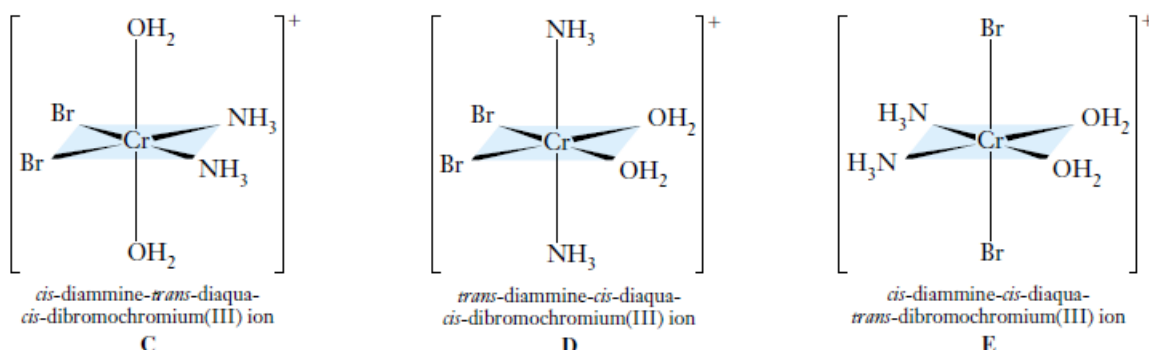


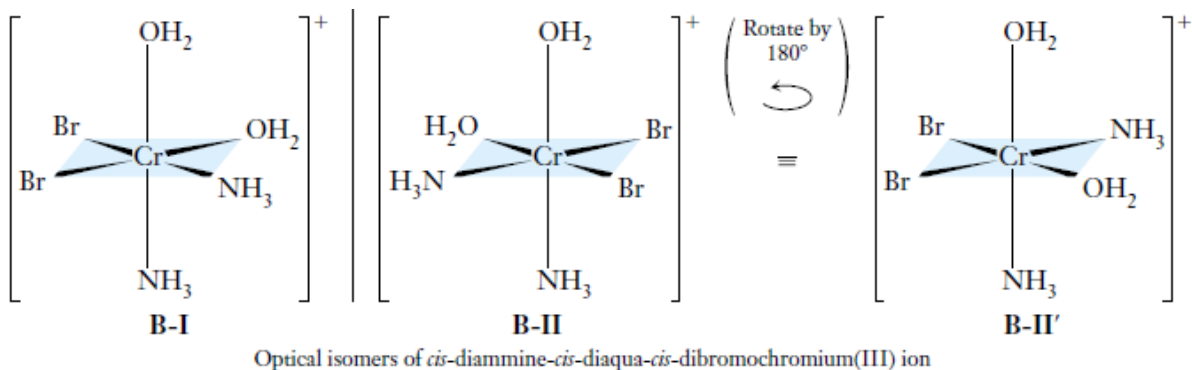
Then, members of one of the pairs may be *trans* to each other, but the members of the other two pairs are *cis*.



In C, only the two H<sub>2</sub>O ligands are in a *trans* arrangement; in D, only the NH<sub>3</sub> ligands are *trans*; and in E, only the two Br<sup>-</sup> ligands are *trans*. Further interchange of the positions of the ligands produces no new geometric isomers. However, one of the five geometric isomers (B) can exist in two distinct forms called *optical isomers*.

## 2- Optical Isomers

The *cis*-diammine-*cis*-diaqua-*cis*-dibromochromium(III) geometrical isomer (B) exists in two forms that bear the same relationship to each other as left and right hands. They are *nonsuperimposable* mirror images of each other and are called **optical isomers** or **enantiomers**.

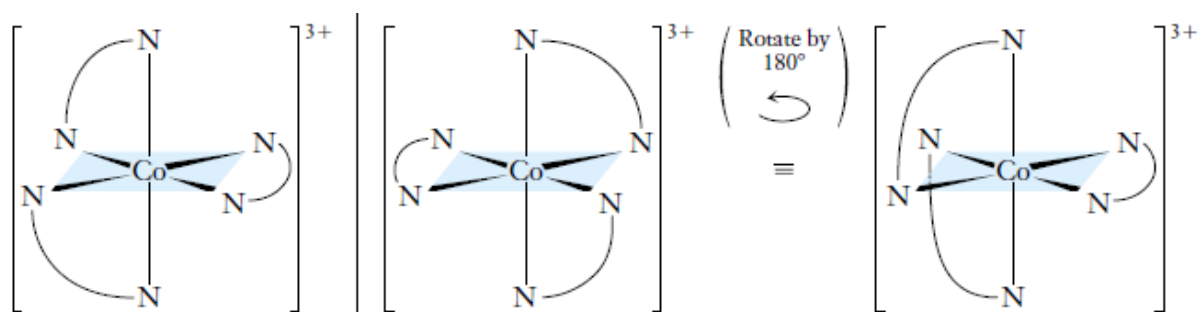


Complexes B-I and B-II are mirror images of each other. To see that they are not identical, imagine rotating B-II about its vertical axis by  $180^\circ$  (B-II), so that the two  $\text{Br}^-$  ligands are at the left, as they are in B-I. Then B-II' has the  $\text{OH}_2$  ligand at the right front position and the  $\text{NH}_3$  ligand at the right rear position, which is not the same as in B-I. No rotation of B-II makes it identical to B-I. Thus these two arrangements are nonsuperimposable mirror images of each other.

**Optical isomers** that are nonsuperimposable mirror images of each other (**chiral**) are called **enantiomers** of one another. Enantiomers can exist in two forms that bear the same relationship to each other as do left and right hands.

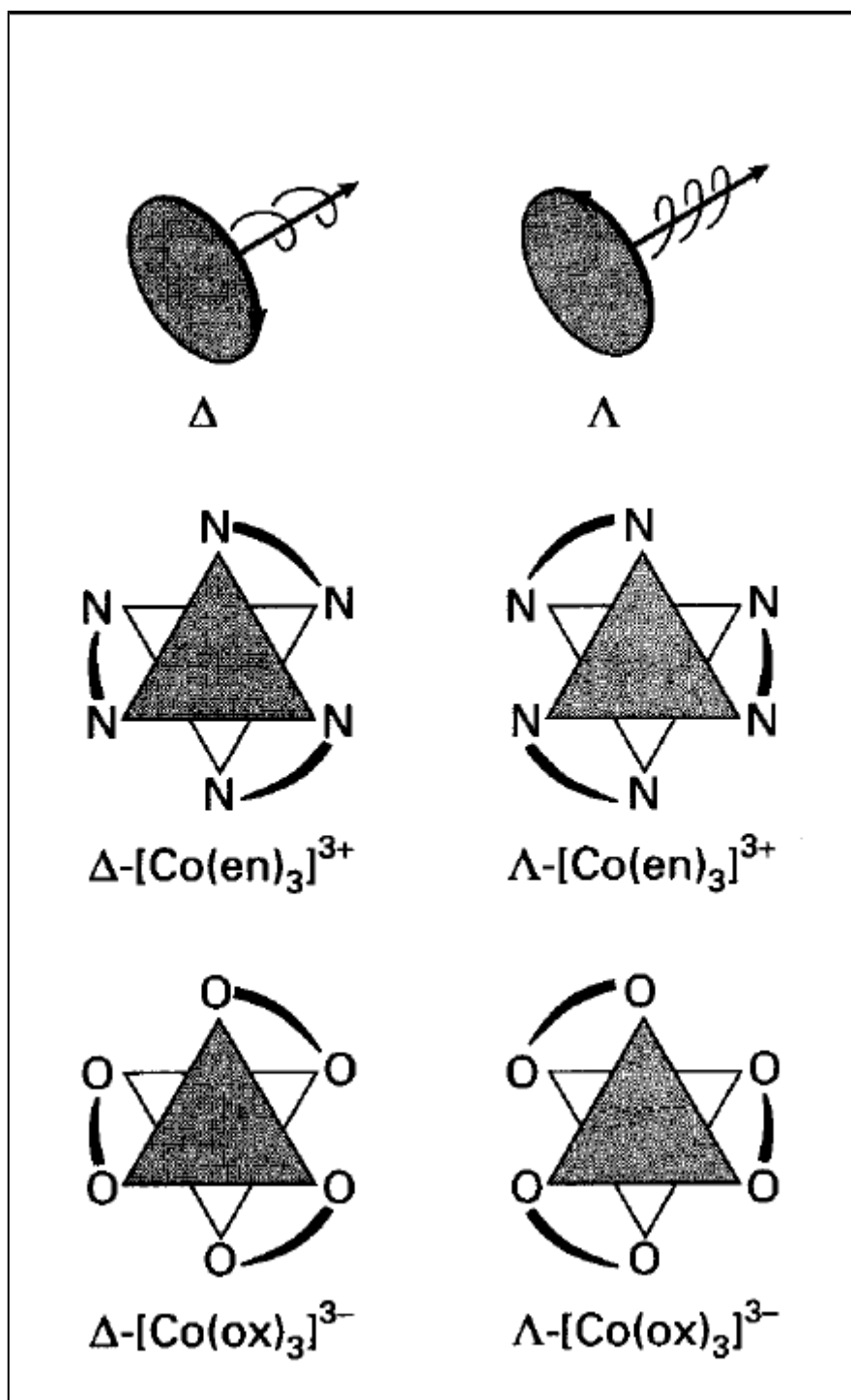
**chiral** (from the Greek word *cheir*, meaning “hand”); an object that is superimposable with its mirror image is said to be **achiral**. Examples of familiar objects that are **chiral** are a screw, a propeller, a foot, an ear, and a spiral staircase; examples of common objects that are **achiral** are a plain cup with no decoration, a pair of eyeglasses, and a sock.

Another pair of optical isomers follows, each of which contains three identical molecules  $[\text{M}(\text{A}\cap\text{A})_3]$  such as  $[\text{Co}(\text{en})_3]^{3+}$  which contains three of ethylenediamine, a bidentate ligand.



The two optical isomers of the *tris*(ethylenediamine)cobalt(III) ion

The notation for the absolute configuration of the  $M(A\cap A)_3$  complex enantiomers follow the rules given on the right-hand side. In case of a right-hand screw, the complex is denoted as  $\Delta$ - $M(A\cap A)_3$ ,  $\Delta$  (delta), in case of a left-hand screw, the complex is denoted  $\Lambda$ - $M(A\cap A)_3$ ,  $\Lambda$  (lambda).

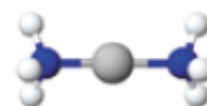
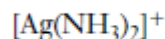
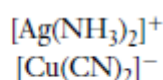


## Coordination numbers (C.N.) and geometries

Coordination number - the number of  $\sigma$ -bonds between ligands and central atom

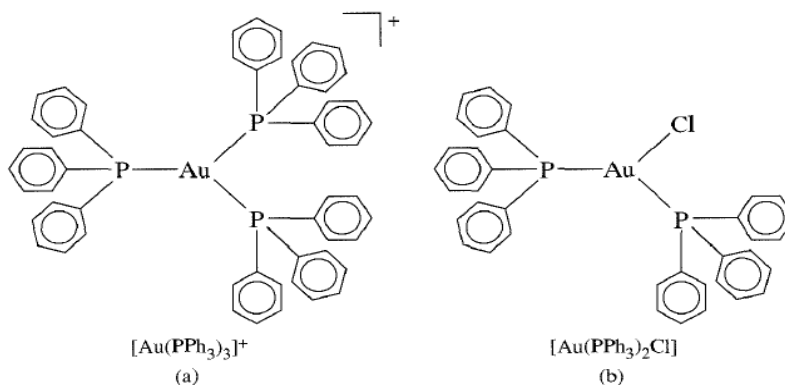
### Low coordination numbers (CN = 2 and 3)

**Coordination number 2** is rare. The best known example is  $[\text{Ag}(\text{NH}_3)_2]^+$ , the diamminesilver(I) ion. The silver 1+ ion is  $d^{10}$ , so the only electrons to be considered in the VSEPR treatment are those forming the bonds with the ammonia ligands, and the structure is linear as expected for two bonding positions.



Other examples are also  $d^{10}$  and linear ;  $[\text{CuCl}_2]^-$ ,  $[\text{Hg}(\text{CN})_2]$ ,  $[\text{Au}(\text{CN})_2]^-$

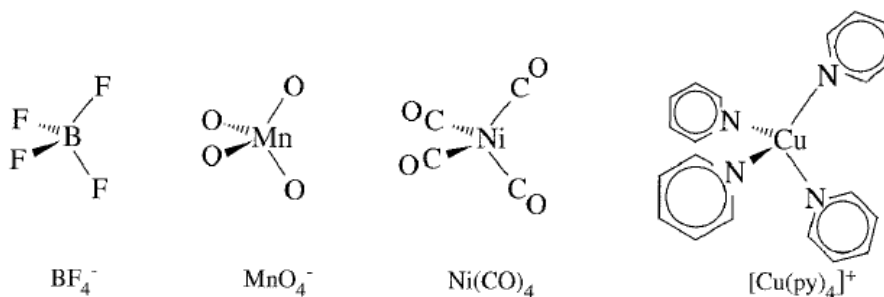
**Coordination number 3** also is more likely with  $d^{10}$  ions, with a trigonal-planar structure being the most common. Three-coordinate Au(I) and Cu(I) complexes that are known include  $[\text{Au}(\text{PPh}_3)_3]^+$  and  $[\text{Au}(\text{PPh}_3)_2\text{Cl}]$ . Most 3-coordinate complexes seem to have a low coordination number because of ligand crowding. **Ligands such as triphenylphosphine,  $\text{PPh}_3$ , is bulky enough to prevent larger coordination numbers even when the electronic structure favors them.** Most the first-row transition metals form such complexes, either with three identical ligands or two of one ligand and one of the other. These complexes have a geometry close to trigonal planar around the metal. Others with three ligands are  $\text{MnO}_3^+$  and  $\text{HgI}_3^-$ .



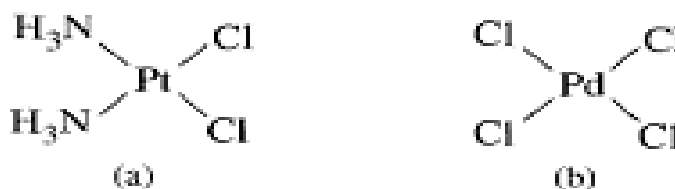
## Coordination Number 4

**Tetrahedral and square-planar** structures are two common structures with four ligands. Another structure, with four bonds and one lone pair, appears in main group compounds such as  $\text{SF}_4$  and  $\text{TeCl}_4$ , giving a "seesaw" structure. Crowding around small ions of high positive charge prevents higher coordination numbers for ions such as  $\text{Mn(VII)}$  and  $\text{Cr(VI)}$ , and large ligands can prevent higher coordination for other ions. Many  $d^0$  or  $d^{10}$  complexes have tetrahedral structures, such as  $\text{MnO}_4^-$ ,  $\text{CrO}_4^{2-}$ ,  $[\text{Ni}(\text{CO})_4]$ , and  $[\text{Cu}(\text{py})_4]^+$  with a few  $d^5$ , such as  $\text{MnCl}_4^{2-}$ .

A number of tetrahedral  $\text{Co(II)}$  ( $d^7$ ) species are also known  $\text{CoCl}_4^{2-}$  is one, as well as some for other transition metal complexes, such as  $[\text{Co}(\text{PF}_3)_4]$ ,  $\text{TiCl}_4$ ,  $[\text{NiCl}_4]^{2-}$ , and  $[\text{NiCl}_2(\text{PPh}_3)_2]$ . Examples of tetrahedral species are given in Figures below.



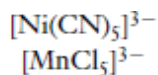
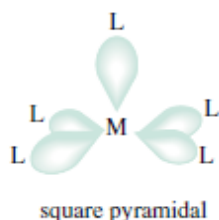
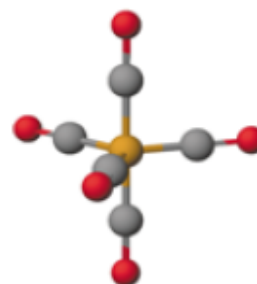
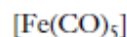
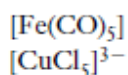
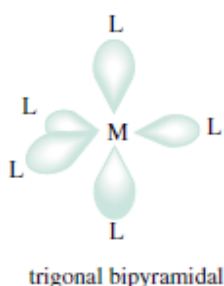
**Square-planar geometry** is also possible for four-coordinate species; with the same geometric requirements imposed by octahedral geometry (both require  $90^\circ$  angles between ligands). Some square-planar complexes are shown in Figures below.



## Coordination Number 5

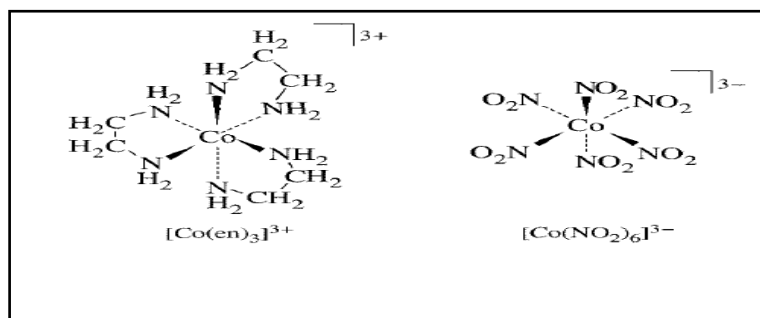
The structures possible for coordination number 5 are the **trigonal bipyramid**, and the **square pyramid**. The energy difference between the trigonal bipyramid and the square pyramid is very small. Many 5 coordinate nickel(II) complexes are known. The majority of these complexes are trigonal bipyramidal (tbp), low spin, and diamagnetic. However, high-spin complexes of tbp also exist. Five coordinate nickel(II) can also adopt the square pyramidal geometry, of which the majority of complexes are also high spin and paramagnetic.

Other five-coordinate complexes are shown below.



## Coordination Number 6

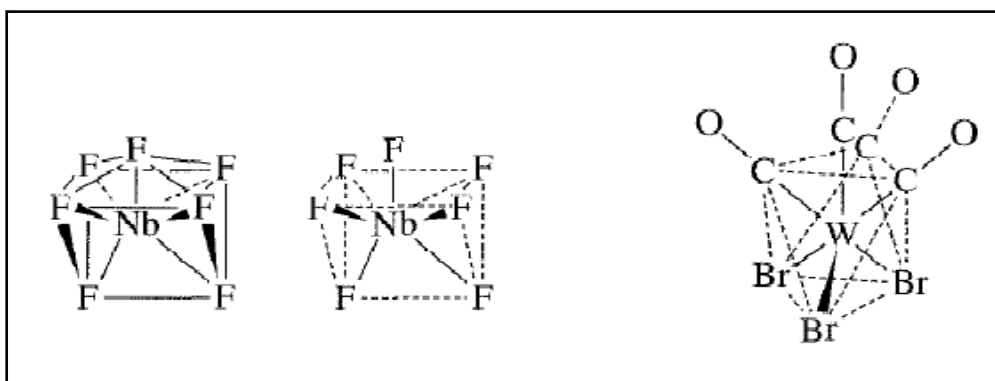
Six is the most common coordination number. The most common structure is octahedral; some trigonal prismatic structures are also known. If a metal ion is large enough to allow six ligands to fit around it and the *d* electrons are ignored, an octahedral shape results from VSEPR arguments. Such compounds exist for all the transition metals with  $d^0$  to  $d^{10}$  configurations, such as tris(ethylenediamine) cobalt(III),  $[\text{Co}(\text{en})_3]^{3+}$  and hexanitritocobaltate(III),  $[\text{Co}(\text{NO}_2)_6]^{3-}$  .....etc.



## Coordination Number 7

Three structures are possible for seven-coordinate complexes, **the pentagonal bipyramid, capped trigonal prism, and capped octahedron**. In the capped shapes, the seventh ligand is simply added to a face of the structure, with related adjustments in the other angles to allow it to fit. Although seven-coordinate is not common, all three shapes are found experimentally, with the differences apparently resulting from different counterions and the steric requirements of the ligands (especially chelating ligands).

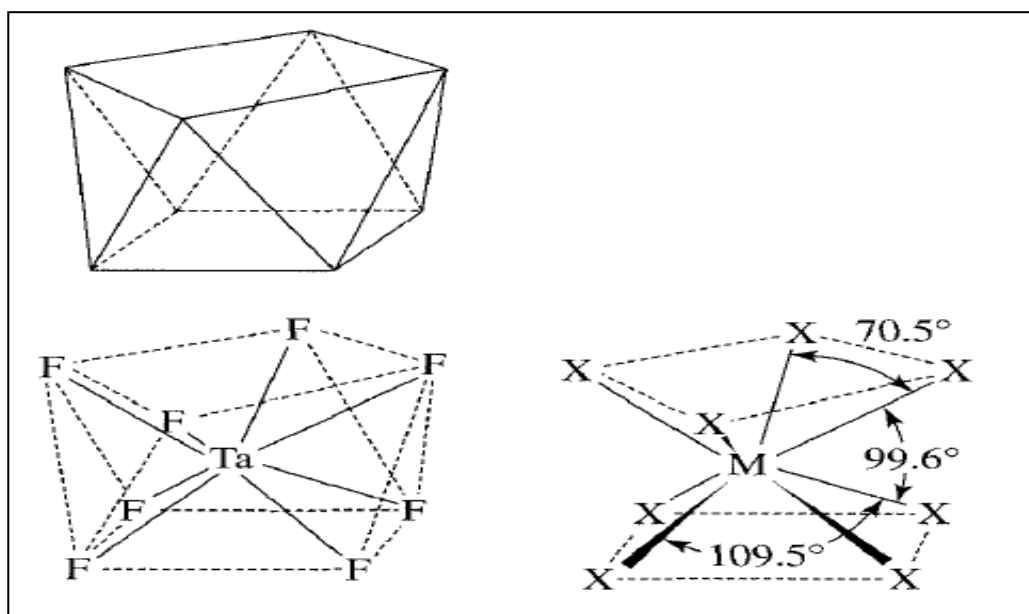
Examples include the following: pentagonal bipyramids;  $[\text{NiF}_7]^{2-}$  and  $[\text{NbF}_7]^{2-}$  in both of which the seventh fluoride caps a rectangular face of a trigonal prism; and  $[\text{W}(\text{CO})_4\text{Br}_3]^-$ , a monocapped octahedron. Some of these complexes are shown below.



## Coordination Number 8

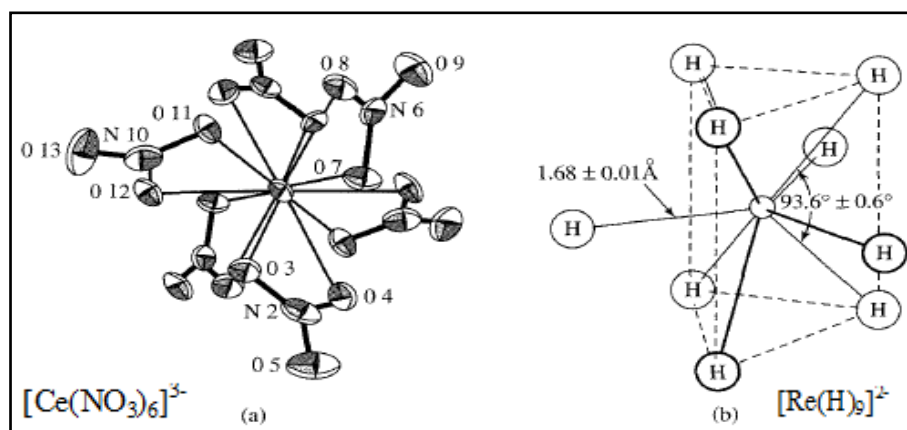
Although the cube has eight-coordinate geometry, it exists only in simple ionic lattices such as CsCl. The square antiprism and dodecahedron are common in

transition metal complexes, and there are many eight-coordinate complexes. Because the central ion must be large in order to accommodate eight ligands, eight-coordinate is rare among the first row transition metals (although it is likely in  $[\text{Fe}(\text{edta})(\text{H}_2\text{O})_2]^+$  in solution). Solid-state examples include  $\text{Na}_3\text{TaF}_8$ ,  $\text{K}_4[\text{Mo}(\text{CN})_8]$ , which have square antiprisms of  $[\text{TaF}_8]^{3-}$  and  $[\text{Mo}(\text{CN})_8]^{4-}$ , and  $[\text{Zr}(\text{acac})_4]$ , a regular dodecahedron. Some figures of these complexes are shown below.



## Larger Coordination Numbers

Coordination numbers are known up to 16, but most over 8 are special cases. Two examples are shown below.  $[\text{La}(\text{NH}_3)_9]^{3+}$  has a capped square-antiprism structure.





## **Bonding theories in coordination complexes**

In the previous lectures, we were talking about old theories in bonding of coordination complexes which are chain theory and Werner theory. In this part of lectures we will talk about of remaining theories such as VBT, CFT, and MOT. These theories have been proposed to explain the nature of metal-ligand bonding in complexes and also explain the color, geometry and magnetic properties of the complexes compounds.

### **Valence Bond theory (VBT)**

This theory is mainly due to (L.Pauling and J.L.Slater, 1935). It deals with the electronic structure of the central metal ion in its ground state, kind of bonding, geometry and magnetic properties of the complexes.

#### **Assumption of VBT**

- 1- The central metal atom or ion makes available a number of empty s, p and d atomic orbital equal to its coordination number. These vacant orbital hybrid together to form hybrid orbitals which are the same in number as the atomic orbitals hybridizing together. These hybrid orbital's are vacant, equivalent in energy and have definite geometry. Important types of hybridization occurring in the first row transition metal (3d metals) complexes and the geometry of the complexes are given in table (8).
- 2- The ligands have a last one  $\sigma$ -orbital containing alone pair of electron.
- 3- Vacant orbital hybrid of the metal atom or ion overlap with the filled(containing lone pair of electrons)  $\sigma$ -orbital of the ligands to form ligand $\rightarrow$ metal  $\sigma$ -bond. This bond which is generally known as coordination bond is a special type of covalent bond and shows the characteristics of both

the overlapping orbitals. However, it also possesses a considerable amount of polarity because of the mode of its formation.

- 4- The non- bonding electrons of the metal atom or ion are often then arrangement in the metal orbitals which do not participate in forming the hybrid orbitals. The rearrangement of non-bonding electrons takes place according to Hund's rule.

Table( 8 ). Important types of hybridization occurring in the first row transition metal (3d metals) complexes and the geometry of the complexes.

Coordination number of metal atom / ion	Type of hybridization	Geometry of complexes	Example
2	$sp(4s, 4p_x)$	linear	$[CuCl_2]^-$ , $[Cu(NH_3)_2]^+$
3	$sp^2(4s, 4p_x, 4p_y)$	Trigonal planar	$[Cu(\text{S}=\text{N}=\text{N})_3]^+$
4	$sp^3(4s, 4p_x, 4p_y, 4p_z)$	Tetrahedral	$[FeBr_4]^-$ , $Ni(CO)_4$
4	$dsp^2(3d_{x^2-y^2}, 4s, 4p_x, 4p_y)$	Square planar	$[Ni(CN)_4]^-$
5	$sp^3d(4s, 4p_x, 4p_y, 4p_z, 3d_{z^2})$	Trigonal bipyramidal	$[CuCl_5]^{3-}$
5	$dsp^3(4s, 4p_x, 4p_y, 4p_z, 3d_{x^2-y^2})$	Square-based pyramidal	$[Ni(CN)_5]^{3-}$
6	$sp^3d^2(4s, 4p_x, 4p_y, 4p_z, 4d_{z^2}, 4d_{x^2-y^2})$	outer-orbital ,Octahedral	$[Co(H_2O)_6]^{+2}$
6	$d^2sp^3(3d_{z^2}, 3d_{x^2-y^2}, 4s, 4p_x, 4p_y, 4p_z)$	Inner-orbital ,Octahedral	$[Co(NO_2)_6]^{3-}$
7	$sp^3d^3(4s, 4p_x, 4p_y, 4p_z, 3d_{xy}, 3d_{x^2-y^2}, 3d_{z^2})$	Pentagonal bipyramidal	$[NiF_7]^{-5}$

## Geometry of 6-coordinate complex ions

The coordination number in these complexes is six and hence these complexes have octahedral geometry. This octahedral geometry arises due to  $sp^3d^2$  or  $d^2sp^3$  hybridization of the central metal atom or ion. These types of two hybridization depend on the number of unpaired or paired electrons present in the complex ion.

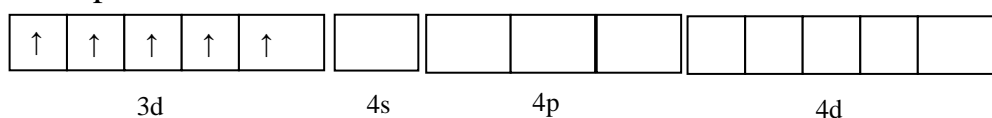
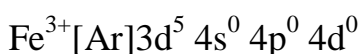
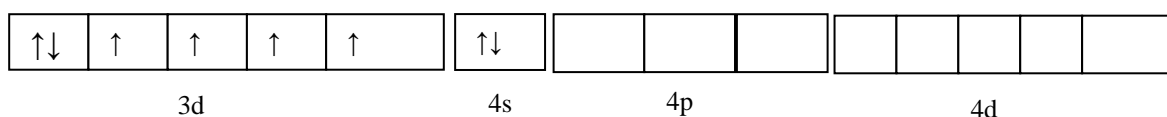
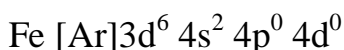
Octahedral complexes in which the central atom is  $sp^3d^2$  hybridized are called outer orbital octahedral complexes while the octahedral complexes in which the central atom is  $d^2sp^3$  hybridized are called inner orbital octahedral complexes.

### $sp^3d^2$ hybridization in outer orbital octahedral complexes

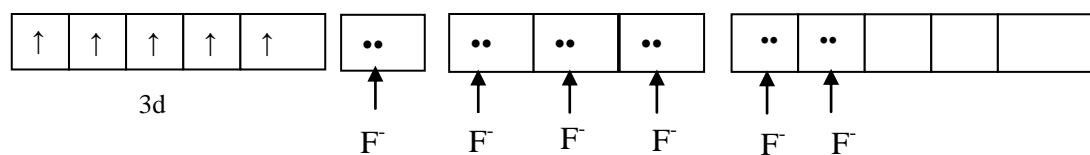
This type of hybridization takes place in those octahedral complex ions which contain weak ligands. Weak ligands are those which cannot force the electrons of  $d_z^2$  and  $d_{x^2-y^2}$  orbitals. In this hybridization,  $(n-1) d_z^2$  and  $(n-1) d_{x^2-y^2}$  orbitals are not available for hybridization. In place of these orbitals, we use  $nd_z^2$  and  $nd_{x^2-y^2}$  orbitals (these d-orbitals belong to the outer shell) and hence  $sp^3d^2$  hybridization can be represented as  $ns, np_x, np_y, np_z, nd_{z^2}, nd_{x^2-y^2}$ . The octahedral complexes resulting from  $sp^3d^2$  hybridization are called **outer orbital octahedral complexes** and also called **high spin** or **spin free octahedral complexes**.

### **Examples of outer orbital octahedral complexes :**

$[FeF_6]^{3-}$  in this ion, the coordination number of Fe is six and hence the given complex ion has octahedral geometry.



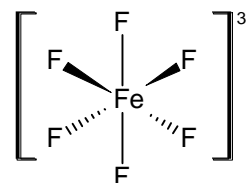
$[\text{FeF}_6]^{3-}$  ion involving  $\text{sp}^3\text{d}^2$  hybridization



Type of hybridization is  $\text{sp}^3\text{d}^2$

Type of geometry is **octahedral**

Type of d-orbital is **outer**



Furthermore, each of the five electrons is unpaired and hence  $n=5$ . Magnetic properties of the given ion is **paramagnetic** corresponding to presence of five unpaired electrons.

### $\text{d}^2\text{sp}^3$ hybridization in inner orbital octahedral complexes

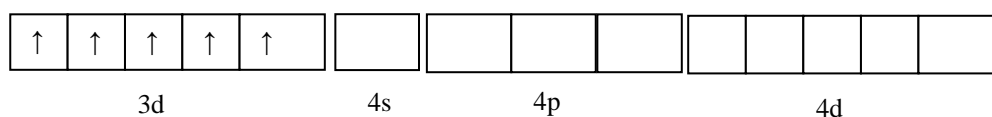
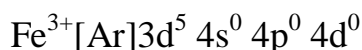
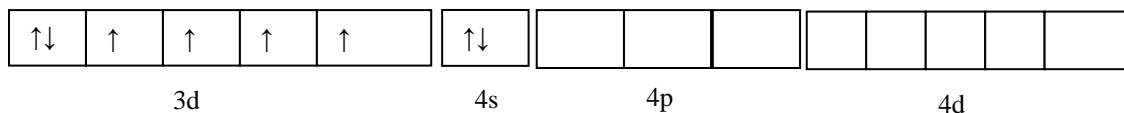
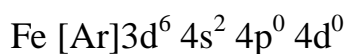
This type of hybridization take place in octahedral complex ions which contain strong ligands . strong ligands are those which force the electrons of  $(n-1)d$  orbital's in this hybridization. In the formation of six  $\text{d}^2\text{sp}^3$  hybrid orbitals ,two  $(n-1)d$  orbitals [ $(n-1) d_z^2$  and  $(n-1) d_{x^2-y^2}$  orbitals], one  $ns$  and three  $np$  ( $np_x$ ,  $np_y$  and  $np_z$ ) orbitals combine together and form six  $\text{d}^2\text{sp}^3$  hybrid orbitals.

$(n-1)d_z^2$  and  $(n-1)d_{x^2-y^2}$  orbitals are available and used for hybridization, (these d-orbitals belong to the inner shell) and hence  $\text{d}^2\text{sp}^3$  hybridization can be represent  $(n-1)d_z^2$ ,  $(n-1)d_{x^2-y^2}$ ,  $ns$ ,  $np_x$ ,  $np_y$ ,  $np_z$ . The octahedral complexes resulted from  $\text{d}^2\text{sp}^3$  hybridization are called **inner orbital octahedral complexes** and also called **low spin** or **spin paired octahedral complexes** .

The inner orbital octahedral complexes have comparatively lesser number of unpaired electrons than the outer orbital octahedral complexes.

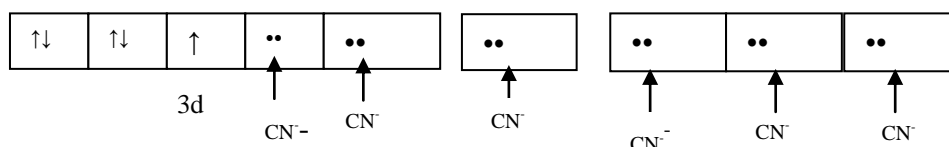
**Example** of inner orbital octahedral complexes :

**1-  $[\text{Fe}(\text{CN})_6]^{3-}$**  In this ion ,the coordination number of Fe is six and hence the given complex ion has octahedral geometry.



Magnetic study of  $[\text{Fe}(\text{CN})_6]^{3-}$  ion has shown that this ion has one unpaired electron ( $n=1$ ) and hence is paramagnetic. Thus ,in the formation of this ion ,two electrons of 3d orbitals( $3d_{z^2}$  and  $3d_{x^2-y^2}$  orbitals) pair up with the three electrons of  $3d_{xy}$  , $3d_{xz}$  and  $3d_{yz}$  orbitals i.e the  $3d_{z^2}$  and  $3d_{x^2-y^2}$  orbitals became vacant and is used in  $d^2sp^3$  hybridization

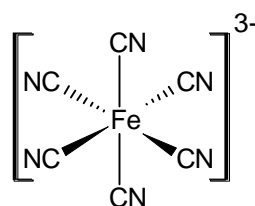
$[\text{Fe}(\text{CN})_6]^{3-}$  ion involving  $d^2sp^3$  hybridization



Type of hybridization is  $d^2sp^3$

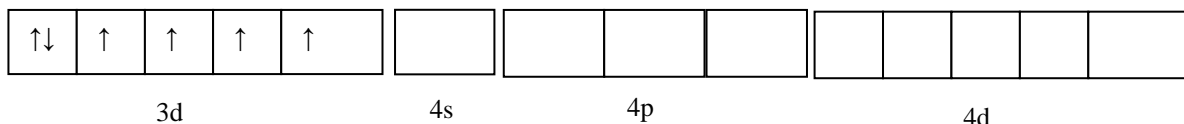
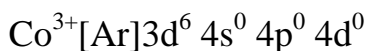
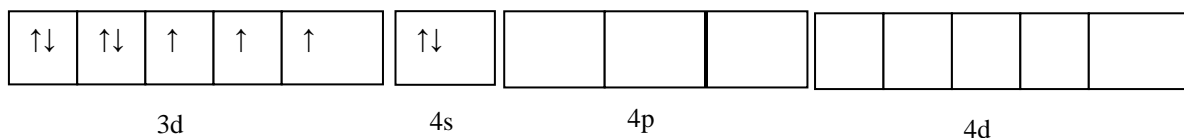
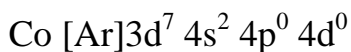
Type of geometry is **octahedral**

Type of d-orbital is **inner**



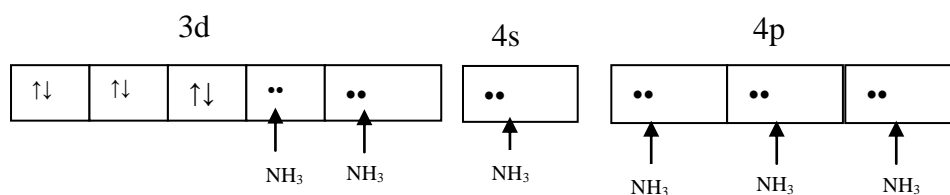
**2-  $[\text{Co}(\text{NH}_3)_6]^{3+}$**

In this ion ,the coordination number of Co is six and hence the given complex ion has octahedral geometry.



Magnetic study of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ion has shown that this ion has zero unpaired electron ( $n=0$ ) and hence is **diamagnetic**. Thus, in the formation of this ion, two electrons of 3d orbitals ( $3d_{z^2}$  and  $3d_{x^2-y^2}$  orbitals) pair up with the two electrons of  $3d_{xz}$  and  $3d_{yz}$  orbitals i.e the  $3d_{z^2}$  and  $3d_{x^2-y^2}$  orbitals became vacant and is used in  **$d^2sp^3$**  hybridization

$[\text{Co}(\text{NH}_3)_6]^{3+}$  ion involving  **$d^2sp^3$**  hybridization



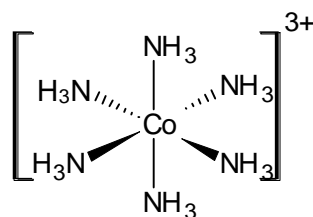
Type of hybridization is  **$d^2sp^3$**

Type of geometry is **octahedral**

Type of d-orbital is **inner**

Magnetic moment,  $\mu$  ( $\mu = 0$ )

i.e The complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$  have diamagnetic property.



## Magnetic properties of complexes

Magnetic measurements are widely used in studying transition metal complexes. The magnetic properties are due to the presence of unpaired electrons in the partially filled d-orbital in the outer shell of these elements.

These magnetic measurements give an idea about the electronic state of the metal ion in the complex.

The resultant magnetic moment of an ion is due to both orbital and spin motions. Chemically useful information can be obtained by proper interpretation of measured values of magnetic moments.

The magnetic moment is given by the following equation:

$$\mu_{s+L} = \sqrt{4s(s+1) + L(L+1)} \quad B.M$$

$\mu$  = magnetic moment

$S$  = spin quantum number

$L$  = orbital quantum number

Although detailed determination of the electronic structure requires consideration of the orbital moment, for most complexes of the first transition series the spin - only moment is sufficient, as any orbital contribution is small.

$$\mu_S = \sqrt{4s(s+1)} \quad B.M$$

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

$S = n \times 1/2$  ,  $n$  = number of unpaired electrons

Experimental, the value of magnetic susceptibility of the complexes at room temperature is calculated using the following equation:

where:

$$\mu_{eff.} = 2.88 \sqrt{X_A} \cdot T \quad B.M$$

$$X_A = X_m + D$$

$$X_m = X_g \cdot M.wt$$

$X_g$  = mass susceptibility

D = Pascal's constant

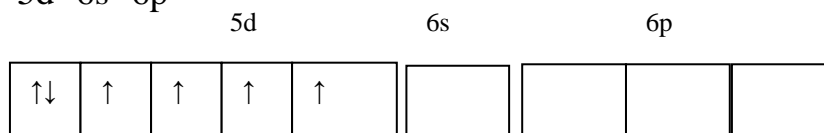
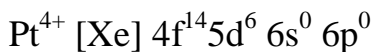
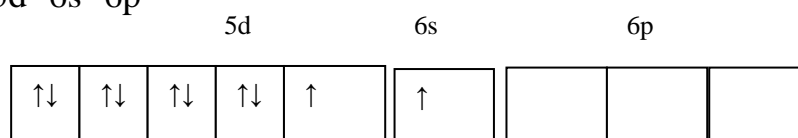
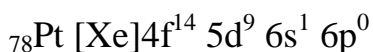
$X_m$  = molar susceptibility

$X_A$  = atomic susceptibility which its corrected from diamagnetic

$\mu_{eff.}$  = effective magnetic moment

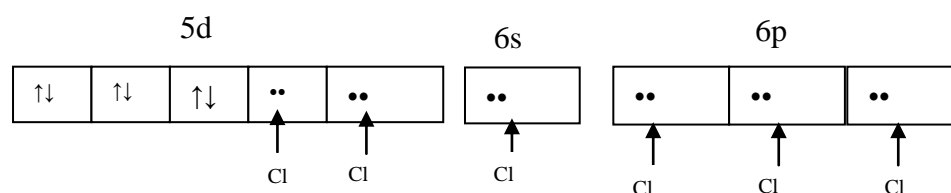
### 3- $[PtCl_6]^-$

In this ion ,the coordination number of Pt is six and hence the given complex ion has octahedral geometry.



Magnetic study of  $[PtCl_6]^-$  ion has shown that this ion has zero unpaired electron ( $n=0$ ) and hence is **diamagnetic**. Thus ,in the formation of this ion ,two electrons of 5d orbitals( $5d_{z^2}$  and  $5d_{x^2-y^2}$  orbitals) pair up with the two electrons of , $5d_{xz}$  and  $5d_{yz}$  orbitals i.e the  $5d_{z^2}$  and  $5d_{x^2-y^2}$  orbitals became vacant and is used in  **$d^2sp^3$**  hybridization

$[PtCl_6]^-$  ion involving  **$d^2sp^3$**  hybridization





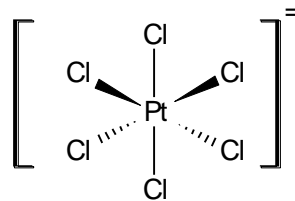
Type of hybridization is  **$d^2sp^3$**

Type of geometry is **octahedral**

Type of d-orbital is **inner**

Magnetic moment,  $\mu$  ( $\mu = 0$ )

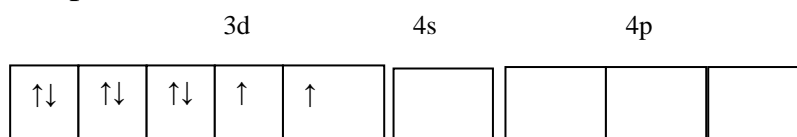
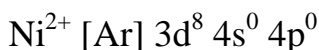
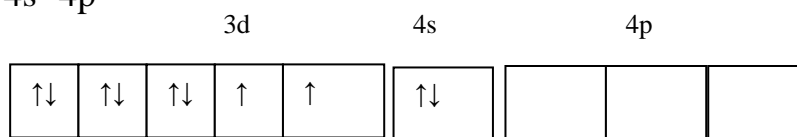
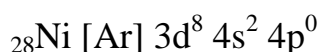
i.e The complex  $[PtCl_6]^-$  have diamagnetic property.



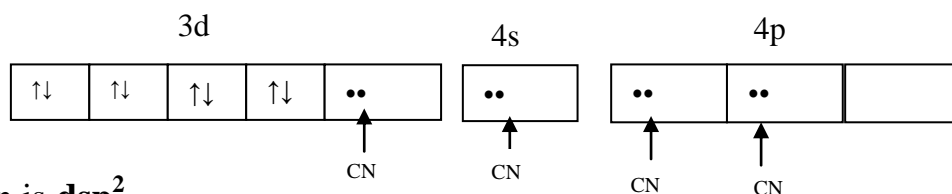
## Square planer complexes

### $[Ni(CN)_4]^-$ ion

In this ion ,the coordination number of Ni is four and hence the given complex ion may be square planar or tetrahedral in shape .in order to decide whether the given complex ion is square planar or tetrahedral, we take the help of magnetic property of the complex ion. Experimentally it has been shown that  $[Ni(CN)_4]^-$  ion has no unpaired electron( $n=0$ ) and hence is diamagnetic, Thus ,in the formation of this ion ,two electrons of 3d orbitals ( $3d_{z^2}$  and  $3d_{x^2-y^2}$  orbitals) are pair up .thereby ,making one of the 3d orbitals empty .this empty 3d orbital(which is  $3d_{x^2-y^2}$  orbital) is used in  **$dsp$**  hybridization.



$[Ni(CN)_4]^-$  ion involving  **$dsp^2$**  hybridization

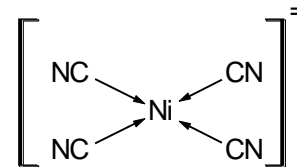


Type of hybridization is  **$dsp^2$**

Type of geometry is **square planar**

Type of d-orbital is **inner**

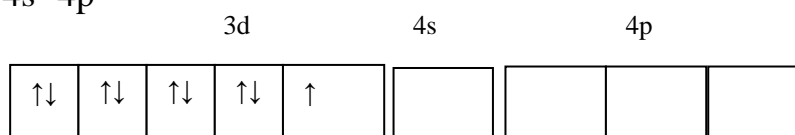
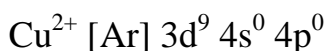
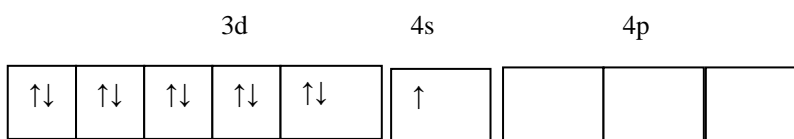
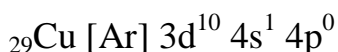
Magnetic moment,  $\mu$  ( $\mu = 0$ )



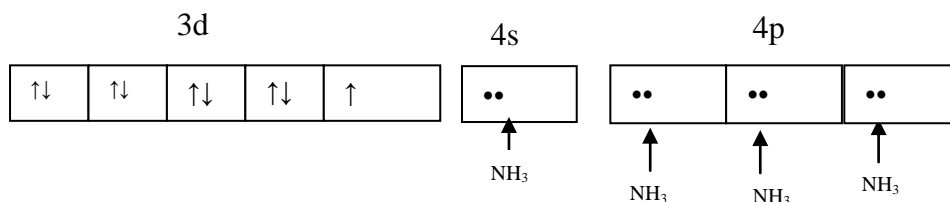
i.e The complex  $[Ni(CN)_4]^{2-}$  have diamagnetic property.



In this ion ,the coordination number of Cu is four and hence the given complex ion may be tetrahedral or planar square in shape. Tetrahedral geometry arises due to  $sp^3$  hybridization of  $Cu^{2+}$



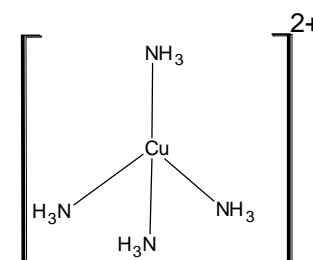
$[Cu(NH_3)_4]^{2+}$  ion involving  **$sp^3$**  hybridization



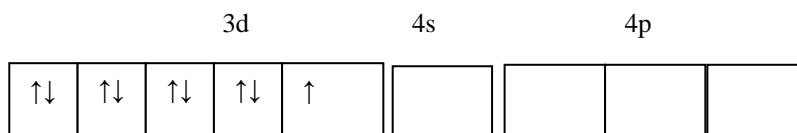
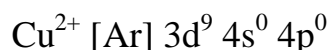
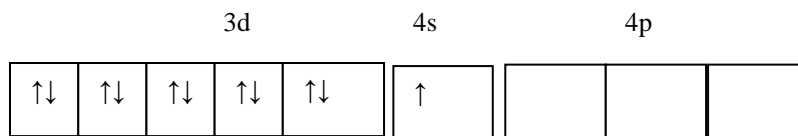
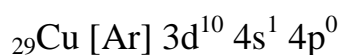
Type of hybridization is  **$Sp^3$**

Type of geometry is **Tetrahedral**

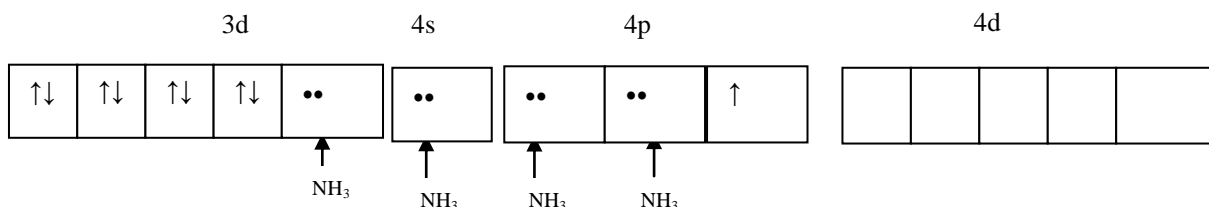
The complex has paramagnetic property ( $n=1$ )



Square planer geometry arises due to **dsp<sup>2</sup>** hybridization of Cu<sup>2+</sup>



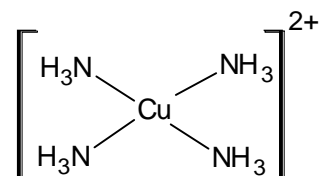
[Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ion involving **dsp<sup>2</sup>** hybridization



Type of hybridization is **dsp<sup>2</sup>**

Type of geometry is **square planar**

The complex has paramagnetic property (n=1)



The above discussion shows that in both the geometries, [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ion has one unpaired electron (n=1). i.e., the magnetic property of [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ion cannot be helpful in deciding as to what is the exact geometry of [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ion. However, physical measurement(x-ray) have indicated that the **square planar** geometry for [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ion is occurred.

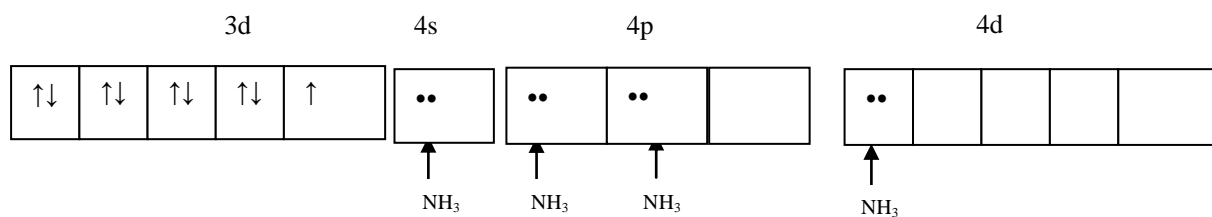
Now if the square planer geometry for [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ion is supposed to be correct, the unpaired electron present in the higher energy 4p orbitals (**dsp<sup>2</sup>** hybridization) should

be expected to be easily lost, i.e.,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion should be easily oxidized to  $[\text{Cu}(\text{NH}_3)_4]^{3+}$  ion by losing the unpaired electron residing in 4p orbital.

However, experiments have shown that the oxidation of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion does not occur. Then how to explain the geometry of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion?

**Huggin's suggestion.** Huggin's has suggested that  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion has square planer geometry and  $\text{Cu}^{2+}$  ion is **sp<sup>2</sup>d** [4s,4p and 4d] hybridized as shown below .the unpaired electron resides in 3d orbital.

**[Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ion involving **sp<sup>2</sup>d** hybridization**



Type of hybridization is  $sp^2d$

Type of geometry is **square planar**

The complex has paramagnetic property (n=1)

A summary of types of complexes formed by first-row metal ions are shown in table below:

<b>Table A Summary of Types of Complexes Formed by First-Row Metal Ions.</b>				
<b>Number of <i>d</i> Electrons</b>	<b>Most Common Ion</b>	<b>Usual Geometry<sup>b</sup></b>	<b>Hybrid Orbital</b>	<b>Example</b>
0	Sc <sup>3+</sup>	Octahedral	<i>d<sup>2</sup>sp<sup>3</sup></i>	Sc(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>
1	Ti <sup>3+</sup>	Octahedral	<i>d<sup>2</sup>sp<sup>3</sup></i>	Ti(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>
2	V <sup>3+</sup>	Octahedral	<i>d<sup>2</sup>sp<sup>3</sup></i>	VF <sub>6</sub> <sup>3-</sup>
3	Cr <sup>3+</sup>	Octahedral	<i>d<sup>2</sup>sp<sup>3</sup></i>	Cr(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>
4 <sup>a</sup>	Mn <sup>3+</sup>	Octahedral (h.s.)	<i>sp<sup>3</sup>d<sup>2</sup></i>	Mn(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>
4 <sup>a</sup>	Mn <sup>3+</sup>	Octahedral (l.s.)	<i>d<sup>2</sup>sp<sup>3</sup></i>	Mn(CN) <sub>6</sub> <sup>3-</sup>
5	Fe <sup>3+</sup>	Octahedral (h.s.)	<i>sp<sup>3</sup>d<sup>2</sup></i>	Fe(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>
5	Fe <sup>3+</sup>	Octahedral (l.s.)	<i>d<sup>2</sup>sp<sup>3</sup></i>	Fe(CN) <sub>6</sub> <sup>3-</sup>
5	Fe <sup>3+</sup>	Tetrahedral	<i>sp<sup>3</sup></i>	FeCl <sub>4</sub> <sup>-</sup>
6	Co <sup>3+</sup>	Octahedral (h.s.)	<i>sp<sup>3</sup>d<sup>2</sup></i>	CoF <sub>6</sub> <sup>3-</sup>
6	Co <sup>3+</sup>	Octahedral (l.s.)	<i>d<sup>2</sup>sp<sup>3</sup></i>	Co(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>
7	Co <sup>2+</sup>	Octahedral (h.s.)	<i>sp<sup>3</sup>d<sup>2</sup></i>	Co(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>
7	Co <sup>2+</sup>	Trigonal bipyramid	<i>dsp<sup>3</sup></i>	Co(CN) <sub>5</sub> <sup>3-</sup>
7	Co <sup>2+</sup>	Tetrahedral	<i>sp<sup>3</sup></i>	CoCl <sub>4</sub> <sup>2-</sup>
7	Co <sup>2+</sup>	Square planar	<i>dsp<sup>2</sup></i>	Co(CN) <sub>4</sub> <sup>2-</sup>
8	Ni <sup>2+</sup>	Tetrahedral	<i>sp<sup>3</sup></i>	Ni(NH <sub>3</sub> ) <sub>4</sub> <sup>2+</sup>
8	Ni <sup>2+</sup>	Octahedral	<i>sp<sup>3</sup>d<sup>2</sup></i>	Ni(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>
8	Ni <sup>2+</sup>	Trigonal bipyramid	<i>dsp<sup>3</sup></i>	Ni(CN) <sub>5</sub> <sup>3-</sup>
8	Ni <sup>2+</sup>	Square base pyramid	<i>sp<sup>2</sup>d<sup>2</sup></i>	Ni(CN) <sub>5</sub> <sup>3-</sup>
8	Ni <sup>2+</sup>	Square planar	<i>dsp<sup>2</sup></i>	Ni(CN) <sub>4</sub> <sup>2-</sup>
9 <sup>a</sup>	Cu <sup>2+</sup>	Octahedral	<i>sp<sup>3</sup>d<sup>2</sup></i>	CuCl <sub>6</sub> <sup>4-</sup>
9 <sup>a</sup>	Cu <sup>2+</sup>	Tetrahedral	<i>sp<sup>3</sup></i>	Cu(NH <sub>3</sub> ) <sub>4</sub> <sup>2+</sup>
10	Zn <sup>2+</sup>	Octahedral	<i>sp<sup>3</sup>d<sup>2</sup></i>	Zn(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>
10	Zn <sup>2+</sup>	Tetrahedral	<i>sp<sup>3</sup></i>	Zn(NH <sub>3</sub> ) <sub>4</sub> <sup>2+</sup>
10	Ag <sup>+</sup>	Linear	<i>sp</i>	Ag(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>
<sup>a</sup> Irregular structure due to Jahn-Teller distortion.				
<sup>b</sup> h.s. and l.s. indicate high and low spin, respectively.				

### **Limitation in VBT**

- 1- VBT cannot account for the relative stabilities for different shapes and different coordination numbers in metal complexes, e.g., it cannot explain satisfactorily as to why  $\text{Co}^{(+2)}$  ( $d^7$  system) form both  $O_h$  and  $T_h$  complexes while  $\text{Ni}^{(+2)}$  ( $d^8$  system) rarely forms  $T_h$  complexes.
- 2- VBT cannot explain as to why  $\text{Cu}^{(+2)}$  forms only one distorted  $O_h$  complex even when all the six ligands are identical.
- 3- VBT fails to explain the finer details of magnetic properties including the magnitude of the **orbital contribution** to the magnetic moment. e.g., although both tetrahedral ( $sp^3$  hybridization) and outer orbital octahedral ( $sp^3d^2$  hybridization) complexes of  $\text{Co}^{(+2)}$  ( $d^7$  system) have three unpaired electrons and are, therefore, expected to have  $\mu$  value equal to 3.87 B.M., the tetrahedral complexes generally have  $\mu$  value in the range 4.4-4.8 B.M., while the octahedral complexes have still higher value of  $\mu$  value in the range 4.7-5.2 B.M. The increase in the value of  $\mu$  is due to the **orbital contribution**, similar in the case with tetrahedral and octahedral complexes of  $\text{Ni}^{(+2)}$  ( $d^8$  system). VBT cannot explain the increase in the value of  $\mu$ .
- 4- VBT cannot interpret the spectra (colour) of the complexes.
- 5- VBT cannot explain temperature dependent paramagnetism of the complexes.

## Crystal Field Theory(CFT)

This theory is mainly due to (Bethe (1929) and Van Vleck( 1932).This is an electrostatic approach, used to describe the split in metal d-orbital energies. It provides an approximate description of the electronic energy levels that determine the ultraviolet and visible spectra, but does not describe the bonding.

### The octahedral crystal field

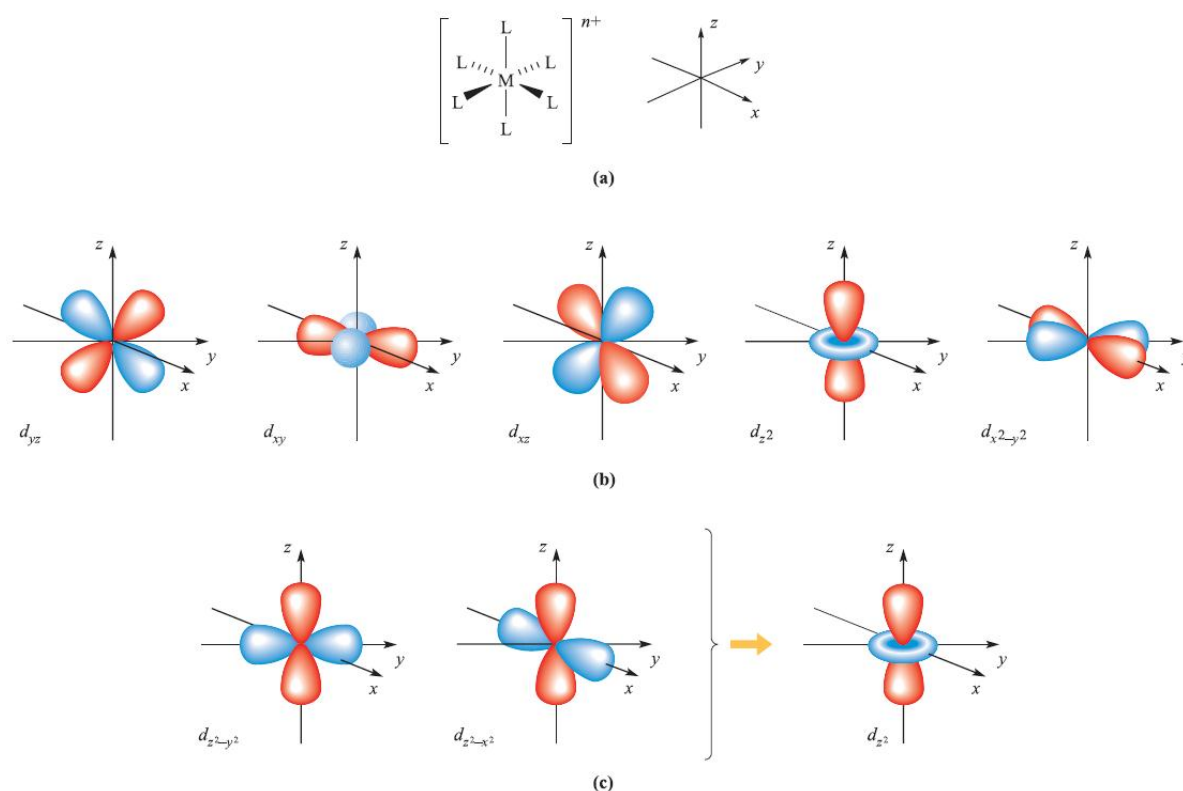


Fig. (a) The six M-L vectors of an octahedral complex  $[ML_6]^{n+}$  can be defined to lie along the x, y and z axes. (b) The five d orbitals; the  $d_{z^2}$  and  $d_{x^2-y^2}$  atomic orbitals point directly along the axes, but the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  atomic orbitals point between them. (c) The formation of a  $d_{z^2}$  orbital from a linear combination of  $d_{z^2-y^2}$  and  $d_{z^2-x^2}$  orbitals.

When the d orbitals of a metal ion are placed in an **octahedral field** of ligand electron pairs, any electrons in them are repelled by the field(see **Fig. above**). As a result, the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals, which are directed at the surrounding ligands, are raised in energy. The  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals, which are directed between the

surrounding ions, are relatively unaffected by the field. From the  $O_h$  character table, it can be deduced that the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals have **eg** symmetry, while the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals possess **t<sub>2g</sub>** symmetry. The resulting energy difference is identified as  $\Delta_{\text{oct}}$ , (oct for octahedral; some older references use the term  $10Dq$  instead of  $\Delta_{\text{oct}}$ ).

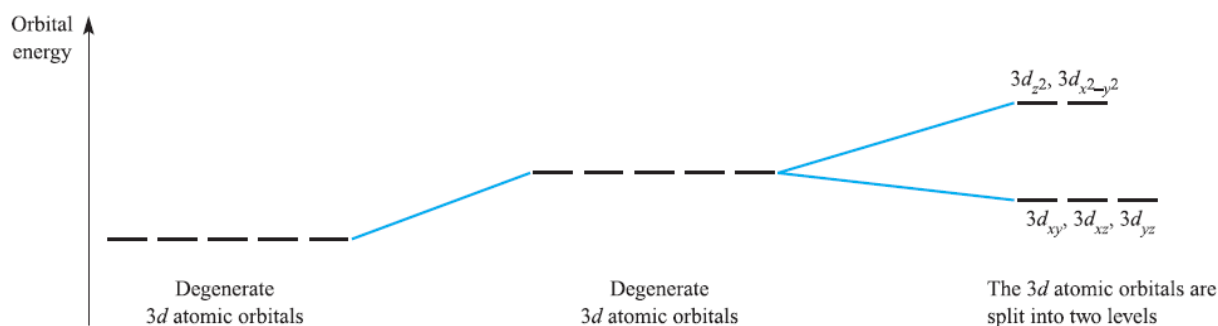


Fig. shows the changes in the energies of the electrons occupying the 3d orbitals of a first row transition ions when it's in an octahedral crystal field. The energy changes are shown in terms of the orbital energies. Similar diagrams can be drawn for second (4d) and third (5d) row metal ions.

The **t<sub>2g</sub>** orbitals are  $0.4\Delta_{\text{oct}}$ , below and the **eg** orbitals are  $0.6\Delta_{\text{oct}}$ , above. The three **t<sub>2g</sub>** orbitals then have a total energy of  $-0.4\Delta_{\text{oct}} \times 3 = -1.2\Delta_{\text{oct}}$  and the two **eg** orbitals have a total energy of  $+0.6\Delta_{\text{oct}} \times 2 = +1.2\Delta_{\text{oct}}$ , compared with the average.

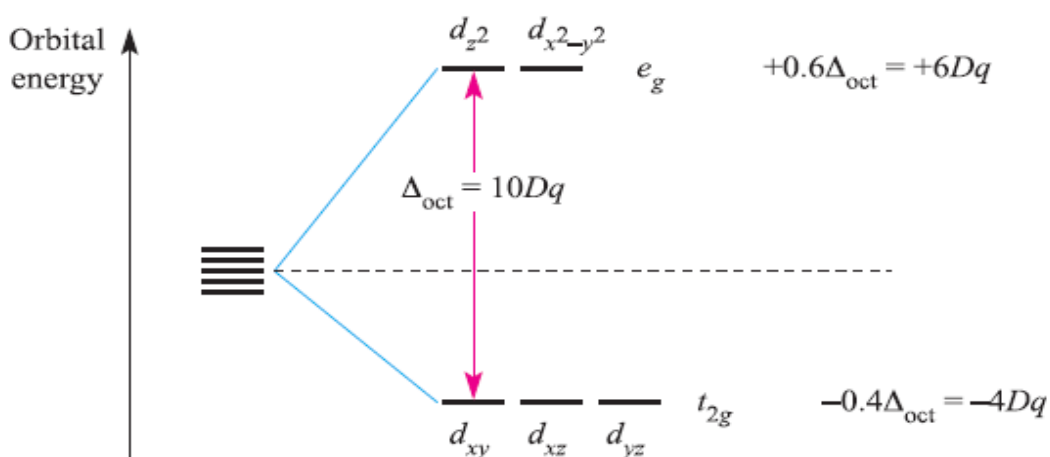


Fig. shows the splitting of the d orbitals in an octahedral crystal field, with the energy changes measured with respect to the barycentre, the energy level shown by the hashed line.



The stabilization and destabilization of the  $t_{2g}$  and  $e_g$  sets, respectively, are given in terms of  $\Delta_{\text{oct}}$ . The magnitude of  $\Delta_{\text{oct}}$  is determined by the strength of the crystal field, the two extremes being called weak field and strong field as shown in equation below.

$$\Delta_{\text{oct}} \text{ weak field} < \Delta_{\text{oct}} \text{ strong field}$$

Values of  $\Delta_{\text{oct}}$  can be evaluated (experimental) from electronic spectroscopic data. Consider the  $d^1$  complex  $[\text{Ti}(\text{OH}_2)_6]^{3+}$ , for which the ground state is represented by following Fig. as shown below or the notation  $t_{2g}^1 e_g^0$ .



The absorption spectrum of the  $[\text{Ti}(\text{OH}_2)_6]^{3+}$  ion exhibits one broad band for which  $\lambda_{\text{max}} = 20,300 \text{ cm}^{-1}$  corresponding to an energy change of  $243 \text{ kJ mol}^{-1}$ . (The conversion is  $1 \text{ cm}^{-1} = 11.96 \times 10^{-3} \text{ kJ mol}^{-1}$ .)

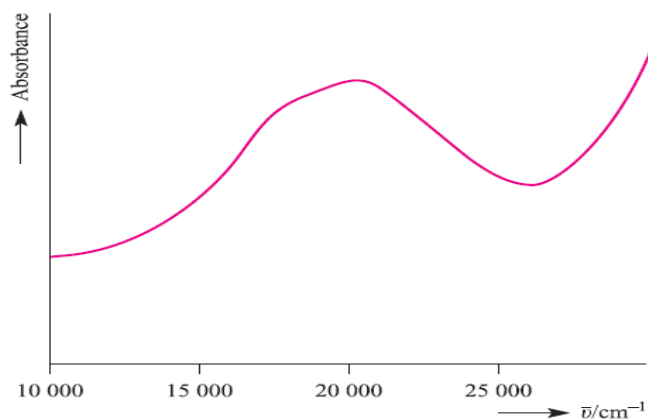


Fig. Shows the electronic spectrum of  $[\text{Ti}(\text{OH}_2)_6]^{3+}$  in aqueous solution.

The absorption results from a change in electronic configuration from  $t_{2g}^1 e_g^0$  to  $t_{2g}^0 e_g^1$ , and the value of  $\lambda_{\text{max}}$  gives a measure of  $\Delta_{\text{oct}}$ . For systems with more than one  $d$  electron, the evaluation of  $\Delta_{\text{oct}}$  is more complicated.