

STUDY MATERIAL



Dumkal College
Basantapur, Dumkal

Topic: Coordination Chemistry-II : Valence Bond Theory

Course Code: CHEMHT-11

Semester: V (Hons)

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Name of the Department: Chemistry

(1) Valence Bond Theory

This theory developed mainly by Pauling. This theory is based on the following assumptions :

- (1) The central metal cation or atom (as the case may be) makes available a number of vacant s , p and or d -orbitals equal to its coordination number to form coordinate covalent bonds with orbitals on the ligands.
- (2) Since the maximum angular overlap of two orbitals forms the strongest bond, therefore, these vacant atomic orbitals of metal are hybridized to form a new set of equivalent bonding orbitals, called hybrid orbitals. These orbitals have same geometry and same energy. These orbitals also have definite directional properties *i.e.*, these orbitals point in the directions of ligands. The geometry and hybridization are related to one another. Once you know the geometry of a complex compound, you automatically know which orbitals of the metal cation or atom uses. The relationship between the geometry of the complex and hybridization is given in Table 4.1.
- (3) The bonding in metal complexes arises when a filled ligand orbital containing a lone pair of electrons overlaps a vacant hybrid orbital on the metal cation or atom to form a coordinate covalent bond (Figure 4.1).

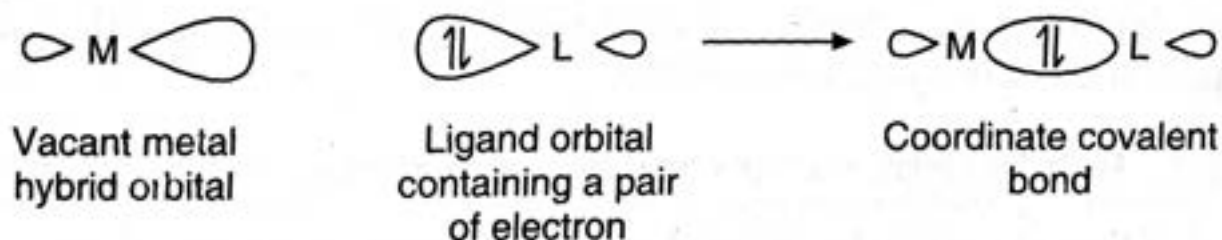


Figure 4.1

- (4) The magnetic moment (*i.e.*, the number of unpaired electrons) and the coordination number of the metal cation or atom decide the hybridization and geometry of the complex. Therefore, magnetic moment, coordination number, hybridization and geometry are related to one

another. The knowledge of magnetic moment can be of great help in ascertaining the nature of ligands and type of complex.

- (5) Each ligand has at least one orbital containing a lone pair of electrons. Pauling classified the ligands into two categories : (i) strong electron donating ligands or simply strong ligands like CN^- , CO etc. (ii) weak ligands or highly electronegative ligands, like F^- , Cl^- , oxygen containing ligands etc.
- (6) Strong ligands have the tendency to pair up the d -electrons of metal cation or atom to provide the necessary orbitals for hybridization. But the pairing of electrons does not violate the Hund's rule of maximum multiplicity. On the other hand, weak ligands do not have the tendency to pair up the d -electrons *i.e.*, in presence of weak ligands electronic configuration of the d -electrons is same as in free metal cation or atom.
- * (7) The bond formed between metal and strong ligand such as CN^- , CO is considered to be covalent. On the other hand, the bond formed between metal and weak or highly electronegative ligand like F^- is not covalent but it is ionic.
- (8) The bond formed between metal and strong ligand like CN^- , CO etc. is considered to be covalent. This would require in many cases the pairing of d -electrons to provide the necessary orbital for hybridization.
- (9) In octahedral complexes, the central metal cation is either $d^2 sp^3$ or $sp^3 d^2$ -hybridized. The d -orbitals involved in $d^2 sp^3$ -hybridization belong to the inner shell *i.e.*, $(n-1)$ d -orbitals and these complex are called as inner orbital complexes. In case of $sp^3 d^2$ -hybridization, the d -orbitals belong to outer most shell *i.e.*, n d -orbitals and the complexes are called outer orbital complexes. The octahedral complexes involving $d^2 sp^3$ -hybridization are more stable than those of $sp^3 d^2$. The d -orbitals involved in hybridization in octahedral complexes are $d_{x^2-y^2}$ and d_{z^2} .
- In tetrahedral complexes, the metal cation or atom is either sp^3 or sd^3 -hybridized. The d -orbitals involved in sd^3 -hybridization are d_{xy} , d_{yz} and d_{zx} .
- In square planar complexes, the metal cation is dsp^2 -hybridized. The p - and d -orbitals involved in dsp^2 -hybridization are p_x , p_y and $d_{x^2-y^2}$ leaving p_z and d_{z^2} orbitals projecting above and below the plane of the complex.
- (10) In case of second and third series transition metal complexes, the d -orbitals involved in hybridization are inner orbitals *i.e.*, $(n-1)$ d -orbitals, because the outer d -orbitals *i.e.*, nd orbitals become too diffuse to bond well.
- (11) The complexes having one or more unpaired electrons are paramagnetic and the complexes having only paired electrons are diamagnetic.

Table 4.1 : Hybrid Orbitals for Common Coordination Geometries

C.N.	Hybridization	Orbitals Involved	Bond Angle (θ)	Geometry	Example
2	sp	s and p_x ✓	180°	Linear	$[\text{Ag}(\text{NH}_3)_2]^+$
3	sp^2	s , p_x and p_y ✓	120°	Triangular planar	$[\text{HgI}_3]^-$

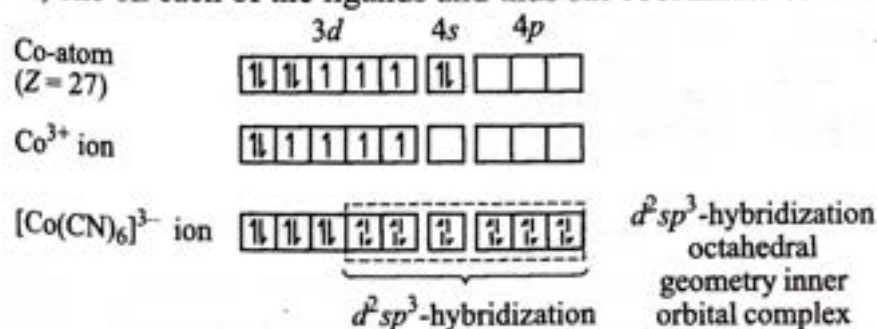
4	sp^3	s, p_x, p_y and p_z	$109^\circ 28'$	Tetrahedral	$[\text{CoCl}_4]^{2-}$, $[\text{NiCl}_4]^{2-}$
4	sd^3	$s, d_{xy}, d_{yz}, d_{zx}$	$109^\circ 28'$	Tetrahedral	MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-}
4	dsp^2	$s, p_x, p_y, d_{x^2-y^2}$	90°	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ (dsp^2)
	or sp^2d	$s, p_x, p_y, d_{x^2-y^2}$	90°	Square planar	$[\text{Cu}(\text{NH}_3)_4]^{2+}$ (sp^2d)
5	dsp^3	$s, p_x, p_y, p_z, d_{z^2}$	$90^\circ, 120^\circ$	Trigonal bipyramidal	$\text{Fe}(\text{CO})_5$
5	dsp^3	s, p_x, p_y, p_z and $d_{x^2-y^2}$	$90^\circ, 90^\circ$	Square pyramidal	$[\text{Ni}(\text{CN})_5]^{3-}$
6	d^2sp^3	$4s, 4p_x, 4p_y, 4p_z,$ $3d_{x^2-y^2}$ and $3d_{z^2}$	$90^\circ, 90^\circ$	Inner orbital octahedral	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{4-}$
6	sp^3d^2	$4s, 4p_x, 4p_y, 4p_z,$ $4d_{x^2-y^2}$ and $4d_{z^2}$	$90^\circ, 90^\circ$	Outer orbital octahedral	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, $[\text{CoF}_6]^{4-}$

Now let us discuss the valence bond theory for octahedral, tetrahedral and square planar complexes taking some examples :

Octahedral Complexes

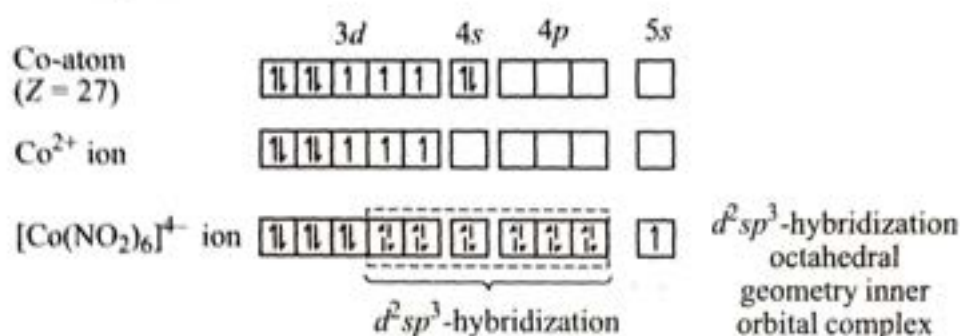
(A) Inner Orbital Complexes : Let us discuss inner orbital complexing taking some examples :

1. $[\text{Co}(\text{CN})_6]^{3-}$ ion : In this complex, oxidation state of cobalt is + 3. The valence shell electronic configuration of Co^{3+} is $3d^6$. Magnetic measurements indicate that $[\text{Co}(\text{CN})_6]^{3-}$ is diamagnetic. All six $3d$ -electrons are, therefore, paired and occupy three of the five $3d$ - orbitals. The CN^- ligands are strong and, therefore, cause pairing of $3d$ -electrons. The vacant two $3d$ -orbitals combine with the vacant $4s$ and $4p$ orbitals to form six d^2sp^3 -hybrid orbitals. These six hybrid orbitals overlap with six filled orbitals of ligands, one on each of the ligands and thus six coordinate covalent bonds are formed.

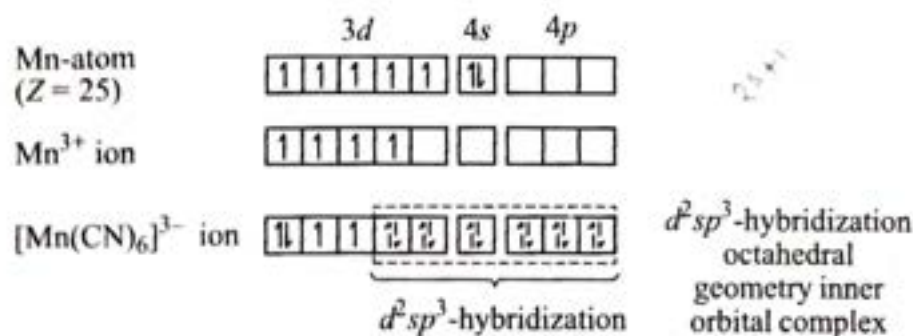


2. $[\text{Co}(\text{NO}_2)_6]^{4-}$ ion : In this complex ion, oxidation state of cobalt is + 2 and its valence shell electronic configuration is $3d^7$. Magnetic moment measurements indicate that this complex ion is paramagnetic corresponding to presence of one unpaired electron. The NO_2^- ligands are strong, they, therefore, cause pairing of metal $3d$ - electrons. Pauling suggested that two vacant $3d$ - orbitals are made available by promotion of an unpaired electron from a $3d$ -orbital to $5s$ -orbital so that Co^{2+} ion gets $d^2 sp^3$ -hybridized.

The presence of an unpaired electron in $5s$ -orbital is supported by the fact that, $5s$ - orbital has very high energy and the electron present in it is loosely bound and can be removed easily. Experimentally it is also observed that $[\text{Co}(\text{NO}_2)_6]^{4-}$ is oxidized by air or H_2O_2 easily to give $[\text{Co}(\text{NO}_2)_6]^{3-}$. This indicates that the complex $[\text{Co}(\text{NO}_2)_6]^{4-}$ is unstable in air. Thus, this complex should be prepared in inert atmosphere.

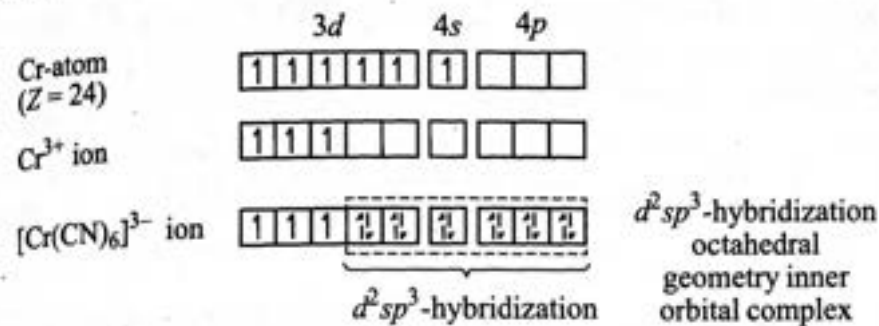


3. $[\text{Mn}(\text{CN})_6]^{3-}$ ion : In this complex ion, oxidation states of Mn is + 3 and its valence shell electronic configuration is $3d^4$. Magnetic measurements show that this complex ion is paramagnetic corresponding to two unpaired electrons. All the four electrons occupy just three of the five $3d$ - orbitals leaving two $3d$ - orbitals vacant. These two vacant $3d$ - orbitals combine with the vacant $4s$ and $4p$ - orbitals to give six $d^2 sp^3$ - hybrid orbitals. These hybrid orbitals form bonds with ligands by accepting six pair of electrons, one pair from each of the six ligands. Since CN^- is a strong ligand and has a tendency to pair up the d - electrons on metal but it causes pairing of two electrons only leaving two electrons as unpaired. If all the electrons become paired, then it will violate the Hund's rule of maximum multiplicity.

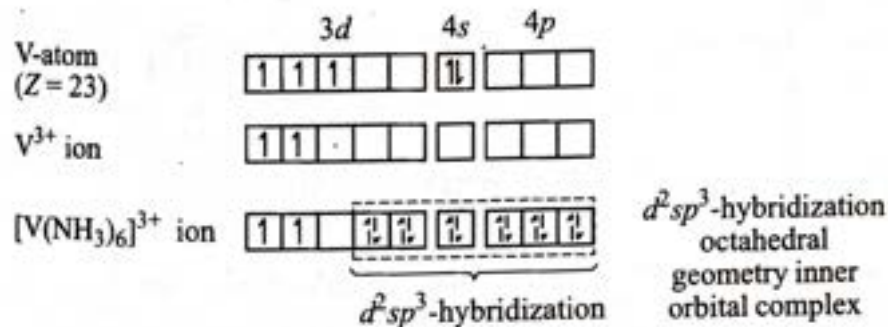


4. $[\text{Cr}(\text{CN})_6]^{3-}$ ion : In this complex ion, oxidation state of Cr is + 3 and its valence shell electronic configuration is $3d^3$. Magnetic measurements show that this complex ion is paramagnetic corresponding to the presence of three unpaired electrons. All the three $3d$ - electrons occupy just three

of the five $3d$ - orbitals leaving two $3d$ - orbitals as vacant. These two vacant orbitals combine with the vacant $4s$ and $4p$ -orbitals to give six d^2sp^3 -hybrid orbitals. These six hybrid orbitals form bonds with ligands by accepting six lone pair of ligands, one pair from each of the six ligands. The three orbitals of the metal cation have three unpaired electrons and are degenerate. Thus, even in the presence of strong ligands pairing of electrons will not occur. If pairing of electrons occur, then it will violate Hund's rule of maximum multiplicity.



5. [V(NH₃)₆]³⁺ ion : In this complex ion, oxidation state of vanadium is + 3 and its valence shell electronic configuration is $3d^2$. Magnetic measurements indicate that this complex ion is paramagnetic corresponding to two unpaired electrons. All the two $3d$ - electrons occupy just two of the five $3d$ - orbitals leaving three $3d$ - orbitals vacant two of which combine with vacant $4s$ and $4p$ - orbitals to give six d^2sp^3 - hybrid orbitals. The d^2sp^3 - hybrid orbitals form bonds with the ligands accepting six pairs of electrons, one pair from each of the six ligands. Out of three $3d$ - unhybridized orbitals, two orbitals have two unpaired electrons one unpaired electron in each and one orbital remains vacant. These three unhybridized $3d$ - orbitals are degenerate. Thus, even in the presence of strong ligands pairing of electrons will not occur. If pairing of electrons occur, then it will violate Hund's rule of maximum multiplicity.



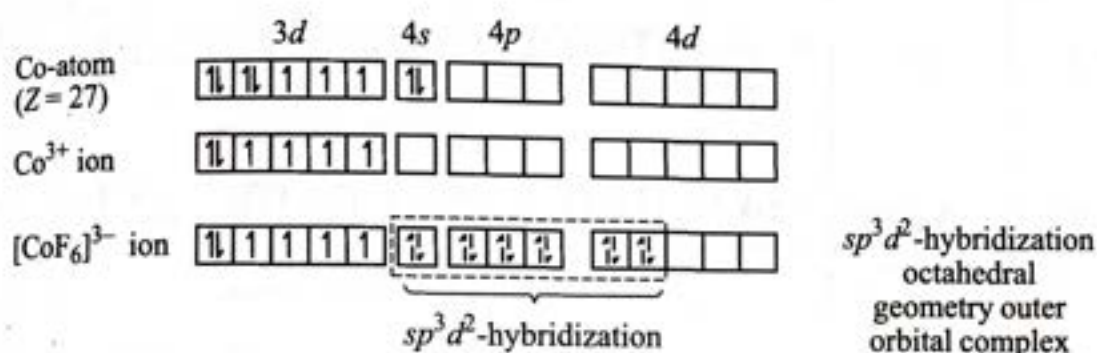
Various inner orbital octahedral complexes are illustrated in Table 4.2.

Table 4.2

Complex Ion	Oxidation State of Metal	Valence Shell Configuration of Metal Cation	Nature of Ligands	Valence Bond Electrons Description	No. of Unpaired Electrons (<i>n</i>)
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	+ 3	$3d^1$	weak	<p>d^2sp^3-hybridization</p>	1
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	+ 3	$3d^2$	weak	<p>d^2sp^3-hybridization</p>	2
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	+ 3	$3d^3$	weak	<p>d^2sp^3-hybridization</p>	3
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	+ 3	$3d^3$	strong	<p>d^2sp^3-hybridization</p>	3
$[\text{Cr}(\text{CN})_6]^{4-}$	+ 2	$3d^4$	strong	<p>d^2sp^3-hybridization</p>	2
$[\text{Mn}(\text{CN})_6]^{4-}$	+ 2	$3d^5$	strong	<p>d^2sp^3-hybridization</p>	1
$[\text{Fe}(\text{CN})_6]^{3-}$	+ 3	$3d^5$	strong	<p>d^2sp^3-hybridization</p>	1
$[\text{Fe}(\text{CN})_6]^{4-}$	+ 2	$3d^6$	strong	<p>d^2sp^3-hybridization</p>	0
$[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$	+ 2	$3d^6$	$\text{CN}^- \rightarrow$ strong $\text{NO}^+ \rightarrow$ strong	<p>d^2sp^3-hybridization</p>	0
$[\text{PtCl}_6]^{2-}$	+ 4	$5d^6$	weak	<p>d^2sp^3-hybridization</p>	0

(B) Outer Orbital Octahedral Complexes : In outer orbital complexes the central metal cation is sp^3d^2 -hybridized. In sp^3d^2 -hybridization, d -orbitals of outer shell (*i.e.*, nd -orbitals) are involved. Let us discuss complexes by taking some examples :

(1) $[\text{CoF}_6]^{3-}$ ion : In this complex ion, oxidation state of cobalt is +3 and its valence shell electronic configuration is $3d^6$. Magnetic moment measurements show that this complex is paramagnetic corresponding to four unpaired electrons. Also, F^- is a weak ligand, there will be no pairing of $3d$ -electrons of the metal cation. Thus, there is no vacant $3d$ -orbital and none of $3d$ -orbitals is available to accept electron pairs from the ligands. Consequently the vacant $4s$, $4p$ and two of the five $4d$ -orbitals combine to give six sp^3d^2 -hybridization. These hybrid orbitals form bonds by accepting six pairs of electrons, one pair from each of the six ligands.



(2) $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$ ion : In this complex ion, oxidation state of Fe is +1 because NO exists in +1 oxidation state in complexes of Fe and its valence shell electronic configuration is $3d^6 4s^1$. Magnetic moment measurements of this complex ion indicate that its experimental magnetic moment is 3.89 B.M. which corresponds to three unpaired electrons in the complex ion. The single NO^+ strong ligand has little tendency to pair up the electrons it pairs up only two unpaired electrons. Since H_2O is a weak ligand, therefore, it has no tendency to pair up the electrons and none of the five $3d$ -orbitals is vacant. Therefore, the $4s$, $4p$ and two of the five $4d$ -orbitals (*i.e.*, $4d_{x^2-y^2}$ and $4d_{z^2}$) combine to give six sp^3d^2 -hybrid orbitals. These hybrid orbitals form bonds with six ligands by accepting six pairs of electrons, one pair from each of the six ligands.

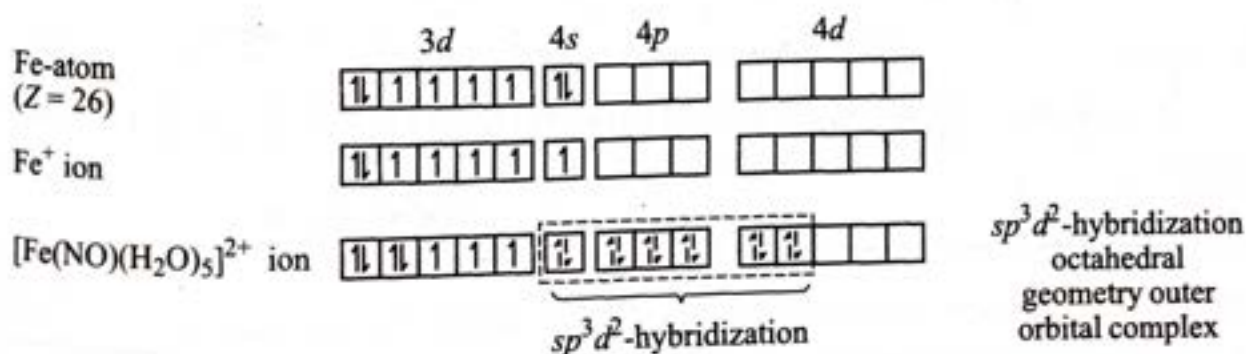


Table 4.3

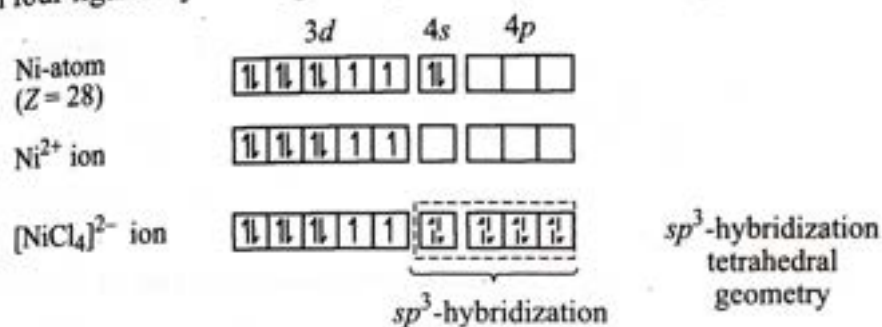
Complex Ion	Oxidation State of Metal	Valence Shell E.C. of Metal Ion	Nature of Ligands	Valence Bond Electrons Description	No. of Unpaired Electrons (<i>n</i>)
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	+2	$3d^4$	weak	 sp^3d^2 -hybridization	4
$[\text{Cr}(\text{NH}_3)_6]^{2+}$	+2	$3d^4$	strong	 sp^3d^2 -hybridization	4
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	+2	$3d^5$	weak	 sp^3d^2 -hybridization	5
$[\text{FeF}_6]^{3-}$ or $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	+3	$3d^5$	weak	 sp^3d^2 -hybridization	5
$[\text{CoF}_6]^{3-}$	+3	$3d^6$	weak	 sp^3d^2 -hybridization	4
$[\text{Co}(\text{NH}_3)_6]^{2+}$	+2	$3d^7$	strong	 sp^3d^2 -hybridization	3
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	+2	$3d^8$	strong	 sp^3d^2 -hybridization	2

From the foregoing discussion it is concluded that the octahedral complexes of d^1, d^2, d^3 -metal cations are always inner orbital complexes whether the ligands are weak or strong. The octahedral complexes of d^8, d^9 and d^{10} metal cations are always outer orbital complexes either the ligands are strong or weak. The complexes of d^4, d^5, d^6 and d^7 metal cations are outer orbital complex if the ligands are weak.

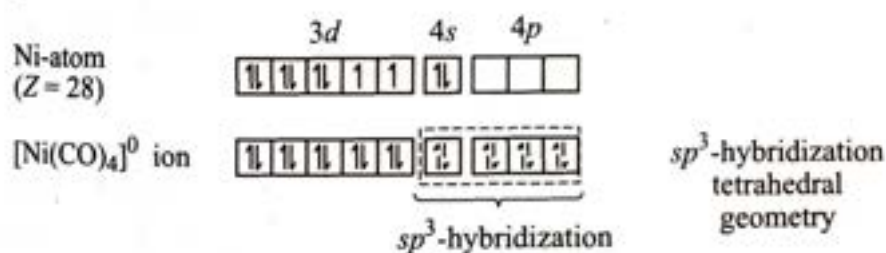
Tetrahedral Complexes

In tetrahedral complexes the metal cation is either sp^3 or sd^3 -hybridized. Let us consider the some example to illustrate the hybridization and geometry :

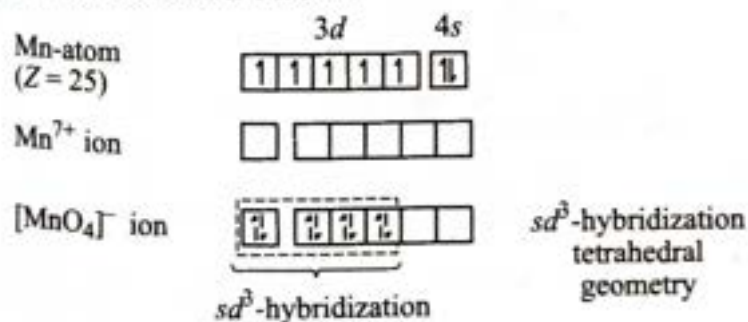
(1) $[\text{NiCl}_4]^{2-}$ ion : In this complex ion, oxidation state of Ni is + 2 and its valence shell electronic configuration is $3d^8$. Magnetic moment measurements indicate that it is paramagnetic corresponding to two unpaired electrons. Since Cl^- is a weak ligand, therefore, no pairing of electrons will occur in $3d$ -orbitals. None of the five $3d$ - orbitals is vacant. Vacant $4s$ and $4p$ -orbitals combine to give four sp^3 - hybrid orbitals because $[\text{NiCl}_4]^{2-}$ is a tetrahedral complex ion. These four hybrid orbitals form bonds with four ligand by sharing four pair of electrons, one pair from each of the four ligands.



(2) $\text{Ni}(\text{CO})_4$: In this compound oxidation state of nickel is zero and its valence shell electronic configuration is $3d^8 4s^2$. Magnetic moment measurements indicate that $\text{Ni}(\text{CO})_4$ is diamagnetic *i.e.*, it has no unpaired electrons. CO is a strong ligand and has the tendency to pair up the $3d$ - electrons. During the pairing of electrons, the two electrons of $4s$ -orbitals shift into one of the five $3d$ - orbitals. Thus, there is no vacant $3d$ - orbital. Thus, the vacant orbitals available for hybridization are $4s$ and $4p$ to give four sp^3 -hybrid orbitals.



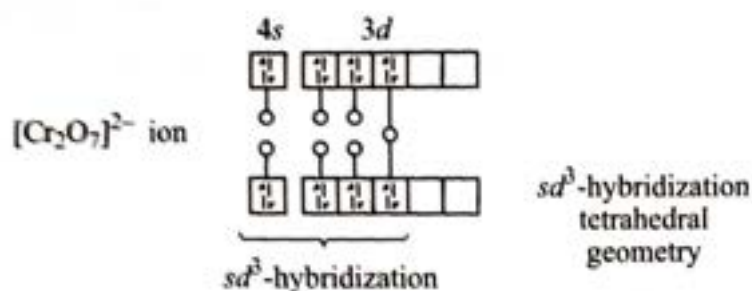
(3) MnO_4^- ion : In this complex ion, oxidation state of Mn is +7. The valence shell electronic configuration of Mn is $3d^5 4s^2$. In Mn^{7+} ion all the five $3d$, $4s$ -orbitals are vacant. The vacant $4s$ and three $3d$ - orbitals combine to give four sd^3 -hybrid orbitals. Thus, Mn^{7+} ion is sd^3 - hybridized in this complex ion as shown below :



In Mn^{7+} ion energy of vacant $4s$ -orbital becomes lower than that of vacant $3d$ - orbitals (aufbau principle).

In sd^3 - hybridization vacant d_{xy} , d_{yz} and d_{zx} orbitals are involved.

(3) $Cr_2O_7^{2-}$ ion : In this complex ion, oxidation state of Cr is + 6 and its valence shell electronic configuration of Cr is $3d^5 4s^1$. Cr^{6+} ion has no electron in $3d$ - orbitals. The $4s$ - and three $3d$ - vacant orbitals of each Cr^{6+} ion combine to give four sd^3 - hybrid orbitals. Thus, each Cr^{6+} ion in $Cr_2O_7^{2-}$ ion is sd^3 - hybridized. One of the seven oxide ions, shares both the Cr^{6+} ions.



It has no unpaired electron, therefore, it is diamagnetic. Some tetrahedral complexes are illustrated in Table 4.4.

Table 4.4

Complex Ion	Oxidation State	Valence Shell E.C.	Valence Bond Electrons Description	No. of Unpaired Electrons (n)
$[Mn X_4]^{2-}$ ($X = Cl^-, Br^-$)	+ 2	$3d^5$	<p>sp^3-hybridization</p>	5
$[FeCl_4]^{2-}$	+ 2	$3d^6$	<p>sp^3-hybridization</p>	4
$[CoCl_4]^{2-}$	+ 2	$3d^7$	<p>sp^3-hybridization</p>	3
$[Cu X_4]^{2-}$ ($X = Cl^-, Br^-, CNS^-$)	+ 2	$3d^9$	<p>sp^3-hybridization</p>	1

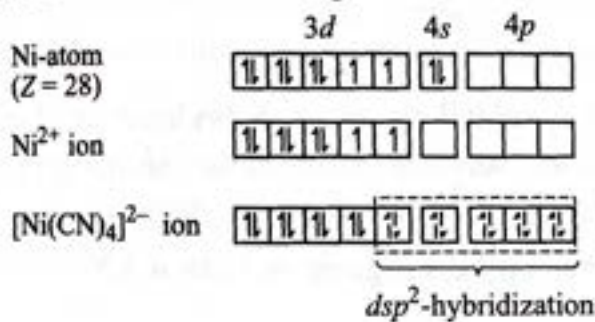
$[\text{Cu}(\text{CN})_4]^{3-}$	+ 1	$3d^{10}$	<p>sp^3-hybridization</p>	0
$[\text{Zn}X_4]^{2-}$ [X = Cl^- , Br^- , I^-]	+ 2	$3d^{10}$	<p>sp^3-hybridization</p>	0

Square Planar Complexes

In square planar complexes, the central metal cation is dsp^2 -hybridized. The dsp^2 -hybrid orbitals point towards the four corners of a square.

Let us consider some examples to discuss the hybridization in square planar complexes :

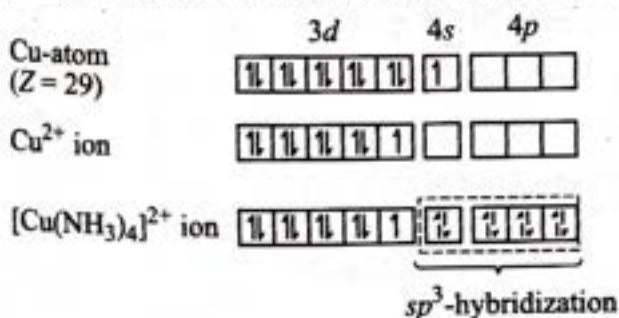
(1) $[\text{Ni}(\text{CN})_4]^{2-}$ ion : In this complex ion, oxidation state of Ni is + 2 and its valence shell electronic configuration is $3d^8$. Magnetic moment measurement indicate that this complex ion is diamagnetic *i.e.*, it has no unpaired electrons. Since CN^- is a strong ligands, therefore, these ligands cause to pair up the two unpaired electrons in one d -orbital resulting in a vacant $3d$ -orbital. This vacant $3d$ -orbital gets hybridized with the vacant $4s$ and two of the $4p$ -orbitals to give four dsp^2 -hybrid orbitals. These hybrid orbitals form bonds to the ligands by accepting four pair of ligand electrons, one pair from each of the four ligands.



dsp^2 -hybridization
square planar
geometry

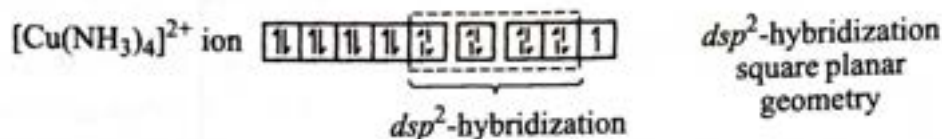
Mo

(2) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion : In this ion, oxidation state of copper is + 2 and its valence shell electronic configuration is $3d^9$. Magnetic moment measurements indicate that this complex ion is paramagnetic corresponding to presence of one unpaired electron. There is no possibility of pairing of electrons by the ligands even the ligand is strong because there is only one unpaired electron in $3d$ -orbitals. Since coordination number of Cu^{2+} ion in $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is 4, therefore, according to VBT, Cu^{2+} ion should be sp^3 -hybridized and the structure is tetrahedral.

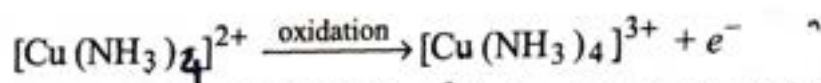


sp^3 -hybridization
tetrahedral
geometry

But according to ESR and X-rays structure determination, the structure of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is found to be square planar. Thus, to make the Cu^{2+} ion dsp^2 -hybridized, it is considered that the unpaired electron in the $3d_{x^2-y^2}$ orbital is to be promoted to $4p_z$ orbital as shown below :

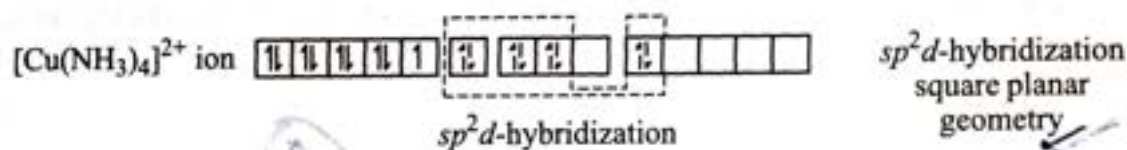


In the above electronic configuration, the unpaired electron is present in the higher energy $4p_z$ orbital and is expected to be lost easily *i.e.*, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion may be easily oxidized to $[\text{Cu}(\text{NH}_3)_4]^{3+}$.



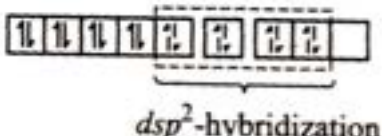
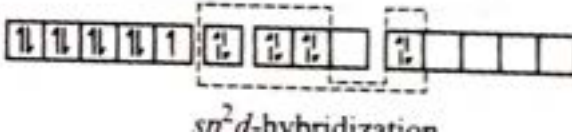
But, experiments have shown that $[\text{Cu}(\text{NH}_3)_4]^{3+}$ ion does not exist *i.e.*, oxidation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ to $[\text{Cu}(\text{NH}_3)_4]^{3+}$ is not possible.

Finally Huggin suggested that in square planar $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion, Cu^{2+} ion is sp^2d -hybridized as shown below :



In this configuration one of the three $4p$ -orbitals, $4p_z$ -orbital remains unhybridized *i.e.*, does not participate in hybridization because p_z -orbitals lies above and below the plane of the ion. $[\text{Cu}(\text{py})_2]^{2+}$, $[\text{Cu}(\text{en})_2]^{2+}$, $[\text{Cu}(\text{CN})_4]^{2-}$ complex ions are square planar and Cu^{2+} ion is sp^2d -hybridized. The valence bond electron description of some square planar complexes is given in Table 4.5.

Table 4.5

Complex	Oxidation State of Metal	Valence Shell E.C. of Metal Cation	Valence Bond Electrons Description	No. of Unpaired Electrons (n)
$[\text{Ni}(\text{Hdmg})_2]$	+ 2	$3d^8$		0
$[\text{Cu}(\text{CN})_4]^{2-}$	+ 2	$3d^9$		1

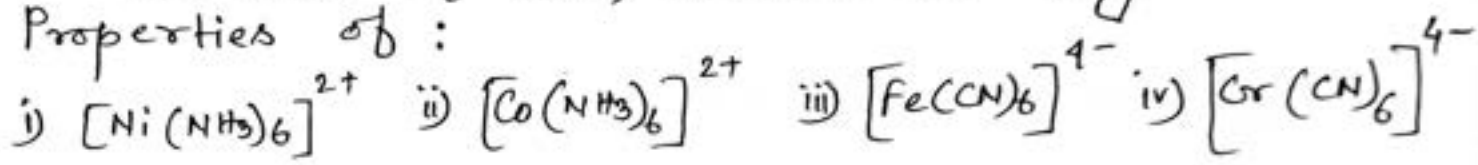
$[\text{PdCl}_4]^{2-}$	+ 2	$4d^8$	<p>The diagram shows five 4d orbitals in a row. The first four orbitals are filled with two electrons each (up and down arrows). The last two orbitals are also filled with two electrons each. A dashed box encloses the last two orbitals, with a bracket underneath labeled dsp^2-hybridization.</p>	0
$[\text{PtCl}_4]^{2-}$	+ 2	$5d^8$	<p>The diagram shows five 5d orbitals in a row. The first four orbitals are filled with two electrons each. The last two orbitals are also filled with two electrons each. A dashed box encloses the last two orbitals, with a bracket underneath labeled dsp^2-hybridization.</p>	0
$[\text{Pt}(\text{NH}_3)_4]^{2+}$	+ 2	$5d^8$	<p>The diagram shows five 5d orbitals in a row. The first four orbitals are filled with two electrons each. The last two orbitals are also filled with two electrons each. A dashed box encloses the last two orbitals, with a bracket underneath labeled dsp^2-hybridization.</p>	0

Limitations of VBT

1. It could not explain the nature of ligands *i.e.*, which ligand is strong and which one is weak.
2. It could not explain why the pairing of electrons occurs in the presence of strong ligands.
3. From this theory magnetic moment can be calculated by knowing the number of unpaired electrons but it could not explain the effect of temperature on magnetic moment. It could also not explain why the experimental value of magnetic moment is greater than the calculated in some complexes.
4. It could not explain the distortion in some octahedral complexes like $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.
5. It could not explain the colour and electronic spectra of complexes.
6. It could not explain reaction rates and mechanism of reactions of complexes.
7. It could not explain the structure of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion.

Model Questions :

1. On the basis of VBT, account for magnetic Properties of :



2. $\text{K}_4[\text{Cr}(\text{NCS})_6]$ has a magnetic moment of 5.0 B.M while $\text{K}_4[\text{Cr}(\text{CN})_6]$ has a value of only 3.2 B.M. Give the geometry of each complex on the basis of VBT.

3. The magnetic moment of $[\text{MnBr}_4]^{2-}$ and $[\text{Mn}(\text{CN})_6]^{3-}$ are 5.9 and 2.9 B.M respectively. Using VBT, assign the geometries of these complex.

4) Discuss the structure, bonding (VBT) and magnetic property of $[\text{Ni}(\text{CO})_4]$.

References :

1. Ajay Kumar (2016); coordination chemistry.

2. ~~Coor~~ Ramanan D. Wijesekera; coordination compounds, Bonding, structure & Nomenclature

3. A.G. Sharpe, Inorganic chemistry, Third Edition