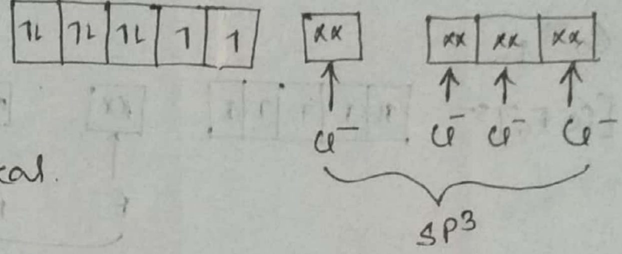


Tetrahedral. Diamagnetic having no unpaired electron.

III. $[NiCl_4]^{2-}$



Ni^{2+} in $[NiCl_4]^{2-}$



Tetrahedral.

Paramagnetic due to presence of unpaired electrons in 3d orbitals.

No. of unpaired electron = 2

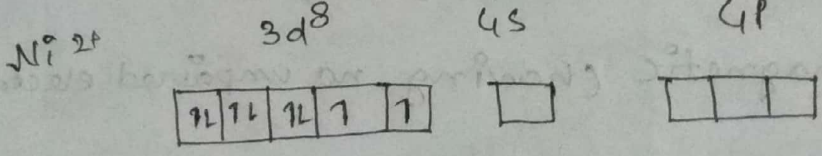
$\therefore$ Magnetic moment $= \sqrt{n(n+2)}$ BM

$= \sqrt{2(2+2)}$

$= 2$ BM.

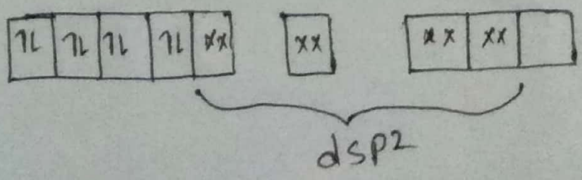
(n = no. of unpaired electrons).

IV. $[Ni(CN)_4]^{2-}$



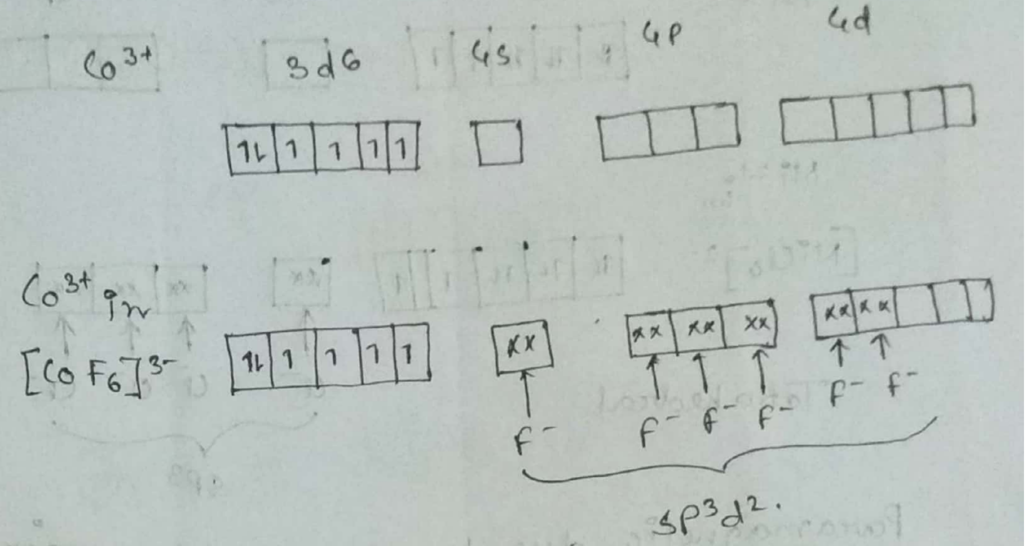
Ni^{2+}

in $[Ni(CN)_4]^{2-}$



Square Planar (Diamagnetic).

V. $[CoF_6]^{3-}$:



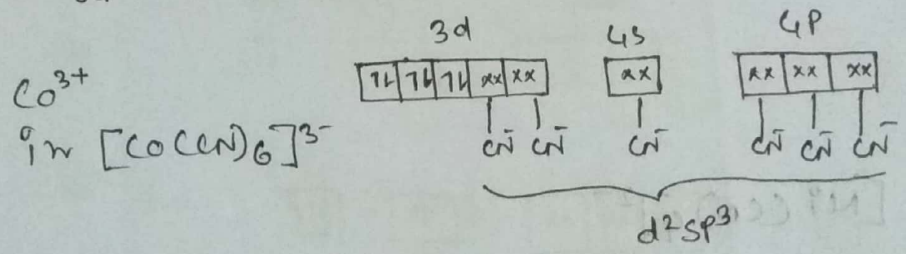
Octahedral (outer orbital).

Paramagnetic, Magnetic moment $= \sqrt{n(n+2)}$ BM

$= \sqrt{4(4+2)}$

$= 4.9$ BM

VI. $[Co(CN)_6]^{3-}$

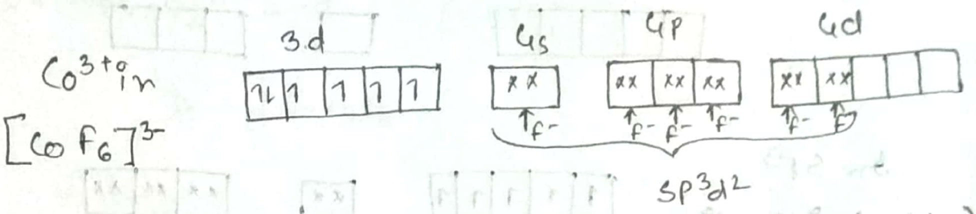


Octahedral (inner orbital)

Diamagnetic (having no unpaired electron).

Outer Orbital Complexes and Inner Orbital Complexes:

To give an explanation about the paramagnetic nature of $[CoF_6]^{3-}$, Huggin suggested that the d orbitals which are hybridised are 4d orbitals but not 3d. Again it was also proposed that all the four unpaired electrons remain unchanged, ie, donot paired up. So, the $[CoF_6]^{3-}$ is paramagnetic in nature.



(outer orbital hybridisation)

($nd_{x^2-y^2}$ & nd_{z^2} are involved in hybridisation).

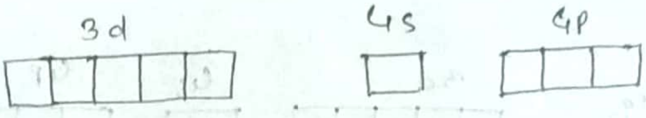
The complexes like $[CoF_6]^{3-}$, ie. where the orbitals undergo in hybridisation are of valence shell, ie; nd orbitals are called as outer orbital complexes. Since here unpaired electrons are present so, their spin is not paired or neutralised. So there complexes are also named as 'spin-free complexes or high spin (H-S) complexes.

Again the complexes like $[Co(CN)_6]^{3-}$, $[Ni(CN)_4]^{2-}$ where the hybridised d orbitals are of (n-1) level ie. (n-1)d orbitals, ie, inner d orbitals are involved in hybridisation, are known as inner orbital complexes. Generally, such type complexes donot contain unpaired electrons so, these complexes also known as spin paired or low spin (LS) complexes.

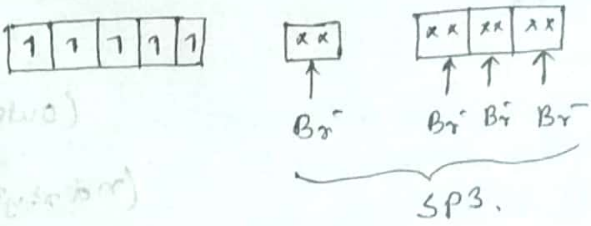
Magnetic moment of $[MnBr_4]^{2-}$ is 5.9 B.M Predict its geometry.

In $[MnBr_4]^{2-}$, the co-ordination no. of Mn^{2+} is 4, i.e, the geometry may be tetrahedral (sp^3) or may be square planar (dsp^2). Now the magnetic moment in sp^3 and dsp^2 hybridisation of Mn^{2+} is as follows-

Mn^{2+} :



In sp^3 hybridisation [in $(MnBr_4)^{2-}$]



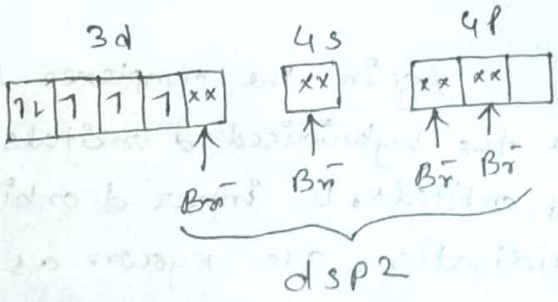
No. of unpaired electrons (n) = 5

$\therefore$ Magnetic moment $(\mu) = \sqrt{n(n+2)}$ BM

$= \sqrt{5 \times 7}$ BM

$= 5.9$ BM.

Mn^{2+} in dsp^2 hybridisation $[MnBr_4]^{2-}$:



No. of unpaired electrons = 3

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

$= \sqrt{3 \times 5}$ BM

$= \sqrt{15}$ B.M $= 3.87$ BM.

Now from the above calculations, we can conclude that the given magnetic moment of $[MnBr_4]^{2-}$ is satisfied when Mn^{2+} exhibits tetrahedral geometry.

ie, the geometry of $[MnBr_4]^{2-}$ is tetrahedral.

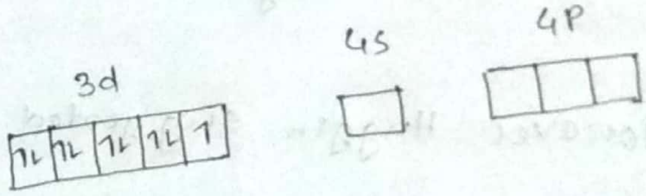
* Predict the magnetic moment of $[Mn(CN)_6]^{3-}$, $[Zn(NH_3)_4]^{2+}$ and $[Ni(NH_3)_4]^{2+}$.

Do yourself.

Structure determination of $[Cu(NH_3)_4]^{2+}$ ⇒

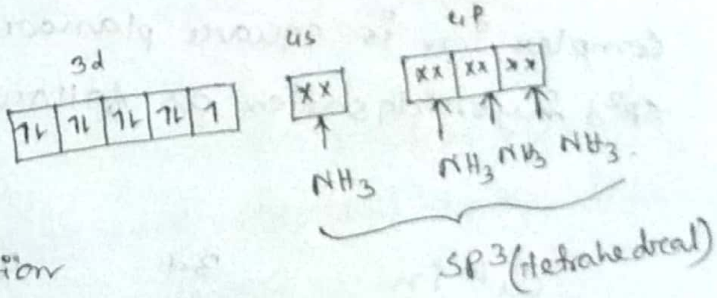
In $[Cu(NH_3)_4]^{2+}$, Cu^{2+} exhibits co-ordination number 4, ie, may be tetrahedral (sp^3) or may be sq. planar (dsP^2). These two cases are as follows—

Cu^{2+}



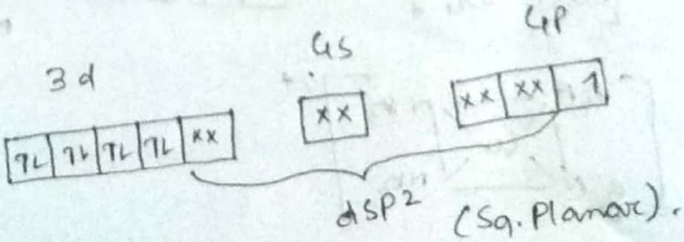
Cu^{2+} in $[Cu(NH_3)_4]^{2+}$

If sp^3 hybridisation



Cu^{2+} in $[Cu(NH_3)_4]^{2+}$

if dsP^2



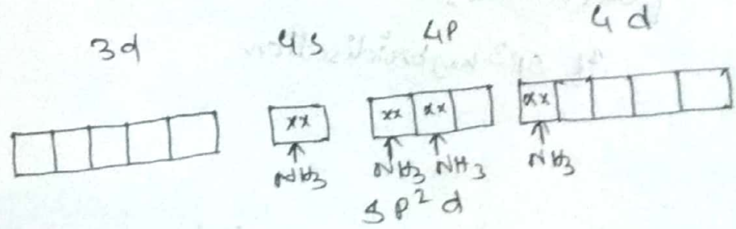
Since in both hybridqsation (dsp^2 and sp^3) there the No. of unpaired electron is 1. So, from magnetic moment value we can not predict the actual geometry of this complex ion. So, from some other physical experiments we can say that it does not exhibit tetrahedral structure.

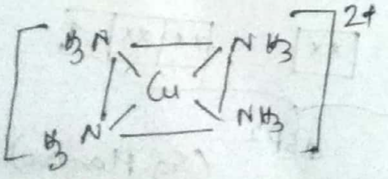
Again if we suppose that the actual structure is square planar, then the unpaired electron of Cu^{2+} will occupy the higher energetic 4P orbital. As a result, it is expected the $[Cu(NH_3)_4]^{2+}$ will undergo oxidation easily, ie, will loose one electron easily. But actually this doesnot loose any electron.

$$[Cu(NH_3)_4]^{2+} \xrightarrow[\text{agent}]{\text{oxidising}} X \quad \text{(No oxidation)}$$

However Huggin suggested that this complex ion is square planar where Cu^{2+} undergoes sp^2d hybridqsation as follows —

Cu^{2+} in $[Cu(NH_3)_4]^{2+}$





Square Planar geometry.

This problem is removed in Crystal field theory.

Drawbacks of VBT :

I. VBT donot consider the splitting of metal d orbital, ie, loss of degeneracy of d orbitals, so it is failure to explain the spectral property of the complexes because in presence of ligands the degeneracy of metal d orbitals is lost.

II. VBT can not satisfactorily explain the magnetic property of all the complexes. for example, in sp^3 hybridisation and octahedral sp^3d^2 hybridisation of Co^{2+} there are three unpaired electrons in both cases. i.e, the expected magnetic moment is 3.87 B.M. But the tetrahedral complexes of Co^{2+} have magnetic moment in the range 4.4 to 4.8 B.M, whereas the μ of octahedral complexes is 4.7 - 5.2 BM. This increase in μ value from the expected value can not be explain by VBT.

III. VBT is failure to explain the abnormal behaviour of Ni^{2+}, Au^{3+} etc (d^8 system) to form sq. planar complexes but not the complexes having coordination no. 5. But this theory only preferes square planar geometry whereas the other geometries such as tetrahedral or trigonal bipyramid should be possible.

IV. VBT can not explain the relative stability of the different geometry and different coordination no. for a particular metal complex.

V. VBT is unable to explain the rate and mechanism of the reactions of a complex.

Electro-Neutrality Principle:

Sidgwick's concept of valency of metal in a complex ie; concept of bonds between the metal atom and ligands suffers from some defects. There are as follows –

When the ligands donate electron pairs to the metal ion then the positive charge on the metal is reduced and a negative charge on the metal is generated. As a result some ionic character is developed in the complex. So the complex becomes unstable.

For example, in $[Fe(CN)_6]^{4-}$ six CN^- ligands donate 6 pairs of electrons to Fe^{+2} ion and as a result some negative charge is generated on Fe^{2+} whereas the two unit positive charge is carried by six CN^- ligands.

So Pauling proposed a principle which is known as electroneutrality principle. According to this principle, electron distribution occurs in such a way that, the charge is ultimately 'zero'. Certain complexes can be explain by this theory. For example-

1. $[Be(H_2O)_4]^{2+}$ exists but $[Be(H_2O)_6]^{2+}$ does not, because 4 water molecule in $[Be(H_2O)_4]^{2+}$ in such a way that the positive charge on Be is just neutralised but in $[Be(H_2O)_6]^{2+}$, six H_2O molecules donate much electrons to Be^{+2}. So a formal -ve charge is created on Be in $[Be(H_2O)_6]^{2+}$ and so this is unstable.

II. $[Al(H_2O)_6]^{3+}$ is stable whereas $[Al(NH_3)_6]^{3+}$ is unstable because due to higher electro negativity the H_2O ligands donates electron pairs in such a way that the charge on 'Al' becomes zero but in case of NH_3 complex, NH_3 ligands donate larger amount of electrons to Al^{+3} which generates a formal negative charge on Al^{+3}, which made the complex unstable.

III. There are some complexes where the ligands can act as a π-acid ligand, ie, act as a π-acceptor. Here π-acid ligands such as CO, CN^-, NO etc. stabilize the complexes by accepting the electron density from the metal through backbonding.

e.g. $Ni(CO)_4$ is stable but $[Zn(CO)_4]^{2+}$ is unstable because due to two (+ve) charge on Zn atom it can not form back bonding and not capable to donate extra electron density to the π* orbital of CO.

Crystal Field Theory (CFT).

This theory was proposed by Bethe and Van Vleck. This theory was originally applied mainly to ionic crystals and is therefore called CFT.

Assumptions of CFT

In the crystal field theory following assumptions are made:

i. The central metal cation is surrounded by ligands which contain atleast one lone pair of electrons.

ii. The ionic ligands (eg; F^-, Cl^-, CN^- etc) are regarded as negative point charges or simply point charges & the neutral ligands (eg; CO, NH_3, H_2O etc) are regarded as point dipoles or simply dipoles. If the ligand is a neutral molecule such as NH_3, H_2O etc, the negative end of the dipole in the molecule is directed towards the central metal cation.

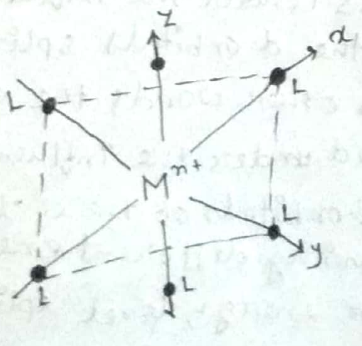
iii. There is no interaction between metal orbitals & ligand orbitals ie, there is no orbitals overlap.

iv. According to this theory, the bonding between central metal cation and ligand is not covalent but it is regarded as purely electrostatic. Thus the bonding in complex may be ion-ion attraction between central metal cation and negative ligands such as Co^{3+} and Cl^-. If the ligand is neutral the bonding may be ion-dipole attraction such as Cr^{3+} and NH_3 or CO. NH_3 has dipole moment with the δ- charge on N & δ+ charge on H atom. Thus in $[Cr(NH_3)6]^{3+}$, the δ- charge on the N atom of each NH_3 molecule point towards the Cr^{3+} ion.

v. The d orbitals on the metal all have the same energy (that is degenerate) in the free atom. However, when a complex is formed the ligands destroy the degeneracy of these orbitals, ie; the orbitals now have different energies. In an isolated gaseous metal ion, the five d orbitals do all have the same energy, and are termed degenerate. If a spherically symmetrical field of negative charges surrounds the metal ion, the d-orbitals remain degenerate. However, the energy of the orbitals is raised because of repulsion between the field & the electron on the metal. In most transition metal complexes, either six or four ligands surround the metal, giving octahedral or tetrahedral structures. In both of these cases the field produced by the ligands is not spherically symmetrical. Thus the d orbitals are not all affected equally by the ligand field.

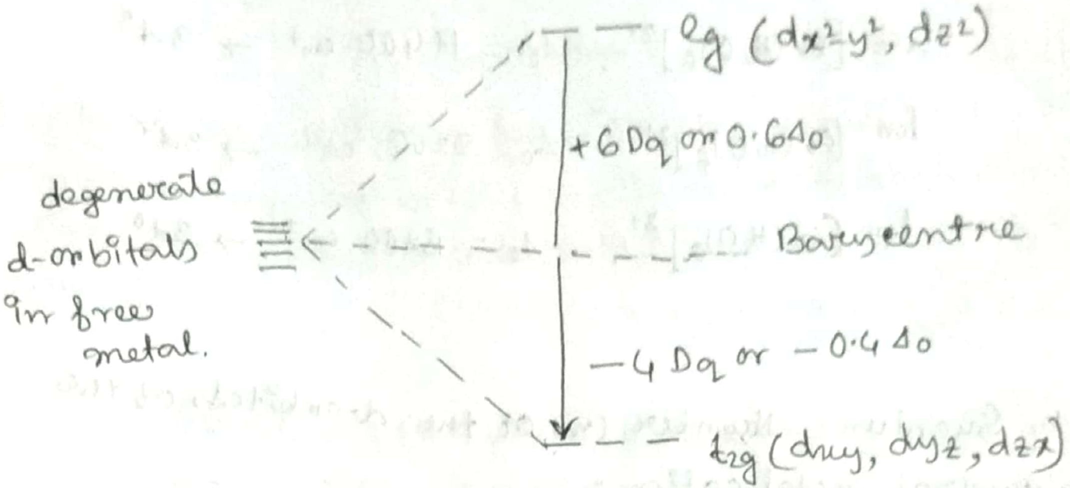
Crystal Field Splitting of d-orbitals in Octahedral Complexes:

In an octahedral complex, the central metal cation is at the centre (origin) of the octahedron and the ligands are at the six corners of the octahedron as shown in the figure. The axes x, y and z point to three adjacent corners of the octahedron.



Now suppose the ligands on each of the three axes are allowed to approach towards the central metal cation (M^{n+}) from both the ends of the axes. In this process the electrons in d-orbitals of the central metal cation are repelled by negative point of point charge or by negative end of the dipole at the ligands. This repulsion will raise the energy of all the five d-orbitals. If all the ligands are symmetrically positioned (ligands are at equal distance from each of the orbitals), the energy of each of five d orbitals will raise by the same amount (ie: all the d-orbitals will still degenerate), but now they will have higher energy than before (free metal cation). This is only a hypothetical situation and this energy state is called barycentre or centre of gravity. It is obvious that not all of the d-orbitals will be affected to the same extent. The lobes of the eg orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the axes x, y & z. The lobes of the t_{2g} orbitals (d_{xy}, d_{yz} & d_{zx}) point in between the axes. The d-orbitals lying along the axes ($d_{x^2-y^2}$ and d_{z^2}) will be more strongly repelled than the orbitals with lobes directed between the axes (d_{xy}, d_{yz} & d_{zx}). Thus the energy of eg orbitals ($d_{x^2-y^2}$ & d_{z^2}) will increase much more than the t_{2g} orbitals (d_{xy}, d_{yz} & d_{zx}). Under the influence of an octahedral ligand field the d-orbitals are, thus split into two sets with eg orbitals at higher energy than t_{2g} orbitals.

Greater is the repulsion, greater will be the increase in energy. Thus under the influence of octahedral ligand field the d-orbitals split into two sets of different energies. In other words the degeneracy of five d-orbitals is removed under the influence of the ligands. The separation of five d-orbitals of the central metal cation into two sets having different energies is called crystal field splitting or energy level splitting.



Crystal field splitting in octahedral field.

The energy difference between t_{2g} and e_g sets is denoted by Δ_o or 10 Dq. Where O in Δ_o standing for octahedral. Δ_o or 10 Dq is called crystal field splitting energy. The energy of the e_g orbitals is 0.6Δ_o / 6 Dq higher than the hypothetical energy state (bary centre) and energy of the t_{2g} orbitals is 0.4Δ_o (= 4 Dq) lower than the hypothetical energy state. In other words we can say that the t_{2g} orbitals are stabilized by amount −0.4Δ_o, while the e_g orbitals are destabilized by 0.6Δ_o with respect to the average energy state.

Factors affecting Δ_o

1. Nature of Metal Cation:

a. Oxidation state of Central Metal Cation:

Higher the oxidation state, higher will be the value of Δ_o for different metal cations having same no. of d-electrons, the cations with a high oxidation state has larger value of Δ_o.

For first row of transition series (3d series metal cation) the value of Δ_o for M^{3+} complexes are roughly 50% lagers than the values of M^{2+} complexes.

For $[V(H_2O)_6]^{2+}$, $\Delta_o = 12400\ cm^{-1} \rightarrow 3d^3$

for $[Cr(H_2O)_6]^{3+}$, $\Delta_o = 17400\ cm^{-1} \rightarrow 3d^3$

for $[Co(H_2O)_6]^{2+}$, $\Delta_o = 9200\ cm^{-1} \rightarrow 3d^7$

For $[Co(H_2O)_6]^{3+}$, $\Delta_o = 18200\ cm^{-1} \rightarrow 3d^6$

b. Quantum Number (n) Of the d-orbitals of the central metal cation:

Δ_o Increases about 30% to 50% from 3d to 4d and by the same amount from 4d to 5d between adjacent members down a group.

Δ_o for 5d > Δ_o 4d > Δ_o 3d.

eg; Δ_o for $[Co(NH_3)_6]^{3+} = 23000\ cm^{-1} \rightarrow 3d^6$

$[Rh(NH_3)_6]^{3+} = 34000\ cm^{-1} \rightarrow 4d^6$

$[Ir(NH_3)_6]^{3+} = 41000\ cm^{-1} \rightarrow 5d^6$

c. NO. Of d-electrons :

The metal ions having same charge but different no. of d-electrons possess different Δ_o. Δ value decreases with increasing the number of d electrons.

Δ_o for $[Co(H_2O)_6]^{2+} = 9300\ cm^{-1} \rightarrow 3d^7$

Δ_o for $[Ni(H_2O)_6]^{2+} = 8500\ cm^{-1} \rightarrow 3d^8$

$\Delta_o \propto$ Charge on cation. (Same no. of d electrons)

$\Delta_o \propto \frac{1}{d\text{-electrons}}$ (same oxidation state)

Nature of the ligands :

The variation of the magnitude of crystal field splitting (Δ) with the nature of the ligand follows a regular order, known as spectrochemical series. The series is as follows with the increasing value of Δ –

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- <$ urea $< OH^- <$
$C_2O_4^{2-} < O_2^- < H_2O < NCS^- < Py \sim NH_3 <$ en $<$ dipy $<$ o-phen $<$
$NO_2^- < PH_3 < CN^- < CO$

The ligands which are π-back bonder such as CO, CN⁻ etc. will produce large Δ. The ligands which are strong σ donor and weak π donor produce large crystal field splitting and again the ligands which are strong π donor and weak σ donor are responsible for small Δ value.

For example :-

a. $[Rh(H_2O)_6]^{3+} \Rightarrow \Delta_o = 27600\ cm^{-1}$

$[Rh(NH_3)_6]^{3+} \Rightarrow \Delta_o = 34100\ cm^{-1}$

$[Rh(en)_3]^{3+} \Rightarrow \Delta_o = 34600\ cm^{-1}$

b. $[NiCl_6]^{4-} \Rightarrow \Delta_o = 7000\ cm^{-1}$

$[NiBr_6]^{4-} \Rightarrow \Delta_o = 7200\ cm^{-1}$

$[Ni(H_2O)_6]^{2+} \Rightarrow \Delta_o = 8500\ cm^{-1}$

$[Ni(NH_3)_6]^{2+} \Rightarrow \Delta_o = 10800\ cm^{-1}$

The spectrochemical series was formed on the basis of electronegativity ; π-bonding ability, dipole moment, polarising power of the ligand.

Similarly, for a given ligand and geometry, the different metal ions can be arranged according to increasing order of Δ_o as follows —

$Mn^{2+} < Ni^{+2} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+}$!

Distribution of d^x electrons ($x = 1$ to 10) of the central metal cation in t_{2g} and e_g orbitals in high spin and low spin octahedral complexes:-

The distribution of d^x electrons of the central metal cation in t_{2g} and e_g orbitals in octahedral complex depends on whether the six ligands are weak or strong. Thus we have the following two cases —

1. When the ligands are weak

This can be shown as:

$$t_{2g}^{1,2,3} \rightarrow e_g^{4,5} \longrightarrow t_{2g}^{6,7,8} \longrightarrow e_g^{9,10}.$$

Here $\Delta_o < P$

d^x ion	Distribution of d^x electrons in t_{2g} and e_g orbitals		$t_{2g}^{p}\, e_g^{q}$ configuration
	t_{2g}	e_g	
d^1	↑ _ _	_ _	$t_{2g}^1\, e_g^0$
d^2	↑ ↑ _	_ _	$t_{2g}^2\, e_g^0$
d^3	↑ ↑ ↑	_ _	$t_{2g}^3\, e_g^0$
d^4	↑ ↑ ↑	↑ _	$t_{2g}^3\, e_g^1$
d^5	↑ ↑ ↑	↑ ↑	$t_{2g}^3\, e_g^2$
d^6	↑↓ ↑ ↑	↑ ↑	$t_{2g}^4\, e_g^2$
d^7	↑↓ ↑↓ ↑	↑ ↑	$t_{2g}^5\, e_g^2$
d^8	↑↓ ↑↓ ↑↓	↑ ↑	$t_{2g}^6\, e_g^2$
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	$t_{2g}^6\, e_g^3$
d^{10}	↑↓ ↑ ↑↓	↑↓ ↑↓	$t_{2g}^6\, e_g^4$

2. When the ligands are strong

This can be shown as $t_{2g}^{1,2,3,4,5,6} \longrightarrow e_g^{7,8,9,10}$

2. When the ligands are strong :

This can be shown as–

$$t_{2g}^{1,2,3,4,5,6} \longrightarrow e_g^{7,8,9,10}.$$

Here $\Delta_o > P$

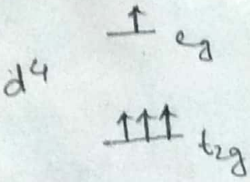
d^x ions	Distribution of d^x electrons in t_{2g} & e_g orbitals		$t_{2g}^p e_g^q$ configuration
	t_{2g}	e_g	
d^1	↑ _ _	_ _	$t_{2g}^1 e_g^0$
d^2	↑ ↑ _	_ _	$t_{2g}^2 e_g^0$
d^3	↑ ↑ ↑	_ _	$t_{2g}^3 e_g^0$
d^4	↑↓ ↑ ↑	_ _	$t_{2g}^4 e_g^0$
d^5	↑↓ ↑↓ ↑	_ _	$t_{2g}^5 e_g^0$
d^6	↑↓ ↑↓ ↑↓	_ _	$t_{2g}^6 e_g^0$
d^7	↑↓ ↑↓ ↑↓	↑ _	$t_{2g}^6 e_g^1$
d^8	↑↓ ↑↓ ↑↓	↑ ↑	$t_{2g}^6 e_g^2$
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	$t_{2g}^6 e_g^3$
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	$t_{2g}^6 e_g^4$

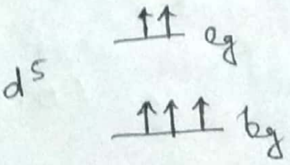
Pairing Energy (P):

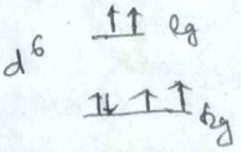
Pairing energy (P) is the energy which is required to pair two electrons against electron-electron repulsion in the same orbital. P is the pairing energy for one electron pair. P is generally expressed in cm^{-1}. Pairing energy depends on the principal energy level (n) of d electrons.

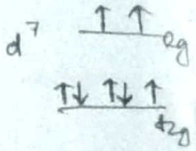
High spin and Low spin Complexes:

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 (HS) or spin free complexes. It is due to the fact that the complexes having most unpaired electrons have higher value of resultant spin and the spin of the electrons do not oppose the spin of one anotherr.

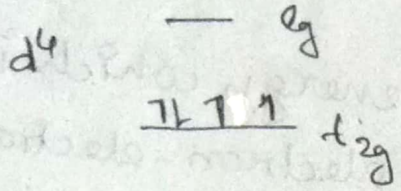


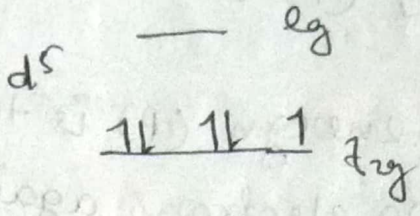


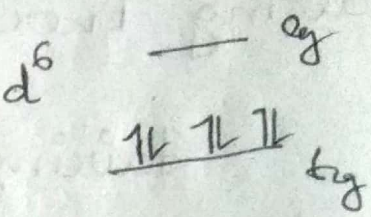


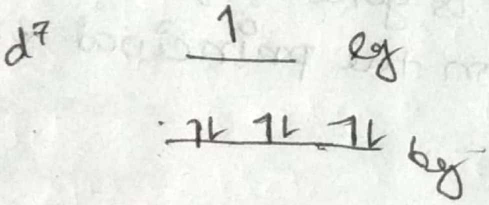


In the octahedral complexes of strong field (ligands), the energy gap Δ_o is greater than the energy required to pair electrons in the same orbital and the t_{2g} level is filled as far as possible. These complexes have lesser no. of unpaired electrons or no unpaired electron so these complexes are called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









i. If $\Delta_o = P$, the low spin complexes have equal energies.

ii. If $\Delta_o > P$, electrons tend to pair and complexes are low spin complexes.

iii. If $\Delta_o < P$, the electrons tend to remain unpaired and hence complexes.

Crystal Field Stabilization Energy:

In octahedral complexes, the d-orbitals of the central metal cation are split into two sets of different energy level (t_{2g} of lower energy & e_g of higher energergy). The energy difference between these two sets is Δ_0 or 10 Dq. The energy of t_{2g} set is lowered by $0.4\Delta_0 (=4Dq)$ while the energy of e_g set is increased by $0.6\Delta_0 (=6Dq)$ relative to the hypothetical energy state. In other words we can say that three of the d-orbitals (ie, t_{2g} orbitals) are stabilised by $0.4\Delta_0$ per electron and two of the d-orbitals (ie e_g orbitals) are destabilised by $0.6\Delta_0$ per electron. Thus energy of each electron in t_{2g} orbitals decreases by $-0.4\Delta_0$ while in e_g orbitals increases by $+0.6\Delta_0$. $-$ and $+$ sign indicate decrease and increase in the energy respectively.

For d^1 case, the electron occupies a t_{2g} orbitals which has an energy of $-0.4\Delta_0$ relative to the barycentre of the d-orbitals. The complex can thus be said to be stabilized to the extent of $0.4\Delta_0$ compared to the barycentre. This quantity is termed as crystal field stabilization energy (CFSE).

Thus for d^1 complex, electronic configuration is- $t_{2g}^1 e_g^0$

$$CFSE = -0.4 \times 1\Delta_0 = -0.4\Delta_0$$

For d^2 complex, electronic configuration is - $t_{2g}^2 e_g^0$.

$$CFSE = -0.4 \times 2\Delta_0 = -0.8\Delta_0$$

for d^3 complex, electronic configuration is $t_{2g}^3 e_g^0$

$$CFSE = -0.4 \times 3\Delta_0 = -1.2$$

Thus in case of an octahedral complex with the configuration $t_{2g}^{p} e_g^{q}$, the crystal field stabilisation is given by –

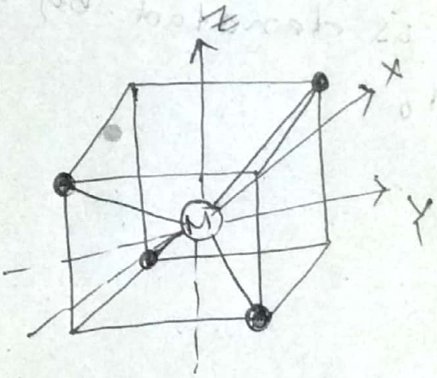
$$CFSE = [-0.4\,p + 0.6\,q]\,\Delta_o$$

CFSE for d^0 to d^{10} for HS and LS octahedral complex –

d^n	Weak field/H.S		Strong field/L.S	
	configuration	CFSE	configuration	CFSE
d^1	t_{2g}^{1}	$-0.4\times1\,\Delta_o = -0.4\,\Delta_o$	t_{2g}^{1}	$-0.4\times1\,\Delta_o = -0.4\,\Delta_o$
d^2	t_{2g}^{2}	$-0.4\times2\,\Delta_o = -0.8\,\Delta_o$	t_{2g}^{2}	$-0.4\times2\,\Delta_o = -0.8\,\Delta_o$
d^3	t_{2g}^{3}	$-0.4\times3\,\Delta_o = -1.2\,\Delta_o$	t_{2g}^{3}	$-0.4\times3\,\Delta_o = -1.2\,\Delta_o$
d^4	$t_{2g}^{3} e_g^{1}$	$[-0.4\times3+0.6\times2]\,\Delta_o = -0.6\,\Delta_o$	t_{2g}^{4}	$-0.4\times4\,\Delta_o = -1.6\,\Delta_o$
d^5	$t_{2g}^{3} e_g^{2}$	$[-0.4\times3+0.6\times2]\,\Delta_o = 0\,\Delta_o$	t_{2g}^{5}	$-0.4\times5\,\Delta_o = -2.0\,\Delta_o$
d^6	$t_{2g}^{4} e_g^{2}$	$[-0.4\times4+0.6\times2]\,\Delta_o = -0.4\,\Delta_o$	t_{2g}^{6}	$-0.4\times6\,\Delta_o = -2.4\,\Delta_o$
d^7	$t_{2g}^{5} e_g^{2}$	$[-0.4\times5+0.6\times2]\,\Delta_o = -0.8\,\Delta_o$	$t_{2g}^{6} e_g^{1}$	$[-0.4\times6+0.6\times1]\,\Delta_o = -1.8\,\Delta_o$
d^8	$t_{2g}^{6} e_g^{2}$	$[-0.4\times6+0.6\times2]\,\Delta_o = -1.2\,\Delta_o$	$t_{2g}^{6} e_g^{2}$	$[-0.4\times6+0.6\times2]\,\Delta_o = -1.2\,\Delta_o$
d^9	$t_{2g}^{6} e_g^{3}$	$[-0.4\times6+0.6\times3]\,\Delta_o = -0.6\,\Delta_o$	$t_{2g}^{6} e_g^{3}$	$[-0.4\times6+0.6\times3]\,\Delta_o = -0.6\,\Delta_o$
d^{10}	$t_{2g}^{6} e_g^{4}$	$[-0.4\times6+0.6\times4]\,\Delta_o = 0.0\,\Delta_o$	$t_{2g}^{6} e_g^{4}$	$[-0.4\times6+0.6\times4]\,\Delta_o = 0.0\,\Delta_o$

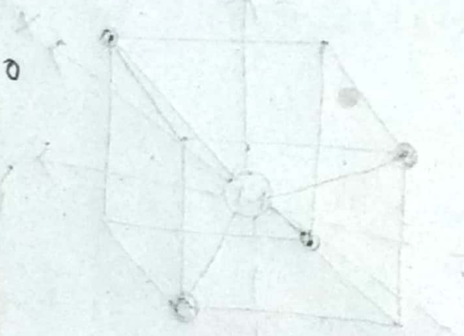
Splitting of d orbitals in Tetrahedral Field →

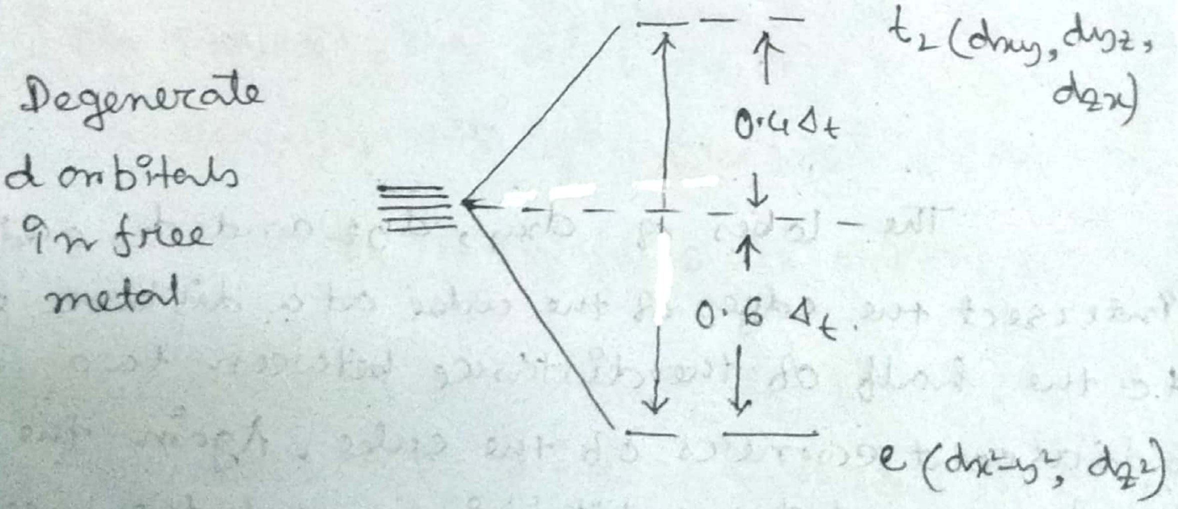
In free metal ion all the five d orbitals are degenerate. Let us consider, a tetrahedral complex of ML_4 type, where the four ligands (L) surround the central metal (M) tetrahedrally. If a tetrahedral complex is placed in a cube to correlate the spatial arrangement of d orbitals in a cartesian co-ordinate, the four ligands occupy the alternative corners of the cube and the metal ion or atom is placed in the centre of the cube.



The lobes of d_{xy}, d_{yz} and d_{zx} orbitals intersect the edges of the cube at a distance equal to the half of the distance between two adjascent corners of the cube. Again the lobes of $d_{x^2-y^2}$ and d_{z^2} orbitals intersect the faces of the cube at a distance equal to the half of face diagonal away from a ligand.

Although the lobes of d_{xy}, d_{yz} & d_{xz} aren't lying along the path of the ligands but are in the path of the ligand, ie, are lying in the closer distance with the path of the ligands than the lobes of $d_{x^2-y^2}$ and d_{z^2}, which are lying along the axes, ie, The lobes of $d_{x^2-y^2}$ and d_{z^2} are lying in space between the ligands. So, d_{xy}, d_{yz} and d_{zx} orbitals experience a greater repulsive force than that of $d_{x^2-y^2}$ and d_{z^2} orbitals. So energy of the former three orbitals are raised whereas the later two orbitals get stabilise, ie, the energy is lowered. So. former three form a set of orbitals named as t_2 and later two form a set of orbitals named as e orbitals Energy difference between e and t_2 is denoted by Δ_t, which is smaller than Δ_o





Why Δ_t is less than Δ_o?

The energy difference between t_{2g} and e_g sets is denoted by Δ_o in case of octahedral and in tetrahedral field energy gap between e and t_2 is named as Δ_t. It has been shown that $\Delta_t < \Delta_o$ as follows—

1. In tetrahedral, only four ligands interact with the metal d electrons whereas in oct, it is 6 ligands. So electrostatic interaction of four ligands would be 2/3 of that produced by six ligands.

ii. The direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field splitting by roughly or further two-third.

$$\therefore \Delta_t = \frac{2}{3} \times \frac{2}{3} \Delta_o = 4/9 \Delta_o.$$

Why tetrahedral complexes are always high spin?

Strong field ligands cause a bigger energy difference between t_{2g} and e_g than weak field ligands. However, in case of tetrahedral splitting Δ_t is always smaller than Δ_o of octahedral splitting ($\Delta_t = 0.45 \Delta_o$). Thus it is never energetically favourable to pair electrons. So, we can say that all tetrahedral complexes are highspin (weak field) and low spin complexes (tδ) are rarely observed.

Distribution of d-electrons in a Tetrahedral Ligand Field:

According to CFT, in tetrahedral ligand field metal d orbitals are splitted into two sets —

i. e ($d_{x^2-y^2}$ & d_{z^2})

ii. t_2 (d_{xy}, d_{yz} & d_{zx}).

The energy gap between e & t_2 is denoted by Δ_t.

Where $\Delta_t = 4/9\,\Delta_0 = 0.45\,\Delta_0$

Now the e orbitals are stabilised by —

$0.6 \times \Delta_t = 0.6 \times 0.45\,\Delta_0 = 0.27\,\Delta_0$

and the t_2 orbitals are disstabilised by $0.4 \times \Delta_t$ $= 0.4 \times 0.45\,\Delta_0 = 0.18\,\Delta_0$ amount of energy.

i.e, Due to introduction of one electron in e orbital the complex get stability by $(-0.27\,\Delta_0)$ amount of CFSE and when one electron is introduced in t_2 orbitals then the complex gets stability of $(0.18\,\Delta_0)$ amount of CFSE. Now the distribution of d-electrons and the corresponding CFSE values for a tetrahedral ligand field is as follows —

No. of d-electron	Distribution	CFSE
d^1	$e^1 t_2^0$	$-0.27\Delta_o$
d^2	$e^2 t_2^0$	$-0.54\Delta_o$
d^3	$e^2 t_2^1$	$-0.54\Delta_o + 0.18\Delta_o = -0.36\Delta_o$
d^4	$e^2 t_2^2$	$-0.54\Delta_o + 0.36\Delta_o = -0.18\Delta_o$
d^5	$e^2 t_2^3$	$-0.54\Delta_o + 0.54\Delta_o = 0$
d^6	$e^3 t_2^3$	$-0.81\Delta_o + 0.54\Delta_o = -0.27\Delta_o$
d^7	$e^4 t_2^3$	$-1.08\Delta_o + 0.54\Delta_o = -0.54\Delta_o$
d^8	$e^4 t_2^4$	$-1.08\Delta_o + 0.72\Delta_o = -0.36\Delta_o$
d^9	$e^4 t_2^5$	$-1.08\Delta_o + 0.90\Delta_o = -0.18\Delta$
d^{10}	$e^4 t_2^6$	$-1.08\Delta_o + 1.08\Delta_o = 0$