

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

**University of karbala**

**Lec: One-B**

**College of pharmacy**

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**3rd Stage**

**Course title:** Inorganic medicinal and Pharmaceutical Chemistry.

**Lec Title: Electronic structure of atoms:(part six)**

**Coordination compounds and complexation :**

**Coordination chemistry which involving metallic elements , its largely transition metal chemistry, but also involves metals beyond the second period out side the transition series to some extent. immediately also can form a stable coordination compounds.**

In these compounds the metallic cation appears to be able to bond with additional anions or molecules after the normal valence requirements have been satisfied .

**The additional bonding species are usually termed ligands and appear to bond directly to metal cation in accordance with maximum coordination number Table(1). The number is a property of metal and its charge.**

●Table(1).

Metal cation	Its coordination no.	Metal cation	Its maximum coordination no
$\text{Cr}^{3+}$	6	$\text{Pt}^{2+}$	4
$\text{Mo}^{3+}$	8	$\text{Cu}^+$	2
$\text{Mn}^{3+}$	6	$\text{Cu}^{2+}$	4
$\text{Fe}^{2+}$	6	$\text{Ag}^+$	2
$\text{Fe}^{3+}$	6	$\text{Au}^+$	2
$\text{Co}^{3+}$	6	$\text{Au}^{3+}$	6
$\text{Ni}^{3+}$	6	$\text{Zn}^{2+}$	4
$\text{Ni}^{2+}$	4	$\text{Cd}^{2+}$	4
$\text{Pd}^{4+}$	6	$\text{Hg}^{2+}$	4
$\text{Pd}^{2+}$	4	$\text{Al}^{3+}$	6
$\text{Pt}^{4+}$	6		

The ligands occupy space about the metal this space is known as coordination sphere.

The ligands may be displaced by other ligands but don't normally dissociate (ionize) from the metal.



**The metal and its associated ligands constitute what is called complex ion ,if its charged the neutral complex or the complex ion with its counter ions known as a coordination compound.**

**Some complexes are stable in  
crystalline form and  
decompose in solution ,while  
other are stable only in  
solution**

The most accepted theory of the formation of complex ions was proposed by **Alfred Werner** a Swiss chemist who devoted twenty years of his life to studying them, an effort which earned him the Nobel Prize in chemistry. The main points of **Werner's theory** are :

(1) The two types of valency are observed for the metals. One is the primary (ionizable) or principal valence, and the other is the secondary (non ionizable) valence.

(2) Each metal exhibits a specific maximum number of secondary valences called the coordination numbers table(1)

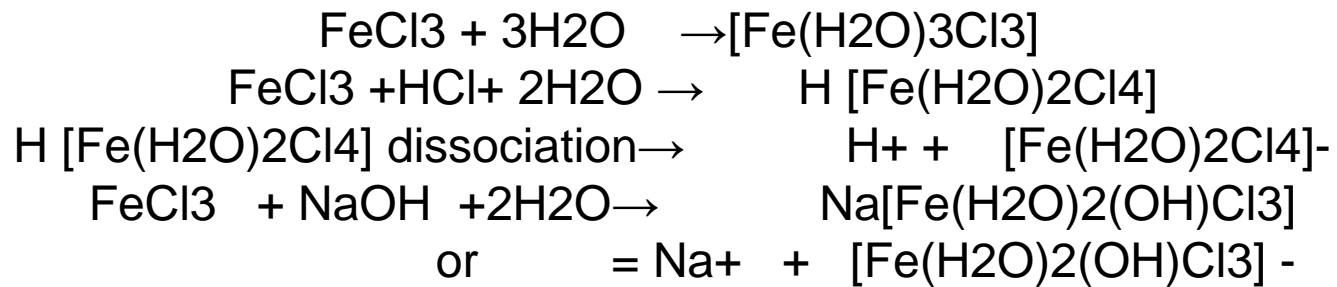
(3) The primary valences of a metal are filled by anions, but the secondary valences (in the coordination sphere) may be satisfied by anions and or neutral molecules and very rarely cation groups.

(4) the ligands are arranged around metallic ion in certain characteristic geometrics as in table (2) .

Maximum coordination number	geometry
2	Linear or angular
3	Trigonal and coplanar
4	Tetrahedral or square-planar
5	Square -pyramidal or trigonal - bipyramidal
6	octahral

Example:  $\text{FeCl}_3$ , a simple trivalent iron(III) and chlorine.

When this compound is dissolved in water and/ or in HCl, the following coordination compounds are formed.





The most stable complexes are formed by the cations of transition series and particularly the transition elements in group VIII (Ni, Pd, Pt). The groups immediately preceding and following in groups VIB (Cr), VIIB (Mn), IIB (Zn, Cd, Hg), IB (Cu) and IIIA (B, Al, Ga) also formed stable coordination compounds

For maximal stability of the metal in a complex the following criteria should be found :

- 1-high positive charge
- 2-a small cationic radius
- 3-un occupied d orbitals

## **Properties of ligands.**

The ligand species in complexes are generally anion or neutral compounds or molecules. Neutral atoms are not usually found as coordination agents.

Also they should have at least one non bonded pair of electrons which is used to form a coordinate covalent bond with the metal ion.

The more stable complexes are formed with anionic or molecular ligands involving the elements of Groups VA, VIA or VIIA.

The order of stability of a ligand in a complex follows the order of basicity of the ligand

TABLE 1-8. COMPLEXING LIGANDS

<i>Neutral Ligands</i>			<i>Anionic Ligands</i>	
decreasing stability ↓	NH <sub>3</sub>	H <sub>2</sub> O	R <sub>3</sub> As	CN <sup>-</sup>
	NH <sub>2</sub> R	HOR	R <sub>3</sub> P	S <sub>2</sub> O <sub>3</sub> <sup>-2</sup>
	NHR <sub>2</sub>	ROR	R <sub>2</sub> S	F <sup>-</sup>
	NR <sub>2</sub>	RCOR	PX <sub>3</sub>	OH <sup>-</sup>
	RCHO		Cl <sup>-</sup>	
			Br <sup>-</sup>	
			I <sup>-</sup>	

decreasing stability  
↓

R = Alkyl or aryl radical; X = halogen.

According to the numbers of pairs to be donated the ligands are of many type :

1- unidentate one coordinate covalent bond (one pair of elements eg.  $\text{NH}_3$  ,  $\text{H}_2\text{O}$ ).

2-bidentate ligands have two positions arranged so that they both can act as donor sites in a complex. Eg ethyl diamine (en)  $\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{NH}_2$ ) glycinate (y)  $\text{H}_2\text{N}-\text{CH}_2\text{COO}^-$  and the Anion of 8-hydroxy-quinoline (oxinate) other polydentate ligands are similarly classified as bidentate, tridentate, tetradentate, pentadentate and hexadentate.

Hexadentate ligand ethylene  
diamine.EDTA .

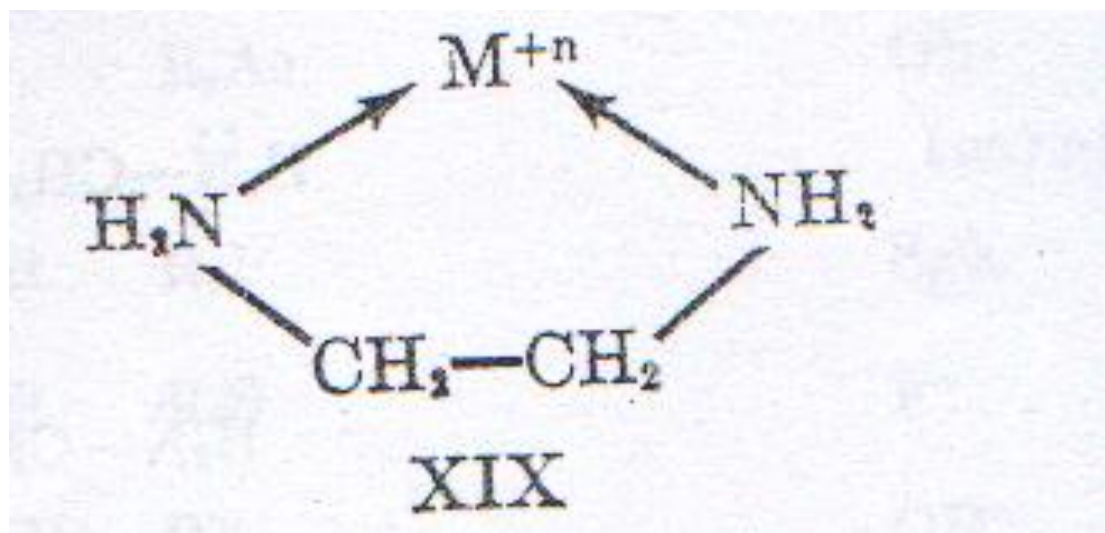
Octadentate ligand eg. Diethylene tri  
amine-penta acetate DTPA.

When poly ligand complex a metal ion a  
ring structure is produced composed of  
the metal and ligand molecule.

These ring structure is named chelates  
from the Greek word *chele* ,meaning  
(المخالب).claw(



The more stable chelates are those where the total number of atoms in the ring including the metal are five, six or seven. Four and eight-member rings are usually unstable



The process of chelation is employed in pharmaceuticals and in drug therapy.

They poly dentate ligand used for chelates formation are generally referred as chelating agents.

The term sequestering agent is usually applied when polydentate ligand used to prove the solubility and or to stabilize a metal ion by chelation( sequestration) .

## **Bonding in complex:**

There are several approaches to a discussion of bonding in metal complexes, none of which is entirely satisfactory in explaining all the properties of these compounds

*Pauling* developed a valence bond theory which is a useful qualitative picture of bonding in coordination compounds.

A round the same time that this theory was introduced (late 1920s to early 1930s), *Bethe and Van Vleck* independently introduced an electrostatic approach called *crystal field theory*

The other is *molecular orbital theory* which probably offers the most complete qualitative and quantitative picture of bonding. But has many computational problems (المشاكل الحسابية). Only two of two orbitals are oriented along the axes of Cartesian system  $[(dx^2-y^2)]$  and  $dz^2$ .

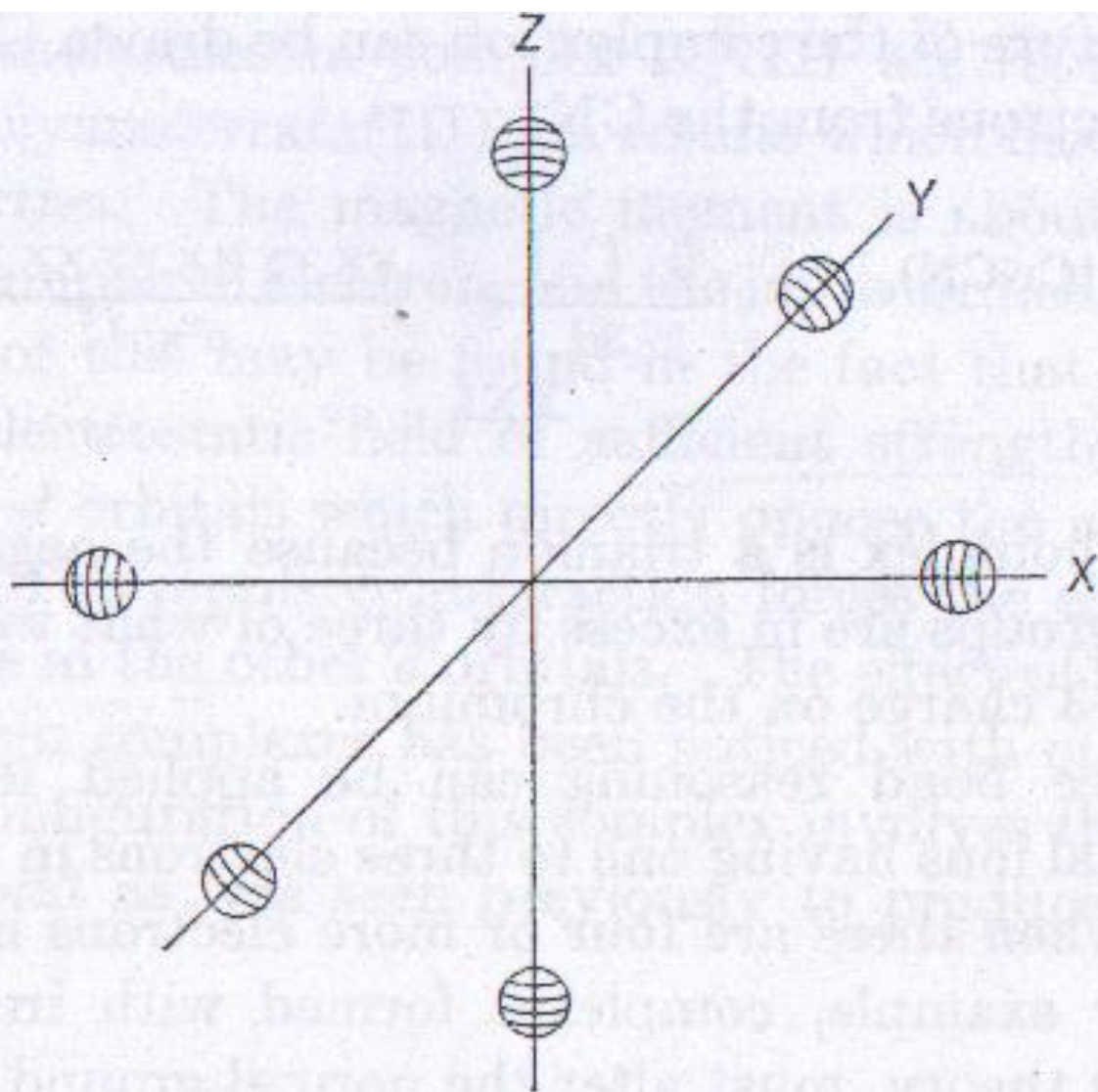


FIG. 1-6. Six ligands organized on the axes of a three-dimensional cartesian coordinate system.

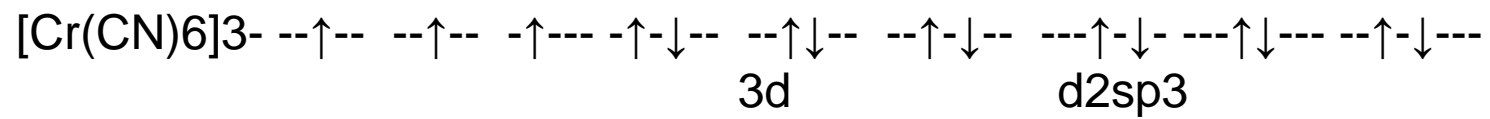
The other d orbitals are directed  
between the axes.

Its generally accepted that the  
( $n-1$ )d, ns and np orbitals are  
close enough in energy to  
become hybridized in to six  
bonding orbitals along the same  
axes occupied by the ligands.





These electrons are unpaired and these occupy the three off-axis d orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ). Thus leaving 2d orbitals, one s, and the three p orbitals empty for bonding with six cyanato groups



*Bidentate Ligands*

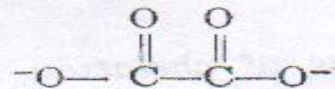
Ethylenediamine (en)



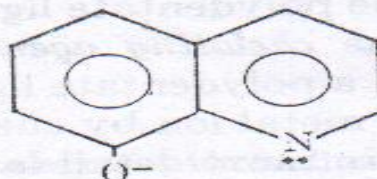
Glycinate (gly)



Oxalate



Anion of 8-hydroxy-quinoline (oxinate)



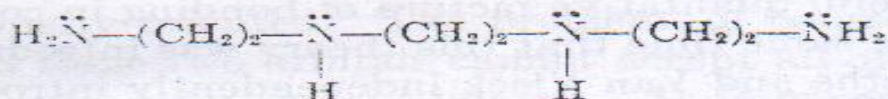
*Tridentate Ligand*

Diethylenetriamine (den)



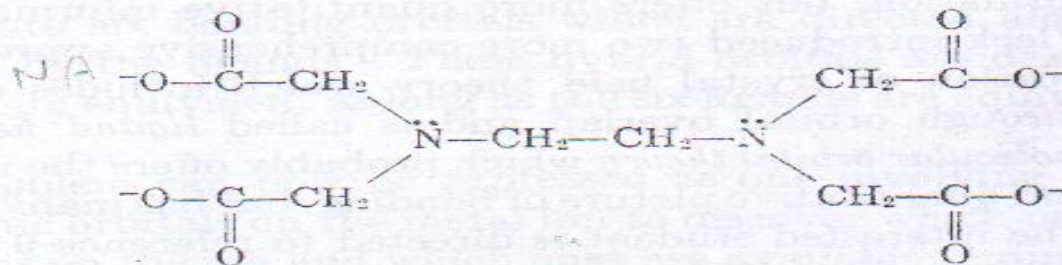
*Tetradentate Ligand*

Triethylenetetramine (trien)



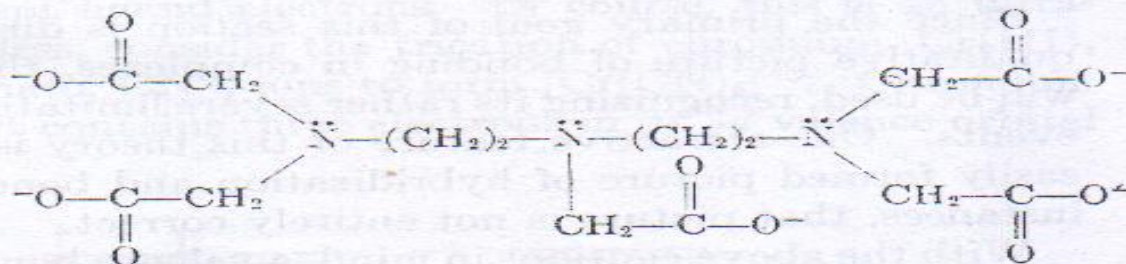
*Hexadentate Ligand*

Ethylenediamine-tetraacetate (EDTA)



*Octadentate Ligand*

Diethylenetriamine-pentaacetate (DTPA)



## **Four or more electrons in d orbitals :**

Similar valence bond reasoning can be applied to other complexes formed with metal ions having one to three electrons in their d orbitals a problem arises when there are four or more electrons in these orbitals on the metals

Complexes formed with Iron(III) which is (a  $d^5$  ion). according to this theory, We must change the normal ground state arrangement of the electrons; we use different orbitals for bonding, or bond in anoncovalent manner.

If the electron configuration on the metal is changed it could be measured experimentally by determine the magnetic moment of the complex.

Magnetic moment is a measured of ( unpaired ness )of electrons in that un paired of electrons are attached to magnetic field (paramagnetic).

And Paired electrons are  
repelled by magnetic field  
(diamagnetic)

Now the electron structure of  
the valence shell of iron(III) is  
shown



$\mu_{\text{eff}}$  values for typical  $d^3$  and  $d^5$  transition metal complexes. [\[5\]](#)

<b>Material</b>	<b><math>\mu_{\text{eff}}/\mu_{\text{B}}</math></b>
$[\text{Cr}(\text{NH}_3)_6]\text{Br}_3$	3.77
$\text{K}_3[\text{Cr}(\text{CN})_6]$	3.87
$\text{K}_3[\text{MoCl}_6]$	3.79
$\text{K}_4[\text{V}(\text{CN})_6]$	3.78
$[\text{Mn}(\text{NH}_3)_6]\text{Cl}_2$	5.92
$(\text{NH}_4)_2[\text{Mn}(\text{SO}_4)_2] \cdot 6\text{H}_2\text{O}$	5.92
$\text{NH}_4[\text{Fe}(\text{SO}_4)_2] \cdot 12\text{H}_2\text{O}$	5.89



When complexed with water molecules the hexaquoiron (III) ion is formed and has the same magnetic properties as would be expected from electronic structure shown above.

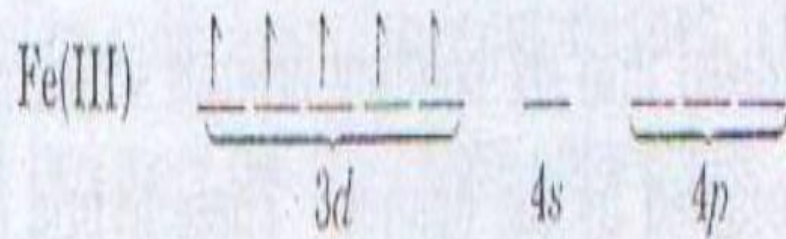
The magnetic moment is **5.9** (Bohr magnetons) which is consistent with five unpaired electrons.

This is general referred to as *a high-spin complex* because the electrons are unpaired as much as possible.

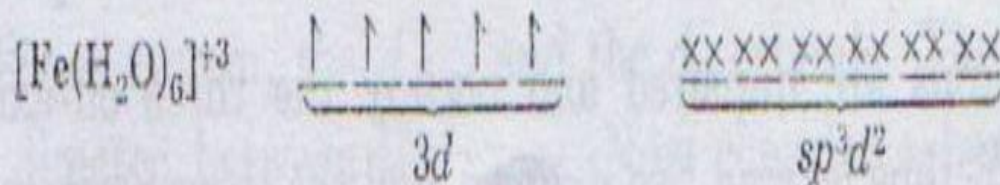
Within the framework of valance bond

The problem of finding six empty atomic orbitals to overlap with the donor water molecules can be accomplished by assuming that the 4d orbitals are of appropriate energy to hybridize with 4s and 4p orbitals.

Hybridization of this type is termed outer orbital hybridization, provides six octahedral arranged hybrids designated  $sp^3d^2$



XXII



XXIII

If the water molecules in complex XXIII are replaced with cyanato groups, the hexacyanoferrate (III) is the result which has distinctly different magnetic properties.

The magnetic moment is about 2B.M., which is indicative of one unpaired electron, and the ion is termed a *low-spin complex*.

An explanation of this may be found in the fact that the cyanato anion has a negative electrostatic field of sufficient strength to repel the electrons in the two d orbitals which directly oppose the approaching ligands ( $d_{x^2-y^2}$  and  $d_{z^2}$ )

The repulsive interaction forces the electrons to become paired with those in the other d orbitals.

The effect of strong field ligands producing low-spin complexes has been noticed with the other metals as well.

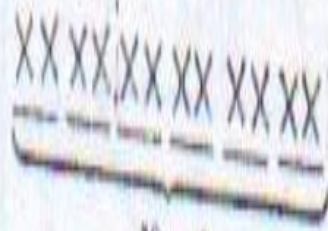


The electron configuration of this complex involves the 3d orbitals in an inner orbital as was seen previously to produce the valence bond picture.  $[\text{Fe}(\text{CN})_6]^{-3}$



3d

XXIV

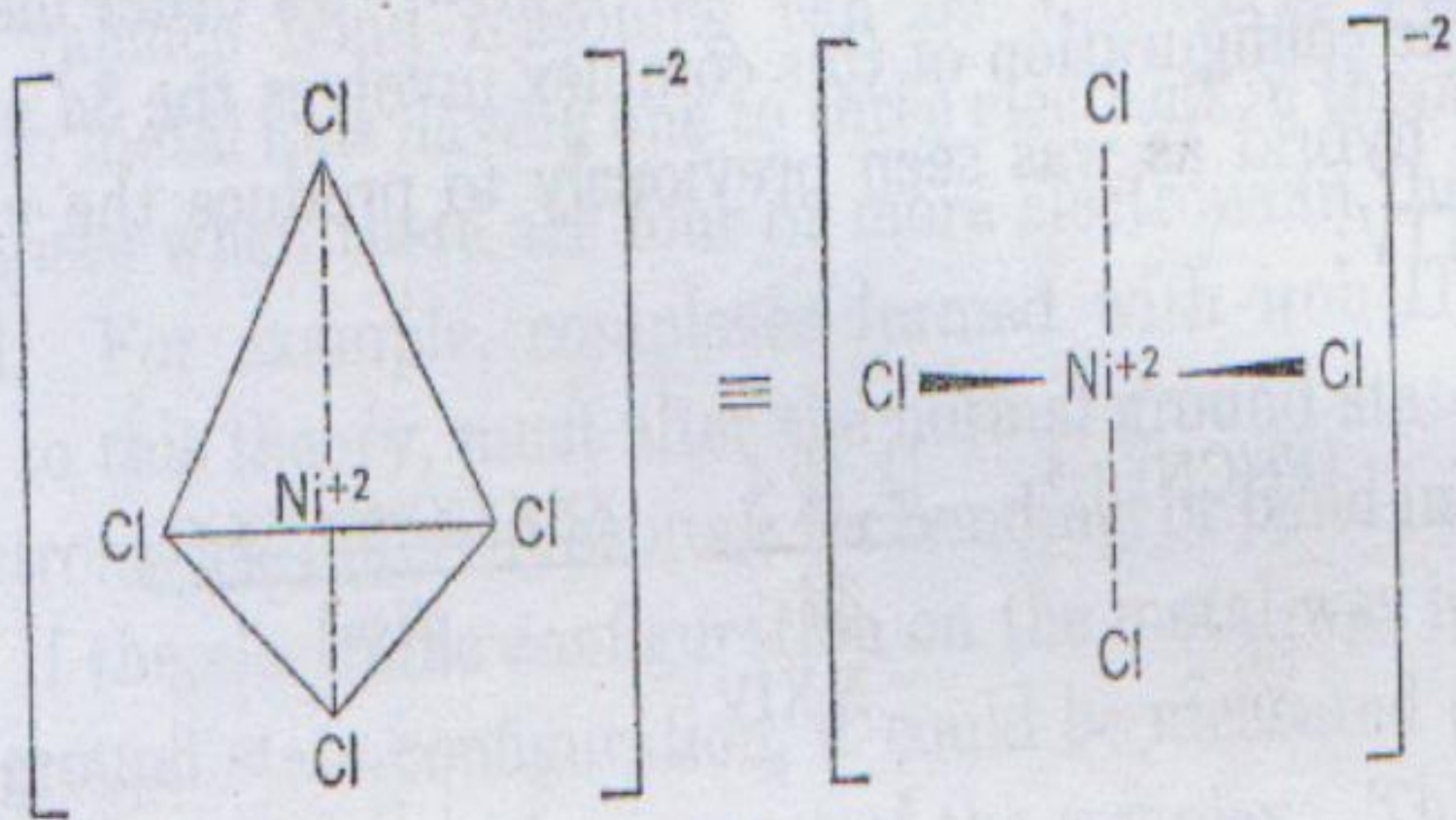


$d^2sp^3$

Metal ions with seven, eight or nine d electrons general have a coordination number of 4 which lead to either square planar or a tetrahedral arrangement of ligands. The field strength of ligand and the formation of high and low-spin complexes may be predictive of the type of hybridization and geometry of complex .

For example  $N_2^+$  which is a d 8 ion complexing with ligand having a relatively weak electrostatic field has no d orbitals available for bonding.

However, The ligand bond through  $sp^3$  hybrids formed on the metal to give a **tetrahedral** complex .

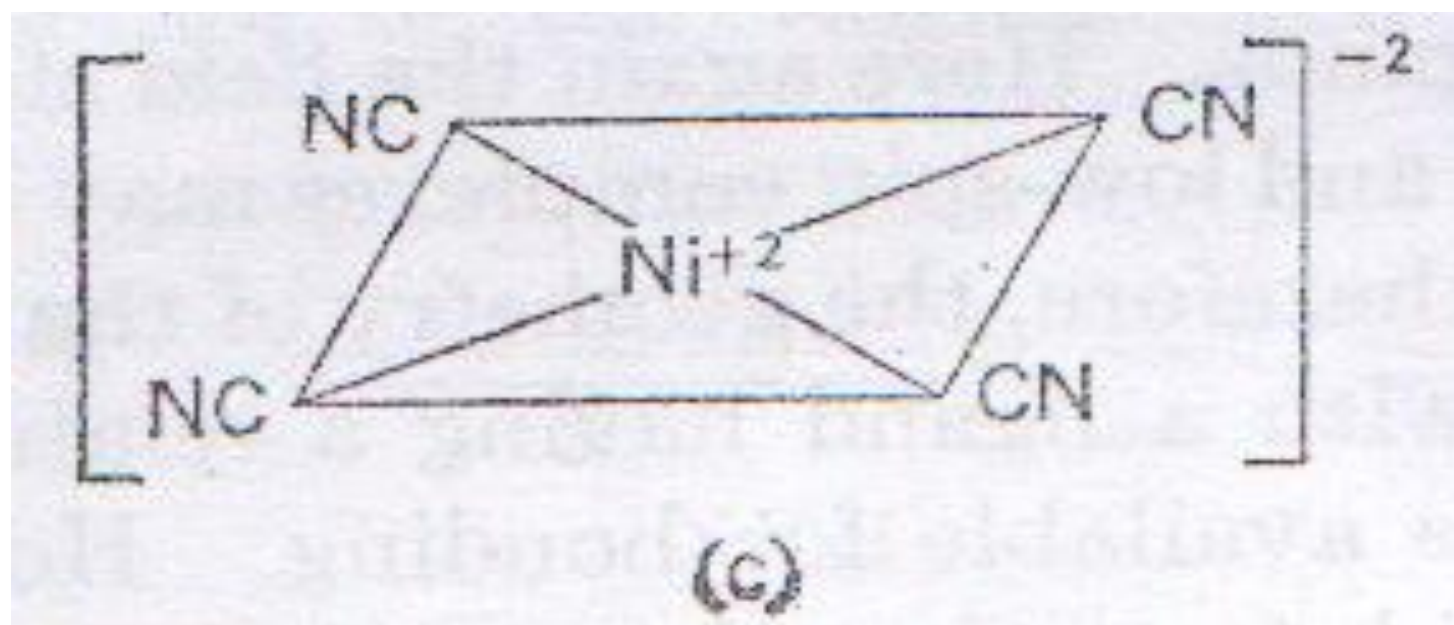


(b)

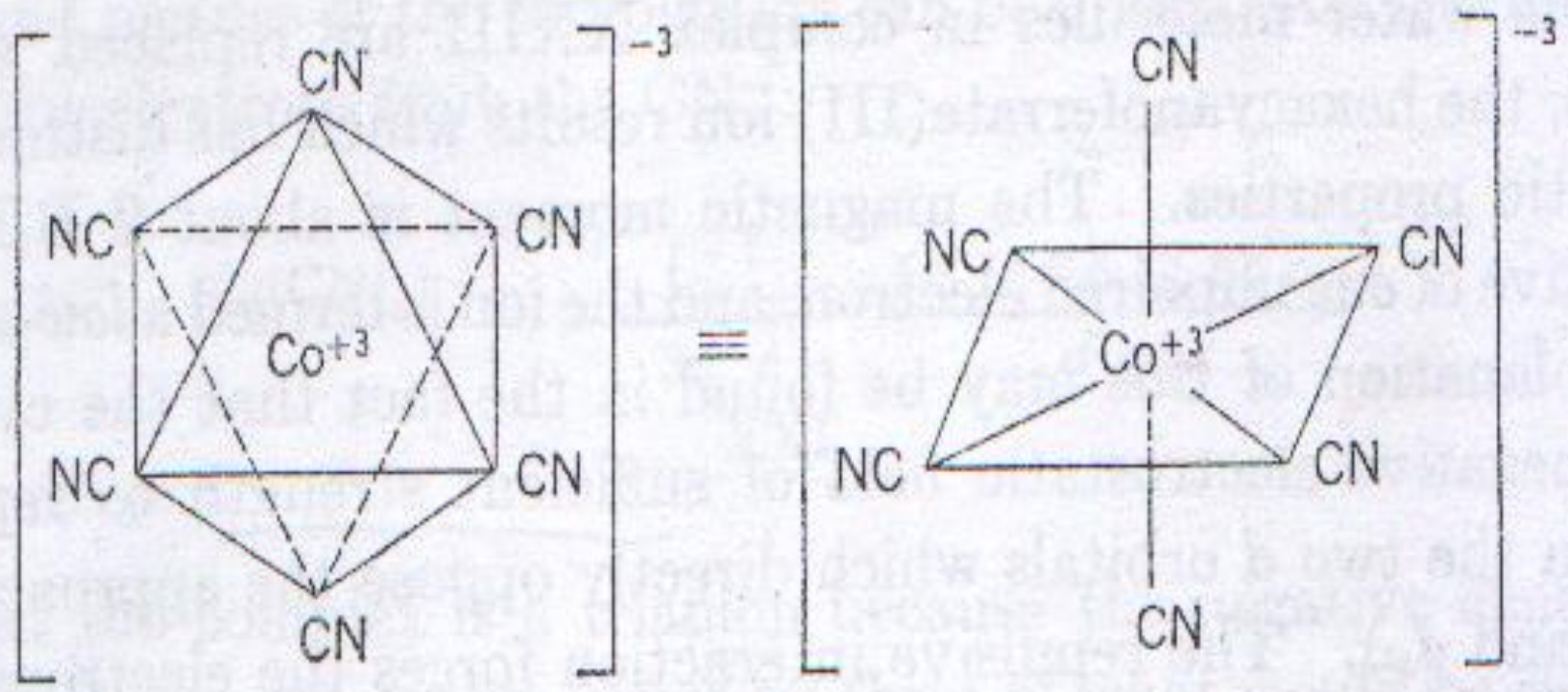
If the ligand field strength is sufficient to force the metal into a low-spin diamagnetic state.

So only one d orbital would be vacant and could be used to form a square planar  $dsp^2$  hybrid. Both of these geometries are illustrated in fig.1-7b and 1-7c, respectively. The valence bond theory approach to bonding and the use of magnetic criteria to predict hybridization and geometry are not successful in many cases.

One of the more comprehensive theories (e.g., ligand field or molecule orbital) would actually give a more theoretically satisfying account of bonding.







(a)

↓ Decreased stability	Neutral ligands	anionic ligands	↓ Decreased stability
	NH <sub>3</sub> , H <sub>2</sub> O, R <sub>3</sub> As	CN <sup>-</sup>	
	NH <sub>2</sub> R, HOR, R <sub>3</sub> P	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	
↓	NHR <sup>2</sup> , ROR, R <sub>2</sub> S	F <sup>-</sup>	↓
	NR <sub>3</sub> , RCOR, PX <sub>3</sub>	OH <sup>-</sup>	
	RCHO	Cl <sup>-</sup>	
		Br <sup>-</sup>	
		I <sup>-</sup>	

R alkyl or aryl radical x halogen.