VALENCE BOND THEORY

This theory is sometimes referred to as VBT or VB Theory or Pauling's Theory.

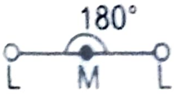
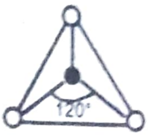
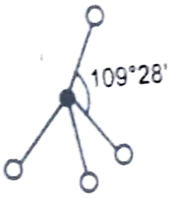
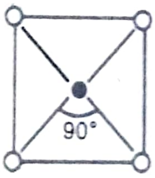
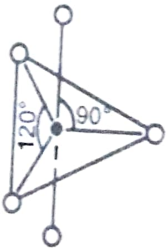
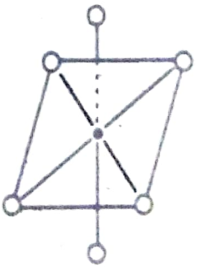
Assumptions / Theory:

1) The central metal atom or ion provides a number or empty *s*, *p* and *d* atomic orbitals equal to its C.N. These orbitals can accomodate electrons donated by the ligands.
2) These vacant orbitals hybridise together to *form* hybrid orbitals which are the same in number as the atomic orbitals hybridising together and have definite geometry. These are vacant equivalent, in energy and have definite geometry.
3) The metal orbitals and ligand orbitals overlap to form strong bonds (co-ordinate bonds).
4) The *d*-orbitals involved in the hybridisation may be inner $(n-1)$ *d*-orbitals (d^2sp^3) or outer (n) d orbitals (sp^3d^2). The complexes formed using these orbitals are referred to as low spin or inner orbital complexes and high spin or outer orbital complexes respectively and high spin or outer orbital complexes.
5) Each ligand donates a pair of electrons to the central metal ions.
6) The non-bonding metal electrons present in the inner orbitals do not take part in chemical bonding.
7) If the complex contains unpaired electrons, the complex is paramagnetic in nature, whereas, if it does not contain unpaired electrons it is diamagnetic.
8) Under the influence of a strong ligand, the electrons can be forced to pair up against Hund's rule of maximum multiplicity.

Explanation of geometry, magnetic properties colour of complex compounds based on the theory:

To explain the magnetic properties of complexes one has to know the hybridisation present in their molecules and their geometries. So we shall first explain the geometry of complexes based on V B theory.

Geometry of complex compound: The complex compounds

C.N	Hybrid-sation	Arrangemnt	Geometrical shape	Examples
2	sp	Linear நேர்கோடு		$Ag(NH_3)_2+$ $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar தள முக்கோண		$[HgI_3]^-$
4	sp^3	Tetrahedral நான்முகி		$[Co(NH_3)_4]^{2+}$ $[Ni(NH_3)_4]^{2+}$ $[Ni(CO)_4]^0$ $[Cu(CN)_4]^{2-}$ $[Cd(CN)_4]^{2-}$ $[FeCl_4]^{2-}$
	dsp^2	Square planar சதுர தளம்		$[NiCl_4]^{2-}$ $[Ni(CN_4)]^{2-}$ $[Pt(NH_3)_4]^{2+}$ $[Cu(NH_3)_4]^{3+}$
5	$dsp^3(sp^3d)$	Trigonal bipyramidal முக்கோண இரு (பிரமிடு)		$[Fe(CO)_5]^0$ $[Cu(Cl)_5]^{2-}$
6	inner outer $d^2sp^3(sp^3d^2)$ low high spine	Octahedral எண்முகி		$[Co(NH_3)_6]^{3+}$ $[Cr(NH_3)_6]^{3+}$ ✓ $[Fe(CN)_6]^{3-}$ $[CoF_6]^{3-}$ $[Ni(NH_3)_6]^{3+}$ ✓ $[FeF_6]^{3-}$

exist in various geometries. They are (i) linear (ii) trigonal planar (iii) tetrahedral (iv) square planar (v) trigonal bipyramidal and (vi) octahedral.

Explanation by V.B. Theory : According to Pauling strong bonds are not formed by pure s,p, or d orbitals. Strong bonds are generally formed by hybridised orbitals. Thus they postulated that hybridisation takes place in the central atom (Refer postulate 2). There are several types of hybridizations. Each hybridisation leads to a definite geometry various hybridisations and the related geometries are given as before.

Magnetic properties of complex compounds:

The complexes having paired electrons do not exhibit magnetic moment and they are said to be diamagnetic. The complexes having one or more unpaired electrons show definite value of magnetic moment and are called paramagnetic complexes. The greater the number of unpaired electrons in a substance the greater is the magnetic moment of the substance. The magnetic moment of a substance can be calculated using the formula.

η = $\sqrt{n(n+2)B.M.}$; μ = Magnetic movement

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

η = Number of unpaired electrons; B.M=Bohr Magneton.

When, η = 1, μ = $\sqrt{1(1+2)}$ = $\sqrt{3}$ =1.73 B.M.

Using this formula the number of unpaired electrons in an ion can be calculated. The values of n calculated for different magnetic moments are as follows:

Magnetic Moment Bohr Magneton	Number of unpaired electrons
0	0
1.73	1
2.83	2
3.87	3
4.90	4
5.92	5

Thus magnetic studies (measurement of m) will reveal whether a co-ordination compound has unpaired electrons in it or not. Now any theory on co-ordination compounds should account for the magnetic properties of the co-ordination compounds.

Explanation by V.B Theory: The magnetic properties of co-ordination compounds can be interpreted successfully by Pauling's V.B. Theory

Octahedral complexes: Octahedral complexes result from either *d^2sp^3 or sp^3d^2 hybridisation.*

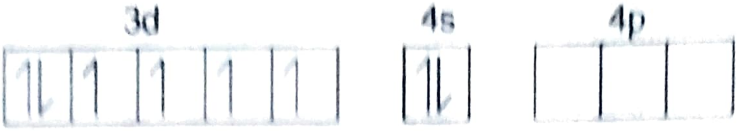
i. $K_4[Fe(CN)_6]$

Fe^{2+} is the central metal ion and $[Fe(CN)_6]^{4-}$ is the complex ion.

Electronic structure of Fe

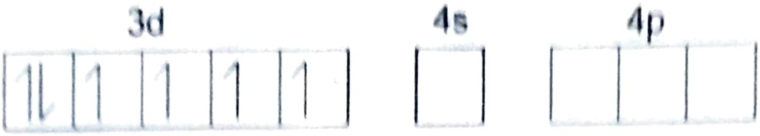
(At No 26)

$3d^6 4s^2$



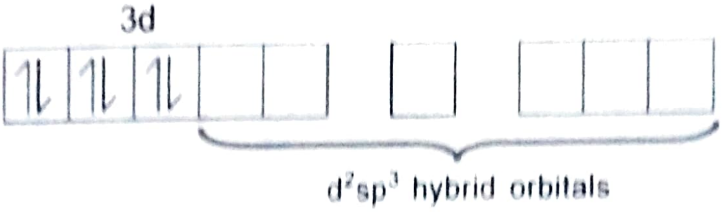
Fe^{2+} ion

$3d^6 4s^0$



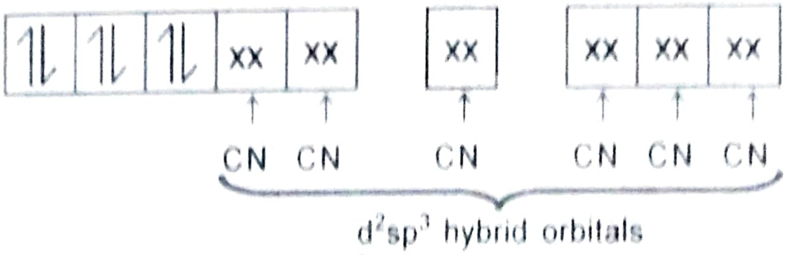
In the presence of CN⁻ ligands the electrons in the *3d* orbitals are forced to pair up against Hund's Rule of maximum multiplicity to make room for the electrons donated by the ligands.

Fe^{2+} in $[Fe(CN)_6]^{4-}$ after rearrangement



In order to give same properties and equal strength to all the metal ligand bonds, all the six orbitals (two 3d one 4s and three 4p orbitals) hybridise to give six equivalent d^2sp^3 hybrid orbitals. These six hybrid orbitals which are vacant accept six electron pairs denoted by six CN⁻ ligands and thus form $[Fe(CN)_6]^{4-}$ ion.

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

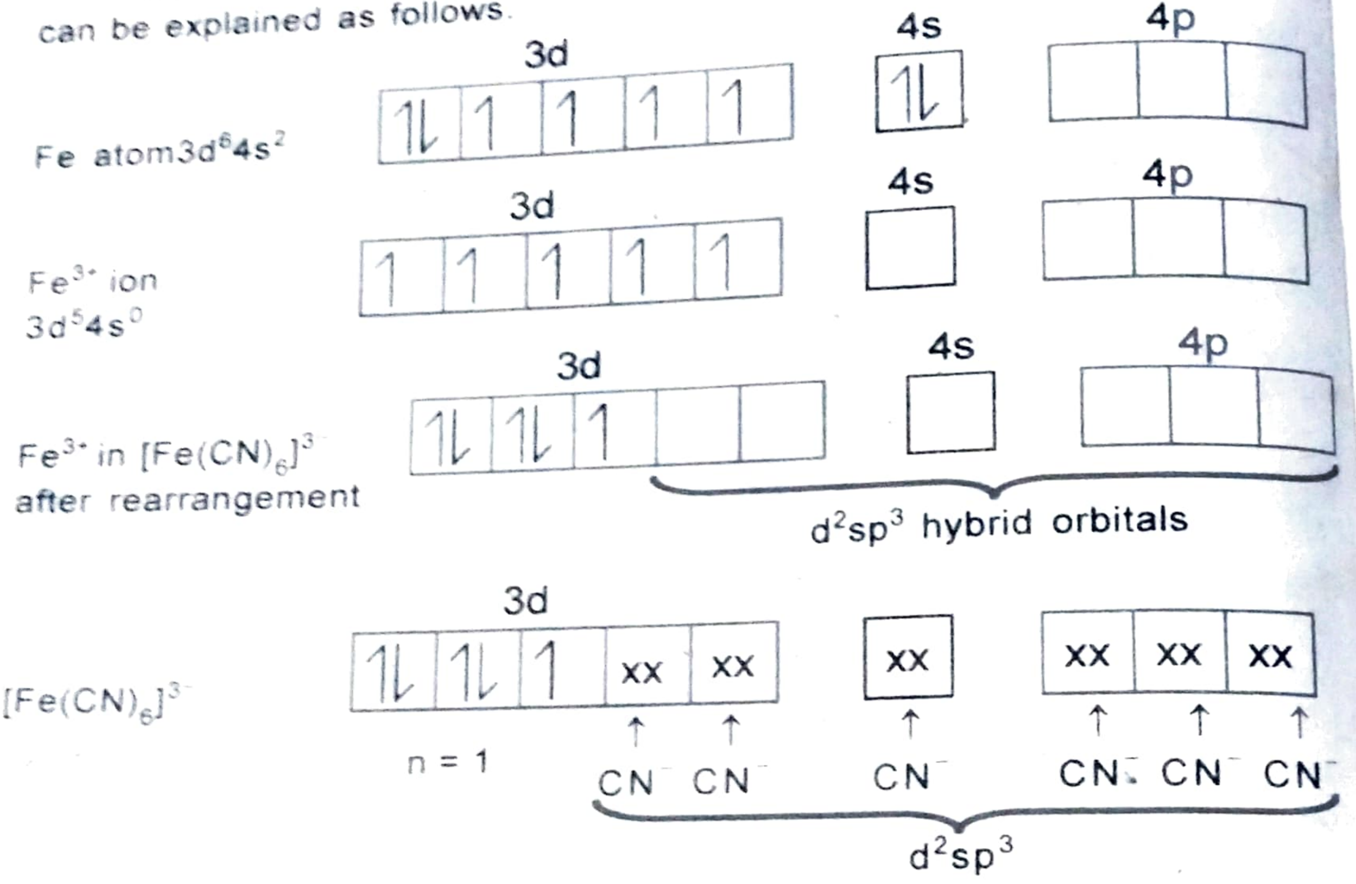


Since the complex results from d^2sp^3 hybridisation, it has octahedral shape. Since there is no unpaired electron in the complex, the complex is diamagnetic. In the above complex the d – orbitals used are from a lower shell (3d) than the s and p orbitals (4s and 4p). Complexes using the inner d- orbitals (3d orbitals) are called inner orbital complexes. They are also known as covalent complex or spin paired or low spin complexes. Other examples: i. $[Co(NH_3)_6]^{3+}$ ii. $[Co(CN)_6]^3$

ii) $K_3[Fe(CN)_6]$: μ = 1.73 BM=1 unpaired electron Fe has Atomic number 26

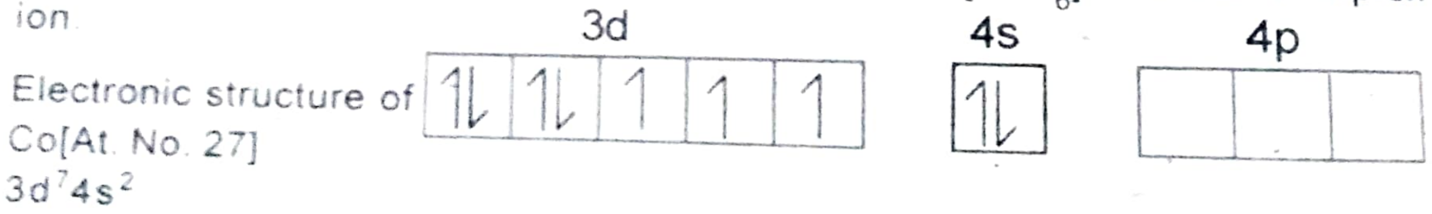
Fe^{3+} is the central metal ion and $[Fe(CN)_6]^{3-}$ is the complex ion.

On the basis of d^2sp^3 hybridisation the nature of bonding in the complex can be explained as follows.

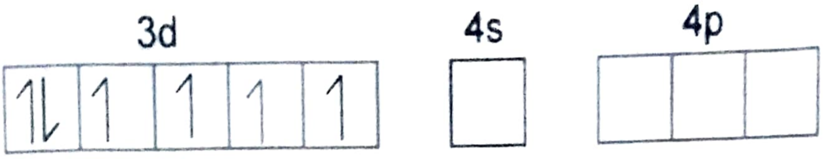


The complex has octahedral shape corresponding to d^2sp^3 hybridisation. The number of unpaired electron is one. So, the complex is paramagnetic. $K_3[Fe(CN)_6]$ is an inner orbital octahedral complex.

iii) $[CoF_6]^{3-}$ ion: Co^{3+} is the central metal ion and $[CoF_6]^{3-}$ is the complex ion.

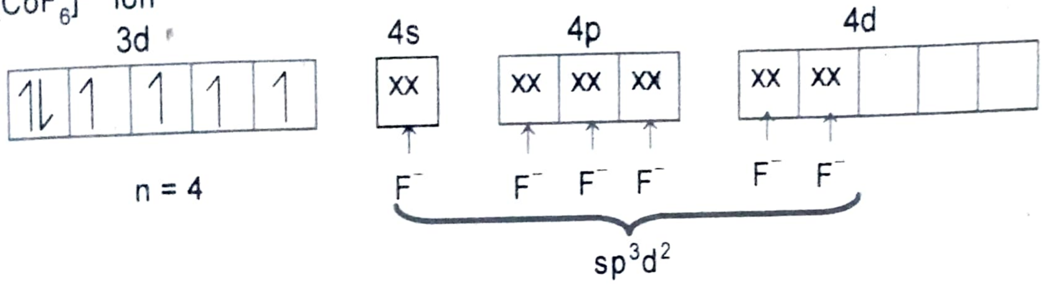


Co^{3+} ion
$3d^6$



In a weak ligand field such as in $[CoF_6]^{3-}$, electrons do not have sufficient energy needed for pairing. Hence there are no vacant orbitals in the *3d* shell. The six ligands donate one lone pair of electrons each to the first six vacant orbitals. Thus in this case one 4s, three 4p and two 4d orbitals hybridise to give six equivalent sp^3d^2 hybrid orbitals. These accept an electron pair from each of the six fluoride ions (ligands).

$[CoF_6]^{3-}$ ion



Complexes such as $[CoF_6]^{3-}$ are called outer orbital complexes since the d orbitals involved in the hybridisation are from the same shell as the s and p orbitals. The outer orbital complexes are also known as ionic complexes or spin free or high spin complexes.

The four *3d*- orbital electrons which remain unpaired explains the paramagnetic character of $[CoF_6]^{3-}$ ion.

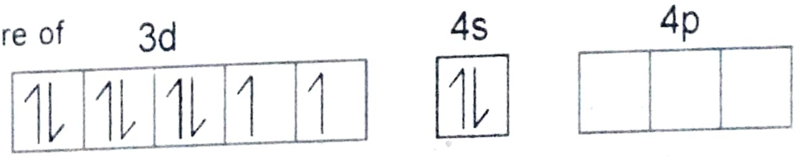
Other examples: i) $[Ni(NH_3)_6)]^{2+}$; ii) $[Fe(H_2O)_6]^{2+}$

iii) $[FeF_6]^{3+}$.

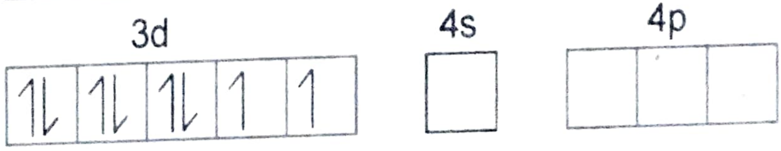
b) ***Tetra hedral complexes:*** These are formed by *sp³* hybridisation.

Example: $[Ni(NH_3)_4)]^{2+}$ ion.

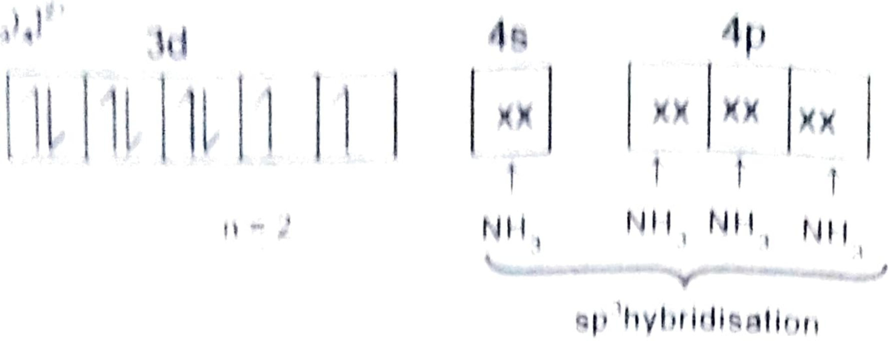
Electronic structure of
Ni (At. No 28)
$3d^84s^2$



Ni^{2+} ion
$3d^84^0$



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



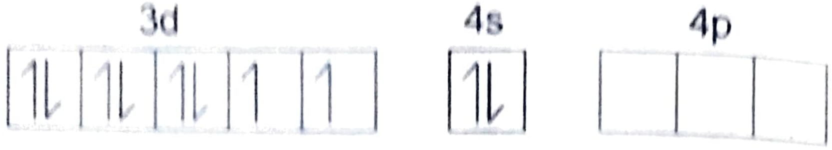
Since sp^3 hybridisation is involved, the complex has a tetrahedr structure. There are two unpaired electrons and the ion is therefo paramagnetic.

Other examples: $[Ni(CO)_4]^0$, $[FeCl_4]^-$, $[ZnCl_4]^{2-}$, $[Zn(NH_3)_4]^{2+}$, $[MnCl_4]^{2-}$, $[CoCl_4]^{2-}$, $[CoBr_4]^{2-}$, $[NiX_4]^{2-}$

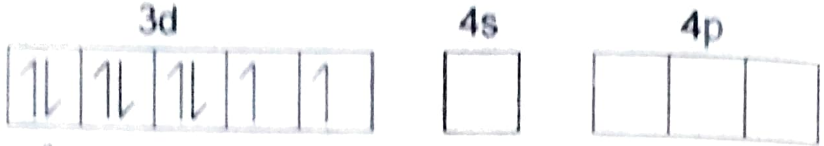
c) Square planar complexes: These are formed by dsp^2 hybridisation.

Example: $[Ni(CN)_4]^{2-}$ $\mu = 0 = 0$ unpaired electrons

Ni(At No 28)
$3d^8 4s^2$

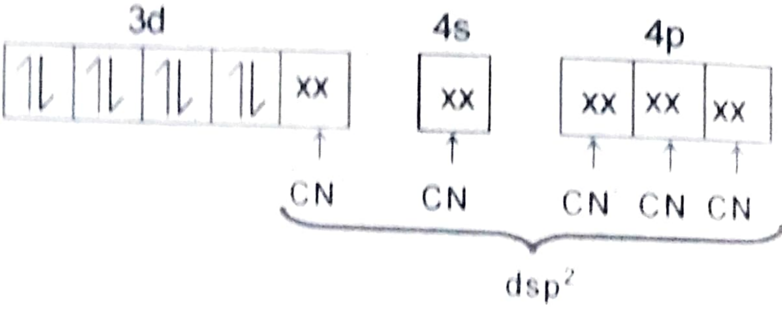


Ni^{2+}
$3d^8 4s^0$



$[Ni(CN)_4]^{2-}$ is diamagnetic. Hence it must involve dsp^2 hybridisatic resulting in square planar structure. The two unpaired $3d$ electrons a coupled making one d orbital empty and available for hybridisation so th dsp^2 hybrid orbitals can be formed.

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



These vacant orbitals accept four electron pairs donated by four C ligands, to form a square planar ion.

Other examples: i) $[Pt(NH_3)_4]^{2+}$, $[PtCl_4]^{2-}$

Colour of complex compound:

Most of the complexes are coloured. For example copper sulphate crystals are blue while anhydrous copper sulphate is white. On adding NH_4OH to $CuSO_4$ solution first is blue precipitate is formed which dissolves in excess NH_4OH giving a deep blue coloured solution.

$CuSO_4$ $5H_2O$ exists as $[Cu(H_2O)_6]SO_4$ $5H_2O$ which is blue in colour. On adding NH_4OH first $[Cu(H_2O)_6]OH_2$ is formed which is insoluble in water. So it is precipitated. On adding excess $NH_4OH[Cu(NH_3)](OH)_2$ is formed which is soluble in water and which is coloured deep blue. Thus when there is an exchange of ligands the colour deepens.

In general when complexes are formed from colourless compounds they are invariably coloured. When complexes are formed from coloured compounds the colour of complex deepens.

Explanation by V.B Theory:

Valence bond theory is NOT in a position to explain the colour of the complexes or depending of colour during complex formation.

Comparison between Werner's theory and V.B Theory:

Similarities :

(i) Both account for the formation of complexes.

(ii) Both recognize the geometry of the complex compounds.

(iii) Both are unable to explain colour of complexes.

Distinctions:

(i) Werner's theory does not rationalise the geometries of complexes through the concept of hybridisation.

(ii) Wener's theory is not in a position to explain the magnetic properties of complexes. V.B theory offers a satisfactory explanation for the magnetic properties of complexes.

Since V.B theory rationalises the geometry of complexes through hybridisation and since it is in a position to offer satisfactory explanation for the magnetic properties it is considered to be superior to the Werner's theory.

Merits of V.B Theory:

1) It provides a satisfactory pictorial representation(geometry) of the complex through the concept of hybridization.

2) It is good model for qualitative prediction of the magnetic behavior and reactively of complexes. Thus V.B theory is an improvement on Werner's theory.

Limitation of V.B Theory:

1) It is limited to qualitative explanations; good model for qualitative interpretation of the stability of the complexes is not possible.
2) V.B Theory is unable to explain colour of complexes. Consequently it is unable to account for spectra of complexes.
3) V.B theory is unable to explain why the same metal is assigned different geometries. In other words in the case of a particular metal, in a particular geometry Hund's rule is shown to be obeyed and in some other cases it is not obeyed. For example $[Ni(CO)_4]^{2-}$ is tetrahedral while $[Ni(CN)_4]$ is square planar.
4) V.B Theory does not explain why some air inner orbital complexes, and some are outer orbital complexes.
5) V.B Theory does not provice suitable explanations from the energy point of the view with respect to complexes.

6) The colour and magnetic moments of transition metal complexes are due to their possessing *d* orbital electrons. So, there should be a quantitative connection is not revealed by Pauling's theory.