Magnetic Criterion :-

In d^2sp^3 and dsp^2 hybridization, it is necessary that there should be pairing of electron in order to make 3d orbital vaccant & available for hybridization.

The no. of unpaired $e^{\ominus}$ in complex ion is reduced as compared to free metal ion. Magnetic properties of complex ion and free metal ion are different.

Pauling made use of magnetic data to find the number of unpaired electrons in given species. The number of unpaired electron and magnetic moments in B.M. (Bohr magneton) are related to each other by following formula:

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$

where,

μ = magnetic moment

n = no. of unpaired $e^{\ominus}$ in species.

B.M. = Bohr magneton

This formula is called 'spin only formula' and applied for complexes of 3d series elements. By using this formula we can show that for given number of unpaired electron in ion, its magnetic moment will be as follows.

No. of unpaired electron	1	2	3	4	5
Magnetic moment (B.M.)	1.73	2.83	3.87	4.90	5.92

Pauling compared value of magnetic moment of species before and after the complex formation and showed that rearrangment of electrons takes place in many complexes. If unpaired electron not disturbed during hybridization, the value of magnetic moment does not

change. Thus free metal ion and corresponding complex show the same value.

Complexes of first Transition series (3d) elements:-

The complexes of first transition series elements are more stable than those formed by 2nd and 3rd transition series element. The stability of these complexes is belived to be due to following reasons.

① The transition metal ion of first series have comparatively smaller size and high positive charge density due to which they can readily accept lone pair of electrons from the ligands resulting in the formation of more stable complex.

② The 3d- orbitals of these metal ions are partially vacant. metal ions use these orbitals to form hybrid orbitals of required energy. These hybrid orbitals posses suitable energy to accept lone pair of electrons from ligands.

③ Most of the metal ions of 1st transition series show the unique property of variable oxidation state. Due to this, metal ion are capable of exhibiting different coordination number. The most common C.N. show by these metals ions are 4 and 6.

① Complexes With d^1, d^2, d^3 configuration:

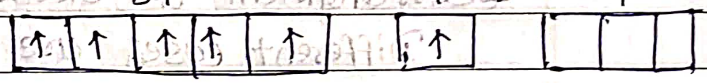
When Cr^{III} possesses 1, 2 or 3 d-electrons they will occupy first three 'd' orbital and remain unpaired. Two 3d- orbitals thus remain vaccant.

Example: Formation of $[Cr(NH_3)_6]^{3+}$.

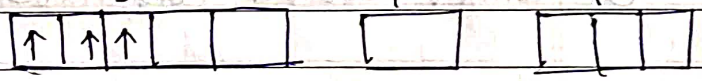
In this chromium is in +3 oxidation state. Atomic no. of Chromium is 24 and its electronic configuration

of $Cr = [Ar]\,3d^5\,4s^1$ and $Cr^{3+} = [Ar]\,3d^3$. In this 3p-orbitals are completely filled, they do not take part in chemical bonding and hence termed as non-bonding orbitals. These are generally neglected in showing the structure of complex ion where only orbitals involved in bond formation are drawn, thus in present case only 3d, 4s and 4P orbitals are drawn because they are involved in chemical bonding. Now as two 3d, one 4s and three 4P-orbitals are used for metal-ligand bonding, i.e, for accommodation of six ligand molecule, they hybridized to yield six d^2sp^3 hybrid orbitals of equal energy so that they give same properties and equal strength to all metal-ligand bonds. The resulting six d^2sp^3 hybrid orbitals are occupied by electron pairs (marked as 'xx') donated by six ligand molecules each donating one lone pair.

i) Cr atom $[Ar]\,3d^5\,4s^1$ =

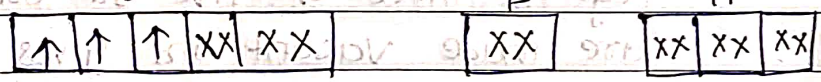


ii) Cr^{3+} ion $[Ar]\,3d^3$ =



Six empty orbitals.

iii) $[Cr(NH_3)_6]^{3+}$

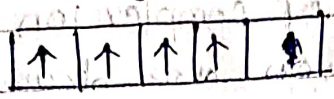


Six d^2sp^3 hybrid bonds formed bet^n Cr^{3+} & NH_3.

This d^2sp^3 hybridization gives octahedral geometry & complex $[Cr(NH_3)_6]^{3+}$ is octahedral. complex has three unpaired electron and hence it is paramagnetic.

② Complexes with d^4, d^5, d^6 configuration :-

In case of these ions 3d- orbitals have following electronic configuration in ground state.

$3d^4$  one orbital vacant

$3d^5$  No orbital vacant

$3d^6$  No orbital vacant.

Two 3d- orbitals are not vacant and hence not available for hybridization in any of above case. Hence these ions will form complexes in which either

① There is rearrangment of electrons and two 3d- orbitals are made vacant.

② Next higher orbital used for hybridization without rearrangment of electron.

Different cases are discussed below -

① Inner orbital complexes involving d^2sp^3 hybridization :-

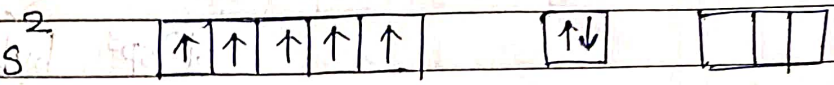
The CMI takes up some amount of energy and in the excited state the unpaired electron are forced to pair up in three of five 3d- orbitals. Thus two 3d-orbitals are made vacant and gives d^2sp^3 hybrid orbitals. The complex is formed is octahedral.

Example :-

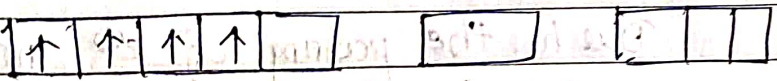
Type	Metal ion	Complex ion
d^4	Mn^{3+}	$[Mn(CN)_6]^{3-}$
d^5	Fe^{3+}	$[Fe(CN)_6]^{3-}$
d^6	Fe^{2+}	$[Fe(CN)_6]^{4-}$
	Co^{3+}	$[Co(H_2O)_6]^{3+}$

Eg of d^4 : ① $[Mn(CN)_6]^{3-}$

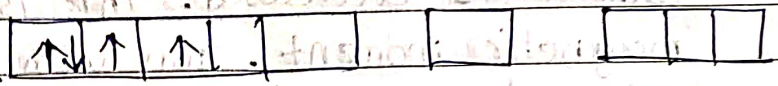
Mn [Ar] $3d^5 4s^2$



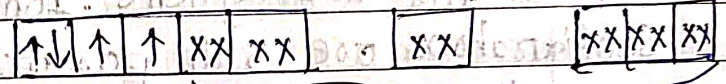
Mn^{3+}



Mn^{3+} (excited state)



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

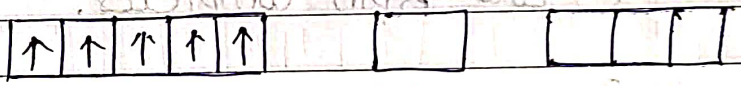


d^2sp^3 hybridization

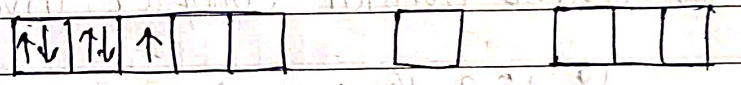
Eg of d^5 : $[Fe(CN)_6]^{3-}$

Fe [Ar] $3d^6 4s^2$

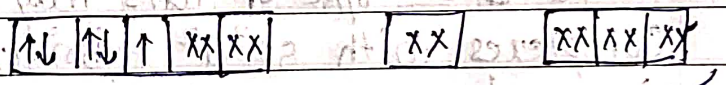
Fe^{3+}



Fe^{3+} (excited state)



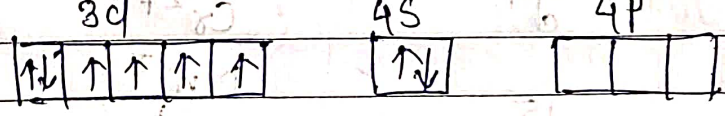
$[Fe(CN)_6]^{3-}$



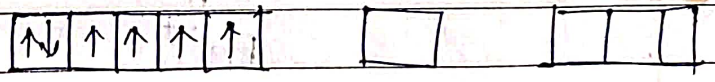
d^2sp^3 hybridization.

Eg of d^6 : $[Fe(CN)_6]^{4-}$

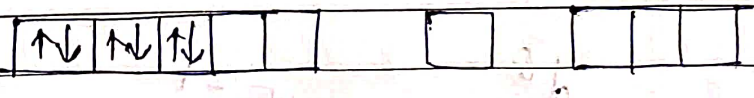
Fe [Ar] $3d^6 4s^2$

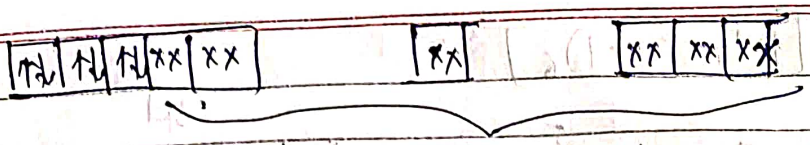


Fe^{2+}



Fe^{2+} (excited state)



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

d^2sp^3 hybridization

Due to the pairing of $e^\ominus$, no. of unpaired $e^\ominus$ in complex is decreased. This is seen by decrease in magnetic moment. Ion with d^6 configuration have all electron paired so it shows zero magnetic moment and diamagnetic. Ion with d^4 & d^5 configurations are still paramagnetic but they show magnetic moment of 2 & 1 unpaired $e^\ominus$ respectively

The magnetic moment value of all above complexes are less than that of free ions, hence these complexes are called low spin complexes. This complexes can be described as (i) octahedral complex, (ii) Inner orbital complex and (iii) Low spin complexes.

(ii) Outer orbital complexes involving sp^3d^2 hybridization:-

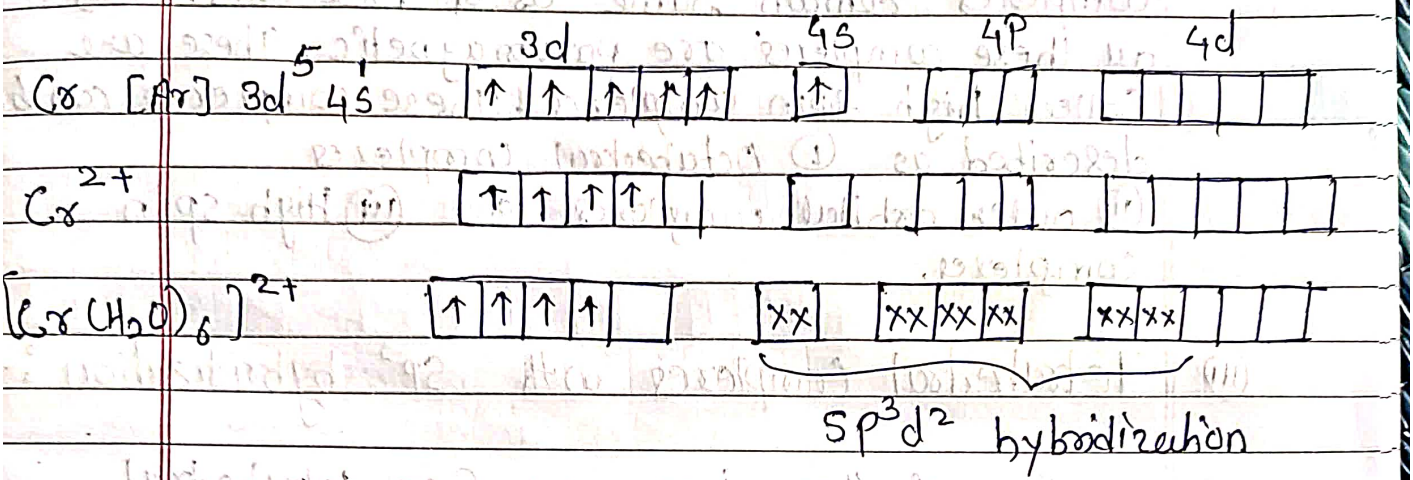
d^4, d^5 & d^6 type of ions may be also octahedral complexes with sp^3d^2 hybridization. The orbital involved are one 4s, three 4P and two 4d. This orbitals hybridize to form six sp^3d^2 hybrid orbitals

Example :-

Type	Metal ion	complex ion
d^4	Cr^{2+}	$[Cr(H_2O)_6]^{2+}$
	Mn^{3+}	$[Mn(H_2O)_6]^{3+}$
d^5	Mn^{2+}	$[Mn(H_2O)_6]^{2+}$
	Fe^{3+}	$[Fe(H_2O)_6]^{3+}$, $[FeF_6]^{3-}$, $[Fe(C_2O_4)_6]^{3-}$
d^6	Fe^{2+}	$[Fe(H_2O)_6]^{2+}$
		$[Fe(NH_3)_6]^{2+}$

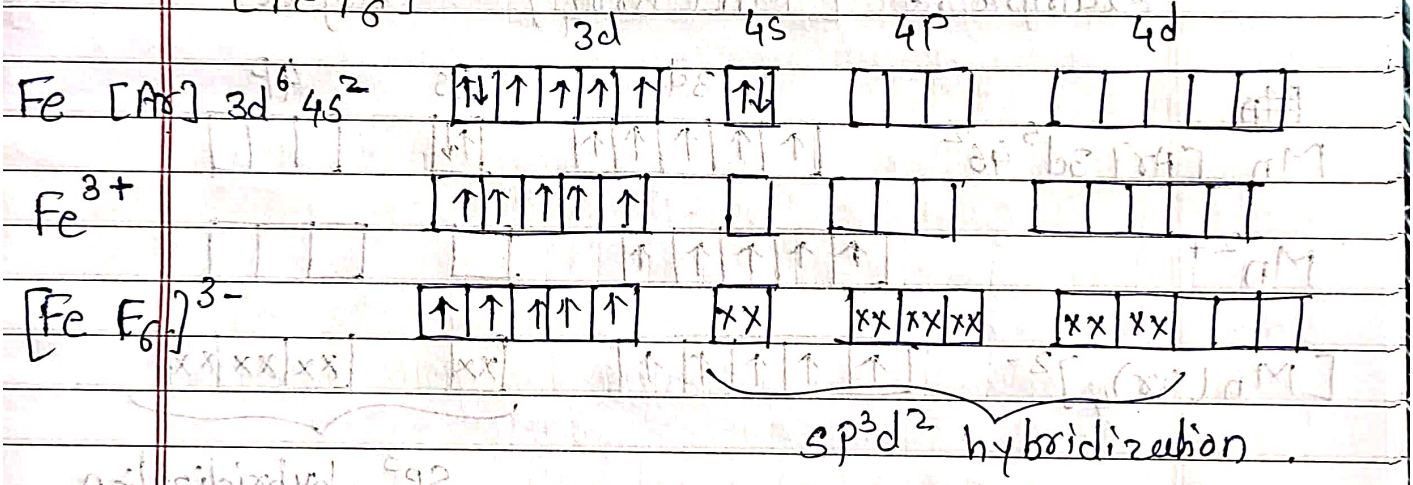
Example of d^4 type:

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



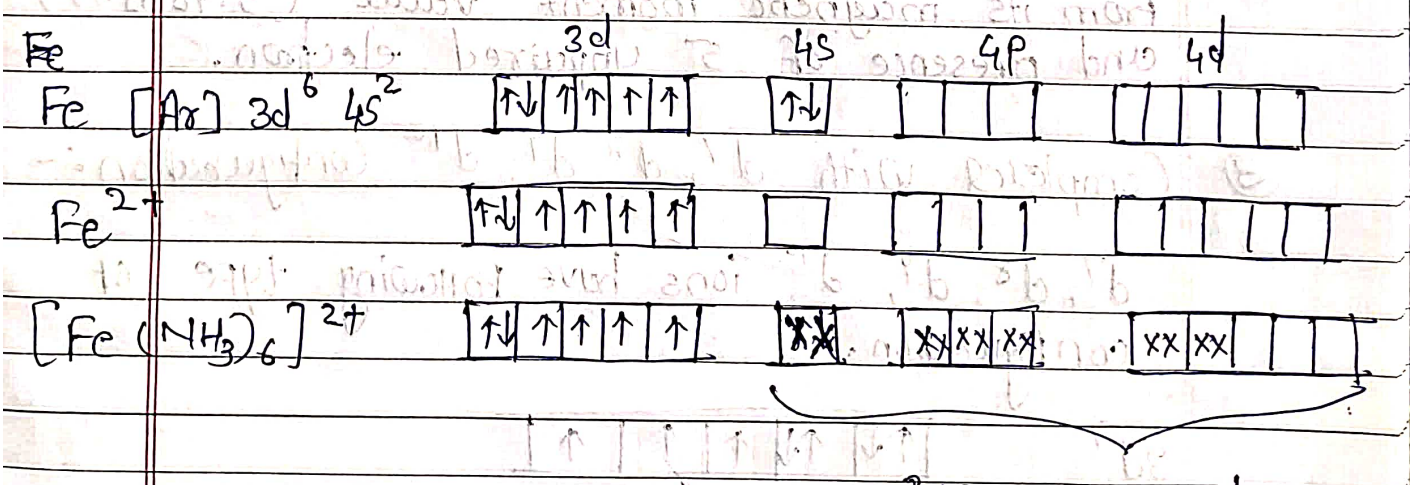
Example of d^5 type

$[FeF_6]^{3-}$



Example of d^6 type

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

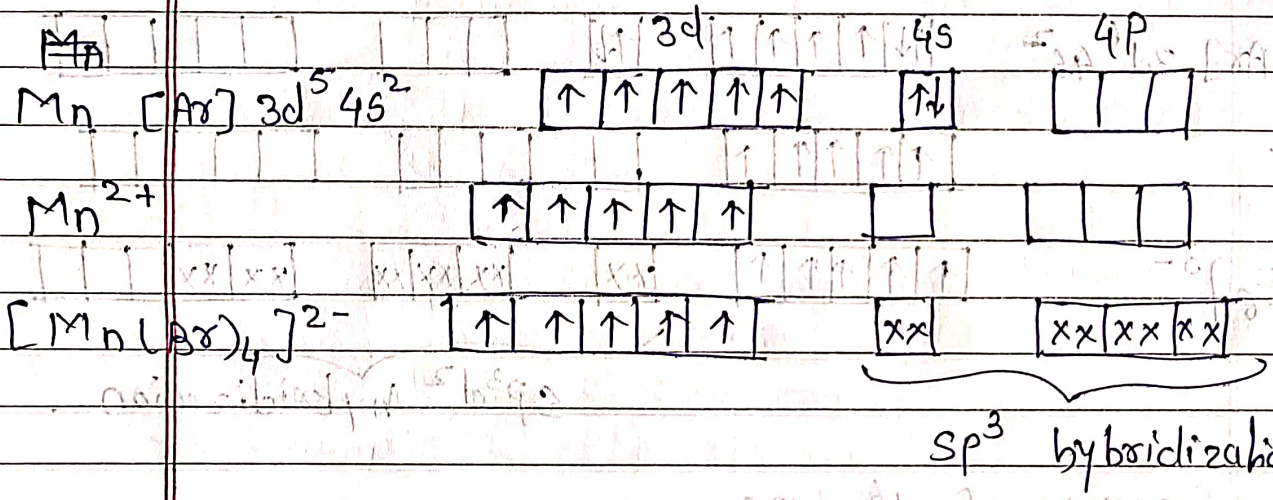


In above cases, the inner 3d-electron are not disturbed. Hence magnetic moment of complexes remain same as of free ions. Thus all these complexes are paramagnetic. These are called high spin complexes. These complexes can be described as (i) Octahedral complexes (ii) outer orbital complexes and (iii) High spin complexes.

(iii) Tetrahedral Complexes with sp^3 hybridization :-

Some of these ions may form tetrahedral complexes with sp^3 hybridization.

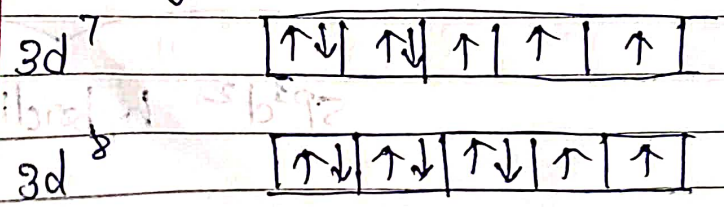
Example :- $[Mn(Br)_4]^{2-}$ complex



The tetrahedral structure of this complex is confirmed from its magnetic moment value (5.90 B.M.) and presence of 5 unpaired electron.

(3) Complexes with d^7, d^8, d^9, d^{10} configuration :-

d^7, d^8, d^9, d^{10} ions have following type of configuration.



$3d^9$ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ |

$3d^{10}$ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ |

In above cases two 3d -orbitals can not be made vacant even after maximum pairing. The formation of inner orbital complexes with d^2sp^3 hybridization is difficult.

Different type of Complexes formed by these ions are given below.

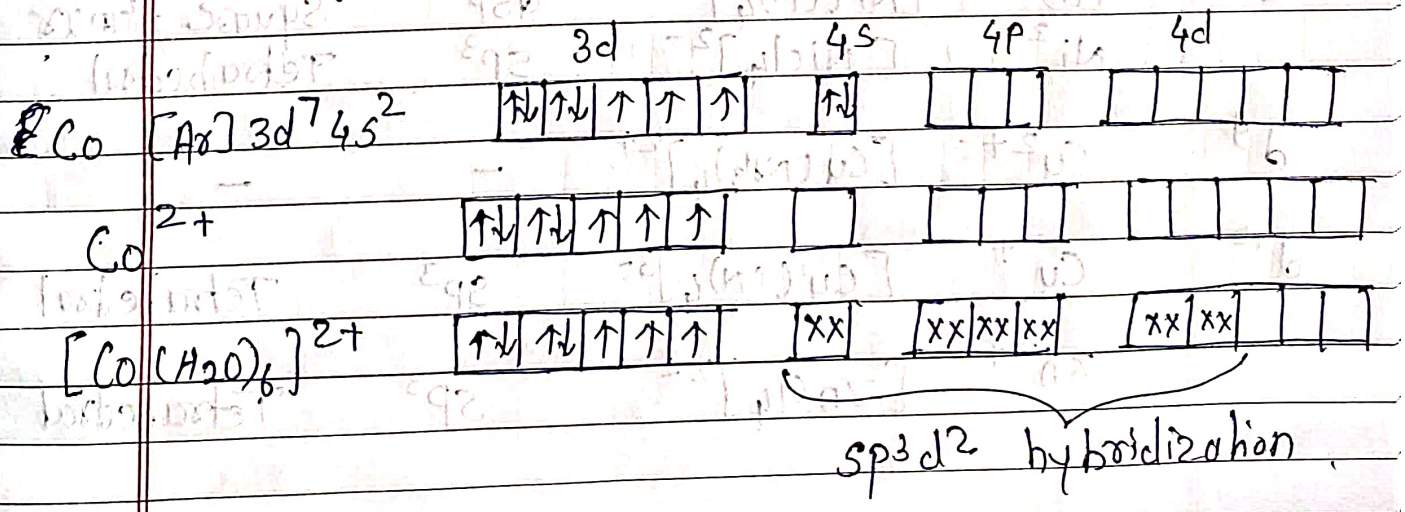
Type	Metal ion	complex ion
d^7	Co^{2+}	$[Co(H_2O)_6]^{2+}$
d^8	Ni^{2+}	$[Ni(NH_3)_6]^{2+}$

(1) Outer orbital complexes with sp^3d^2 hybridization:-

In sp^3d^2 type hybridization one 4s, ~~two~~ three 4p and two 4d orbitals get hybridize to form six sp^3d^2 hybridization. The electronic structure of these complexes are given below.

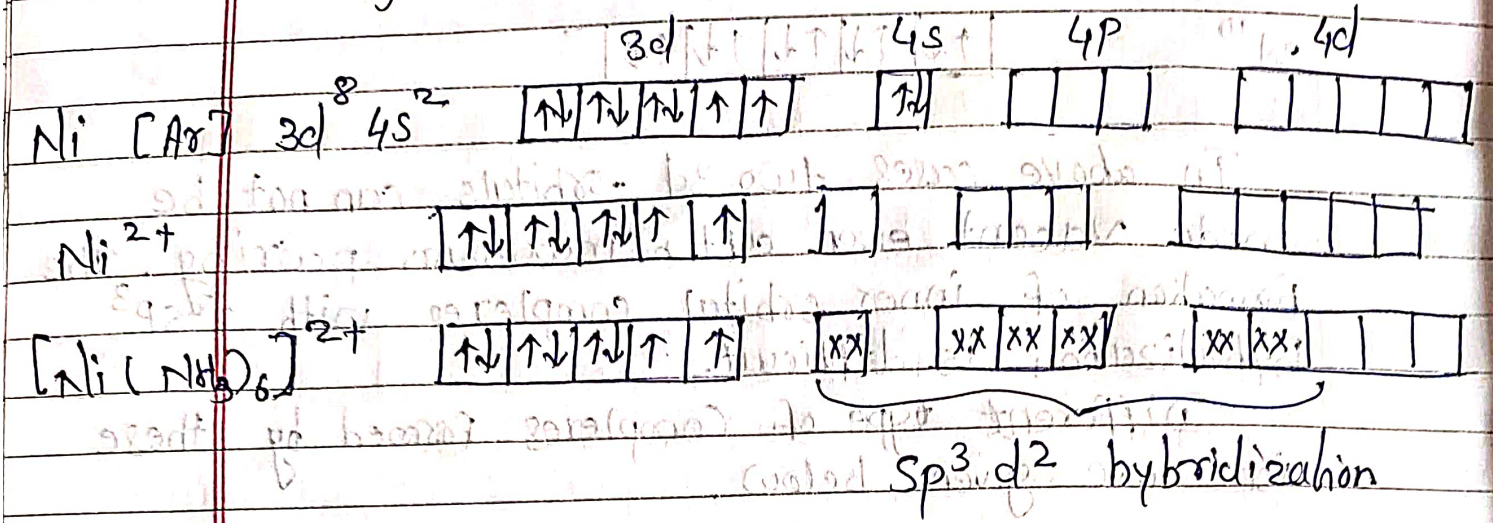
d^7 configuration :-

Example $[Co(H_2O)_6]^{2+}$



d^8 configuration :-

Example $[Ni(NH_3)_6]^{2+}$:-



These complexes are octahedral and paramagnetic The magnetic moment of these complexes are corresponds to presence of 3 and 2 unpaired $e^{\ominus}$.

(11) Tetrahedral or square planar complexes with C.N. 6 :-

Some of these ions can form tetrahedral or square planar complexes using sp^3 or dsp^2 hybridization.

Example :-

Type	metal ion	complex ion	Hybridization	Geometry
d^8	Ni^{2+}	$[Ni(CN)_4]^{2-}$	dsp^2	Square planar
	Ni^{2+}	$[NiCl_4]^{2-}$	sp^3	Tetrahedral
d^9	Cu^{2+}	$[Cu(NH_3)_4]^{2+}$	–	–
d^{10}	Cu^{+}	$[Cu(CN)_4]^{3-}$	sp^3	Tetrahedral
	Zn^{2+}	$[ZnCl_4]^{2-}$	sp^3	Tetrahedral

dsp^2 hybridization forms square planar complexes which is formed by mixing of one d, one s & two p - orbitals and form four equivalent dsp^2 hybrid orbitals which are planar and mutually at right angles pointing toward four corners of square.

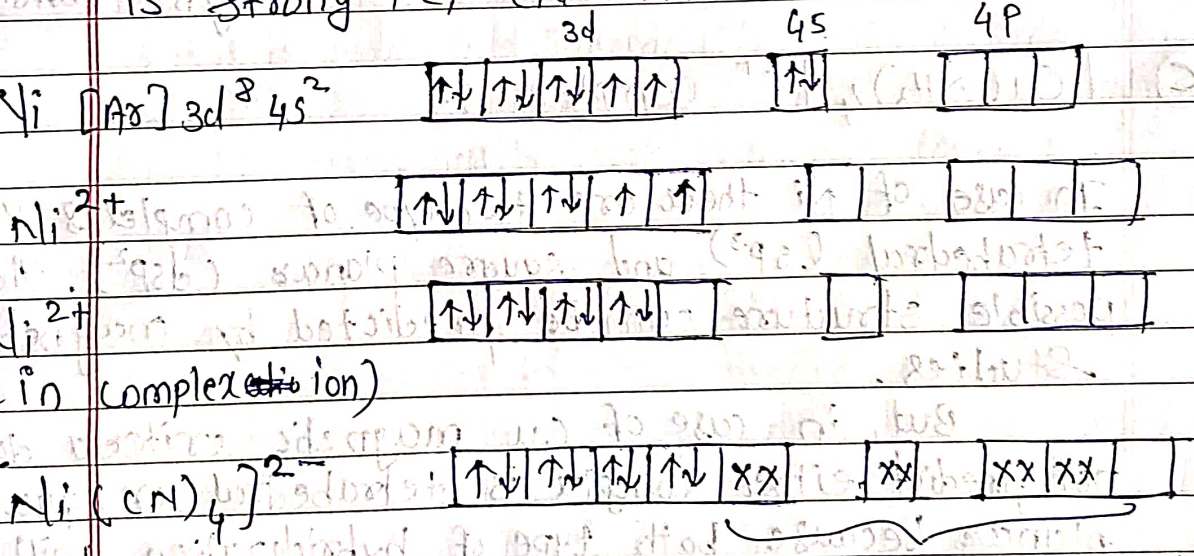
The d-orbital involve is dx^2-y^2 orbital in shell lower than that of s & p - orbitals.

Example :-

(a) formation of $[Ni(CN)_4]^{2-}$ complex :-

Here C.N. of Ni is 4 and configration of Ni^{2+} is $[Ar]\ 3d^8\ 4s^0$ which reveals complex formed by sp^3 hybridization and it is paramagnetic as it is having two unpaired $e^{\ominus}$.

However, experimental data reveals that the complex is diamagnetic i.e. no any unpaired electrons. This is possible only when 3d-$e^{\ominus}$ rearrange against Hund's rule as shown below, it is also accordance with the fact that ligand involved here is strong i.e, CN^- ion.

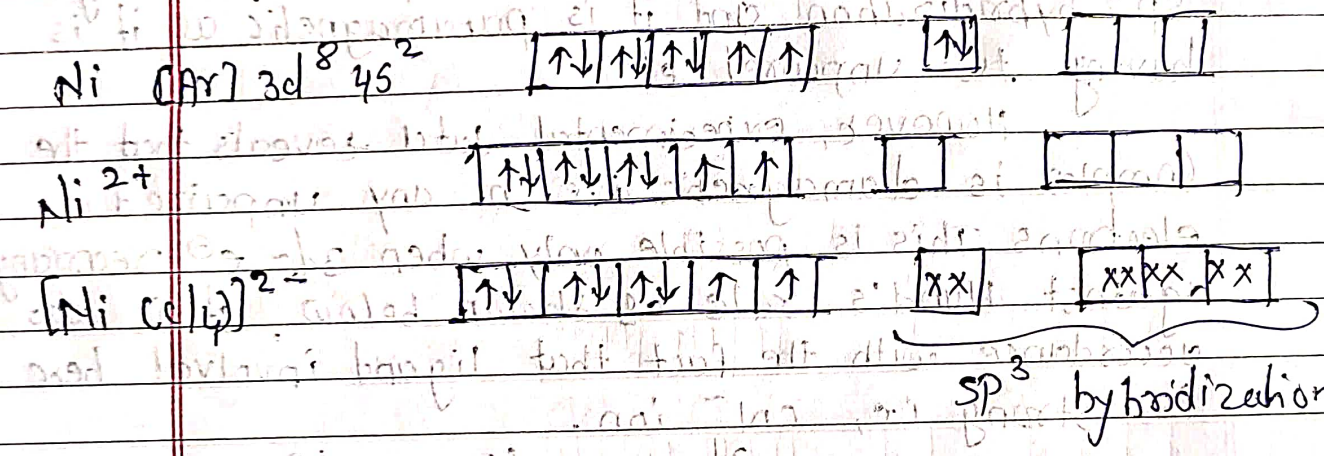


dsp^2 hybridization involves one 3d, one 4s and two 4p orbitals occurs leading to four dsp^2 hybrid orbitals, each of which accepts $e^{\ominus}$ pair from CN^- ion forming $[Ni(CN)_4]^{2-}$ ion.

The resulting complex would be square planar and diamagnetic as it has no unpaired electron.

(b) $[NiCl_4]^{2-}$ complex :-

In this complex formation Ni^{2+} ion uses one 4s and three 4p orbitals for hybridization. sp^3 hybridization gives tetrahedral complex. It is supported from the fact that $[NiCl_4]^{2-}$ is paramagnetic having magnetic moment corresponding to two unpaired electron.

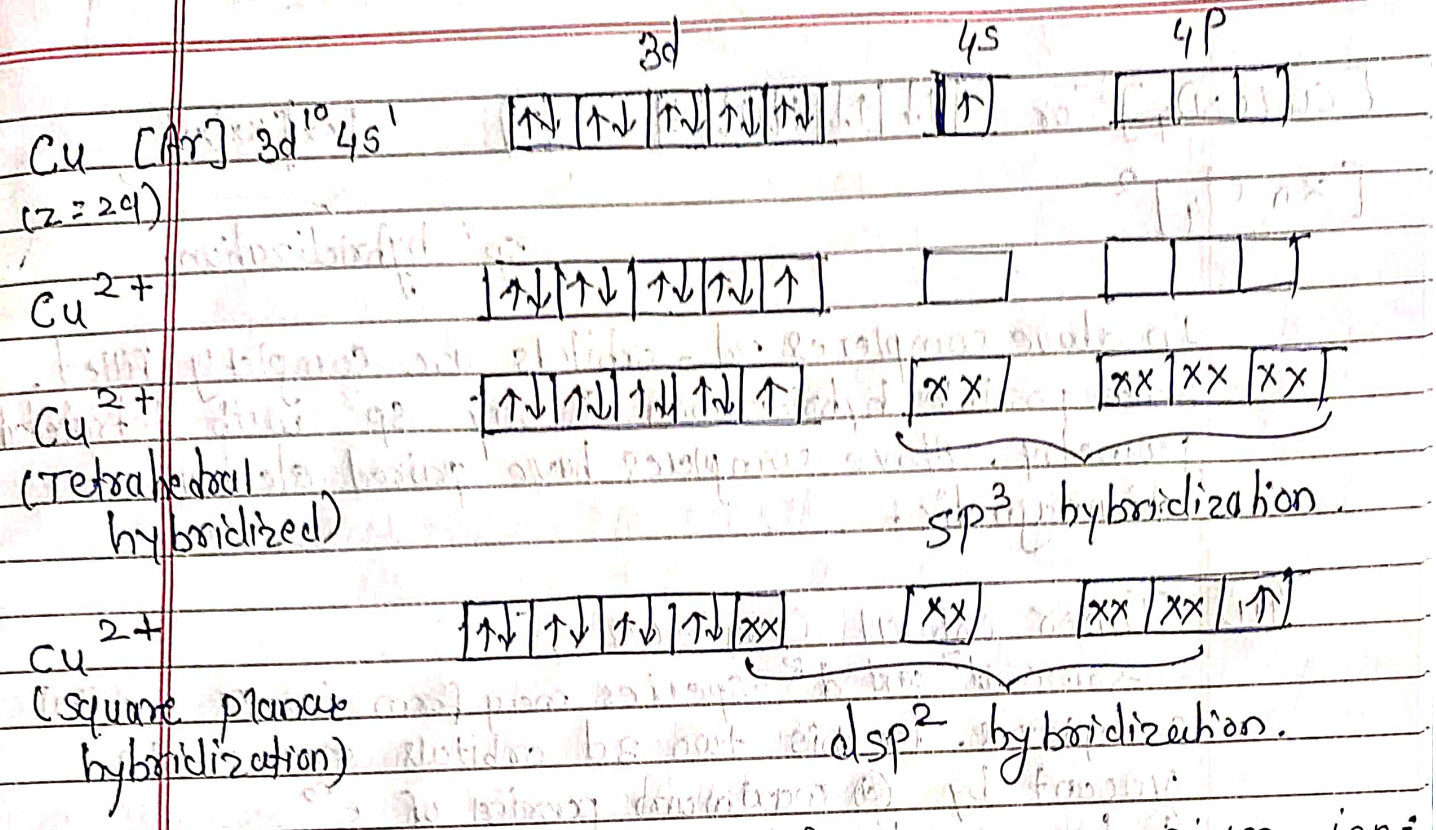


(c) $[Cu(NH_3)_4]^{2+}$ complex :-

In case of Ni there are two type of complexes viz, tetrahedral (sp^3) and square planar (dsp^2). The possible structure can be predicted by magnetic studies.

But, in case of Cu magnetic criteria does not predict either complex is tetrahedral or square planar because both type of hybridization will gives same unpaired electron in 3d and 4p-orbitals.

However, X-ray analysis of Cu(II) complex has settled ambiguity and proved that the ligands are coplanar and hybridization is dsp^2.



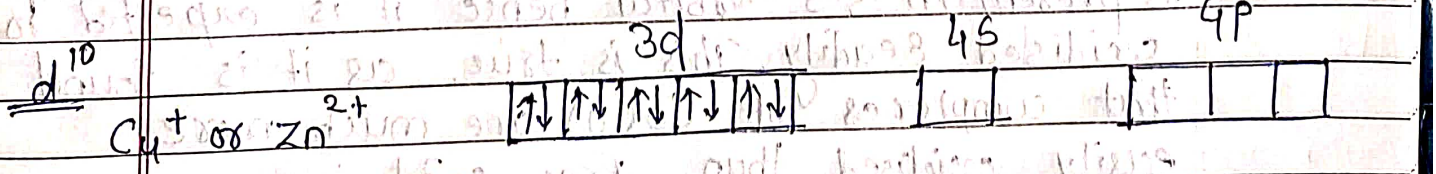
Objection to the shape of Cupercammonium ion:-

(i) placement of the odd electron in 3d level gives sp^3 hybridization which gives tetrahedral structure which is non-existent.

(ii) The necessity to promote one $e^\ominus$ from 3d into a 4p level is not satisfactory. The 4p-$e^\ominus$ would be expected to be easily lost, which would mean that the complex easily oxidized, but this is not so.

According to modern view this complex has distorted octahedral geometry explained on the basis of theories like crystal field theory and molecular orbital theory. According to this theory, the unpaired $e^\ominus$ is accommodated in eg orbital or in antibonding orbital.

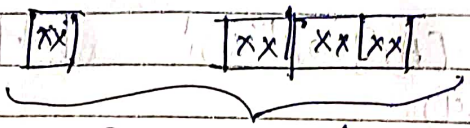
(d) $[Cu(CN)_4]^{3-}$ and $[ZnCl_4]^{2-}$ complex :-



d^{10}

Cu^+ or Zn^{2+}

$[Cu(CN)_4]^{3-}$ or $[Zn Cl_4]^{2-}$



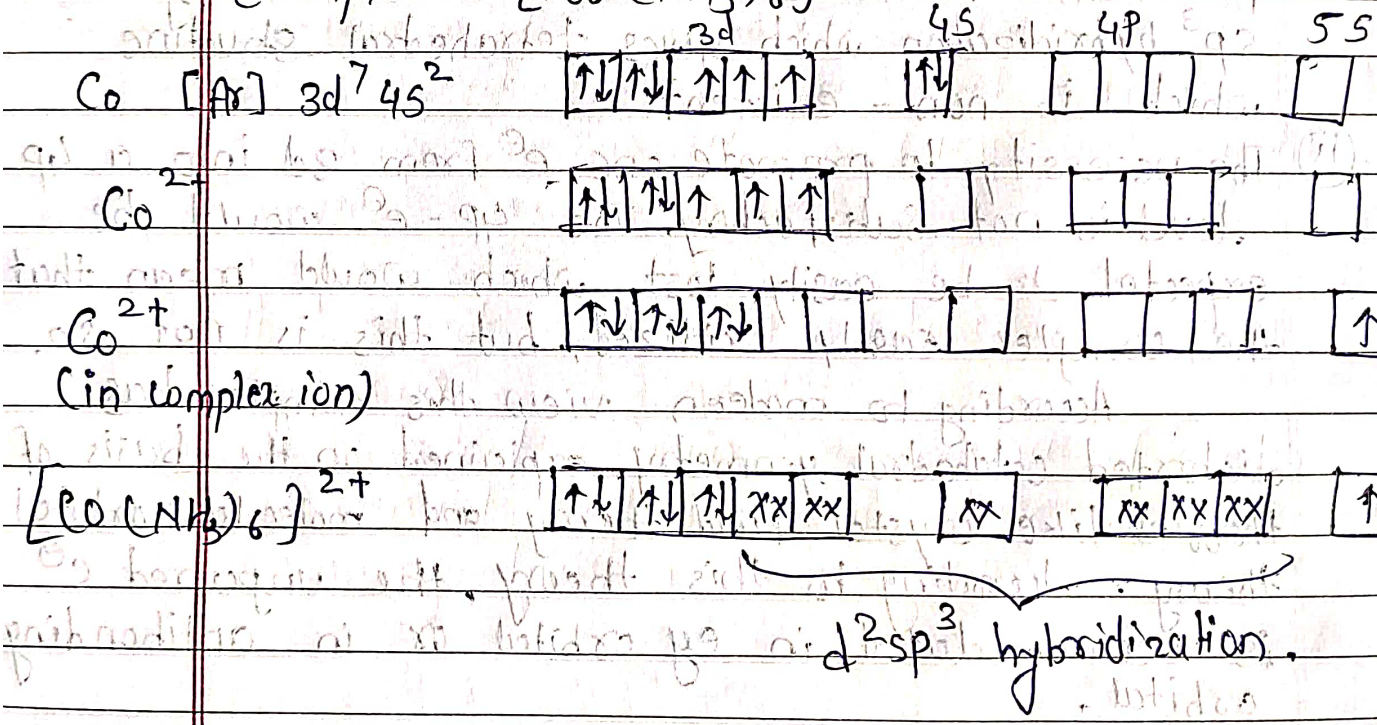
sp^3 hybridization.

In above complexes 3d - orbitals are completly filled. hence possible hybridization is only sp^3 with tetrahedral geometry. Above complexes have paired electron. so diamagnetic.

(iii) Inner orbital complexes :-

Some d^7 and d^8 species may form inner orbital complexes. For this two 3d orbitals are made vacant by (a) maximum pairing of $e^\ominus$ (b) by promotion of remaining unpaired $e^\ominus$ to higher energy level.

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



d^2sp^3 hybridization.

Due to d^2sp^3 hybridization this complex is inner orbital octahedral complex. one unpaired $e^\ominus$ is present in 5s - orbital hence it is expected to oxidised readily. This is true, as it is found that complexes of Co(II) are much more easily oxidised than free Co^{2+} ion.

Inner orbital octahedral complexes (d^2sp^3 hybridization)	outer orbital octahedral complexes (sp^3d^2 hybridization)
① These are formed by d^2sp^3 hybridization. (n-1)d orbitals belongs to inner shell while ns & np belongs to outer shell.	① These are formed by sp^3d^2 hybridization. where all ns, np and nd orbitals belongs to outer shell.
② These complexes have comparatively lesser number of unpaired $e^\ominus$ and hence called as low spin or spin paired octahedral complexes.	② These complexes have comparatively greater number of unpaired $e^\ominus$ and hence called as high spin or spin free octahedral complexes.
③ These complexes are formed by strong	③ These complexes are formed by weak ligands.
④ Generally experimental magnetic moment value (μ_{exp}) of these complexes is lesser than theoretical magnetic moment (μ_s) i.e, $\mu_{exp} < \mu_s$.	④ Generally experimental magnetic moment value (μ_{exp}) is comparable with theoritical magnetic moment (μ_s).

Limitations of Valence bond theory :-

This theory unable to explain following facts.

① It does not predicts magnetic properties except number of unpaired $e^\ominus$ from complex.

② Complex formation of certain metal ions is totally unsatisfactory. Eg : Cu^{2+} is d^9 species, shows ~~d^2sp^3~~ dsp^2 hybridization obtained by promotion of one

one 3d e^0 to 4s orbital. Hence it should lead to ready oxidation of Cu^{2+} to Cu^{3+} which occure occurs rarely.

(iii) The theory does not explain why a particular structure is preferred.
Eg: d^8 ion form square planar complexes (dsp^2 hybridization) after pairing by excitation of electron. d^8 ions may also forms tetrahedral (sp^3 hybridization) complexes without excitation.

(iv) The theory offers no explanation of cause of maximum pairing.

(v) In this theory too much stress has been given of metal ion while the nature of ligand is not properly stressed.

(vi) This theory does not explain reaction rate and mechanism of reaction.

(vii) It does not predict any distortion in symmetrical complexes whereas all the Cu(II) and Ti(III) complexes are distorted.

(viii) It does not explain thermodynamic properties of complexes.

(ix) It does not explain the spectra of complexes.

(x) It can not explain temperature dependent paramagnetism of complexes.