

**Kurdistan region-Iraq
University of Salahaddine
College of Science
Chemistry Department**



Coordinate Bond Theories of Coordination Compounds

**Third stage Chemistry
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Double Salt vs Coordination Compound

A double salt is a crystalline salt having the composition of a mixture of two simple salts but with a different crystal structure from either. Coordination compounds are complex structures composed of a central metal ion surrounded by molecules or ions known as ligands.

1-Composition:

A double salt contains two types of salt compounds crystallized in the same ionic lattice. A coordination compound contains a metal ion surrounded by ligands bonded to that metal ion via coordinate covalent bonds.

2-chemical Bonding:

Double salts contain ionic bonds between cations and anions. Coordinate compounds contain coordinate covalent bonds between metal ion and ligands.

3-Solubility:

When dissolved in water, double salts are dissociated into ionic species. Coordination compounds are soluble compounds and are not separated into ionic species.

Types of Coordination Complexes

1-Cationic complexes: In this co-ordination sphere is a cation. Example: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

2-Anionic complexes: In this co-ordination sphere is anion. Example: $\text{K}_4[\text{Fe}(\text{CN})_6]$

3-Neutral Complexes: In this co-ordination sphere is neither cation or anion.

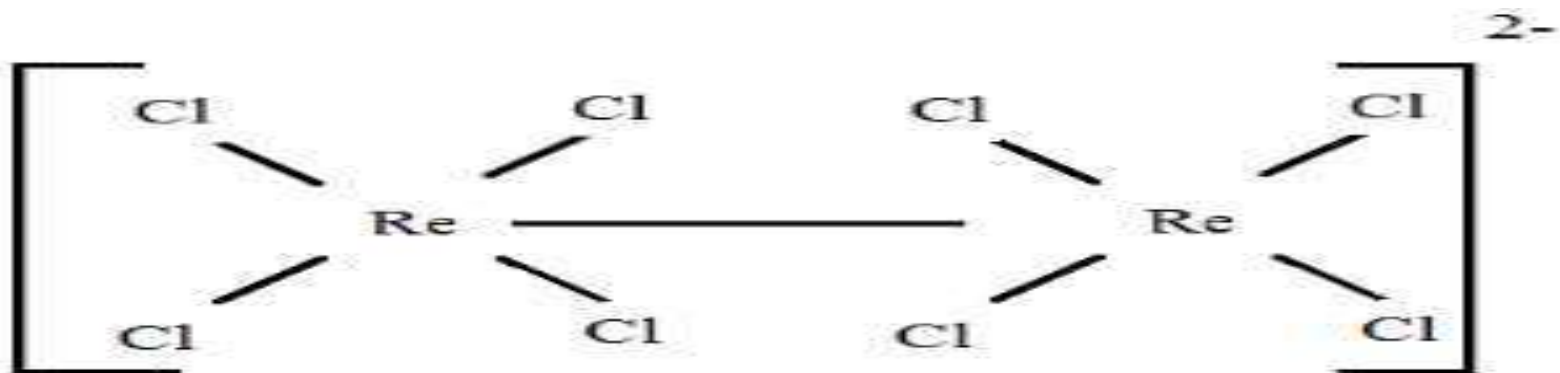
Example: $[\text{Ni}(\text{CO})_4]$

4-Homoleptic complexes: The complex consists of a similar type of ligands. Example: $\text{K}_4[\text{Fe}(\text{CN})_6]$

5-Heteroleptic complexes: These consist of different types of ligands. Example: $[\text{CoCl}(\text{NH}_3)_5]\text{SO}_4$

6-Mononuclear complexes: In this co-ordination sphere has single transition metal ion. Example: $\text{K}_4[\text{Fe}(\text{CN})_6]$

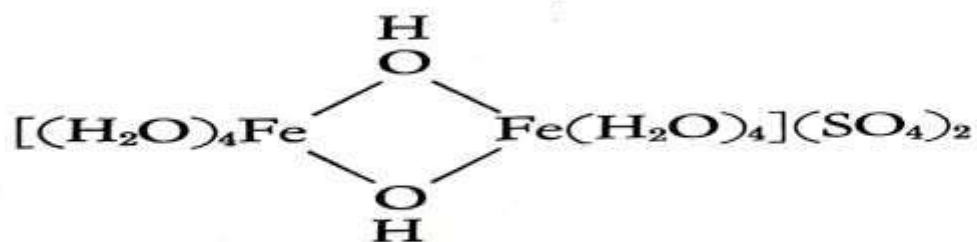
7-Polynuclear complexes: More than one transition metal ion is present. Example:



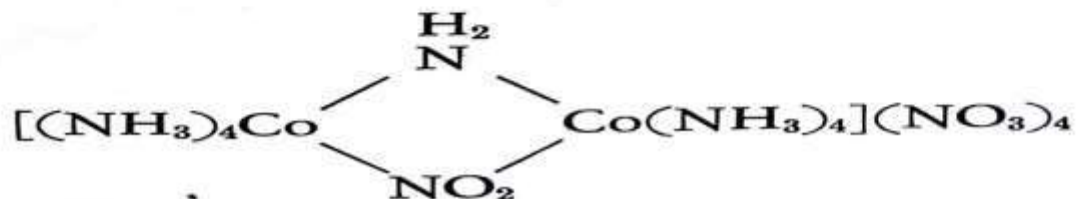
Polynuclear complexes

Bridging Groups

Ligands that bridge two centers of coordination are preceded by the Greek letter μ , which is repeated before the name of each different kind of bridging group.



octaaquo- μ - μ -dihydroxo-
diiron(III) sulfate



octaammine- μ -amido-
 μ -nitrodicobalt(III)
nitrate

Oxidation Numbers



Knowing the charge on a complex ion and the charge on each ligand, one can determine the oxidation number for the metal or knowing the oxidation number on the metal and the charges on the ligands, one can calculate the charge on the complex ion.

Example: $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$

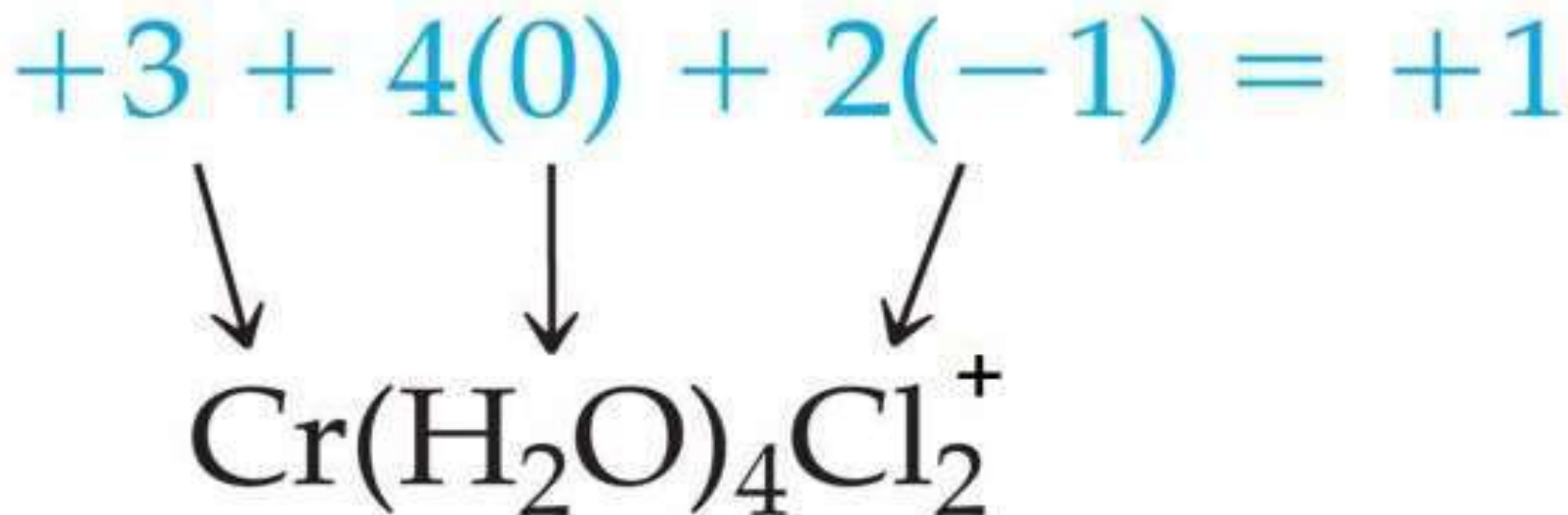


Table :Some Common Ligands in Coordination Compounds

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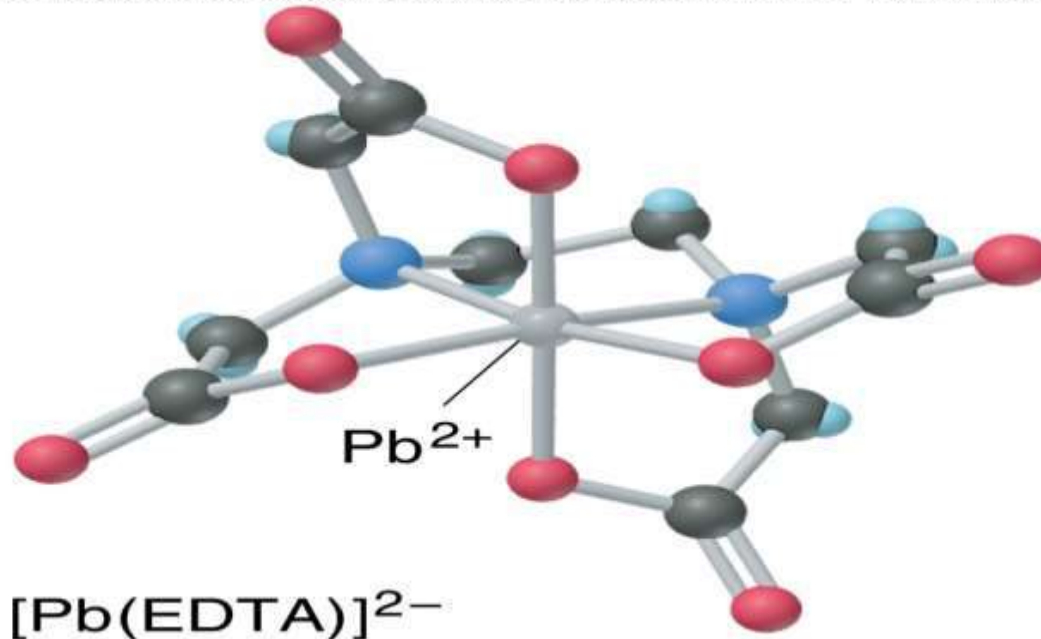
Ligand Type	Examples
Monodentate	$\text{H}_2\ddot{\text{O}}:$ water $:\ddot{\text{F}}:^-$ fluoride ion $:\text{C}\equiv\text{N:}^-$ cyanide ion $:\ddot{\text{O}}-\text{H}^-$ hydroxide ion $:\text{NH}_3$ ammonia $:\ddot{\text{Cl}}:^-$ chloride ion $[\text{:}\ddot{\text{S}}=\text{C}=\ddot{\text{N}}:]^-$ thiocyanate ion $[\text{:}\ddot{\text{O}}-\text{N}=\ddot{\text{O}}:]^-$ nitrite ion <div style="margin-left: 150px;"> or </div>
Bidentate	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ \quad \\ \text{H}_2\text{N} \quad \text{NH}_2 \end{array}$ ethylenediamine (en) $\left[\begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \text{ } \\ \text{C} \\ \text{ } \\ \text{:}\ddot{\text{O}}\text{:} \end{array} - \begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \text{ } \\ \text{C} \\ \text{ } \\ \text{:}\ddot{\text{O}}\text{:} \end{array} \right]^{2-}$ oxalate ion
Polydentate	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2 \\ \quad \quad \\ \text{H}_2\text{N} \quad \text{NH} \quad \text{NH}_2 \end{array}$ diethylenetriamine $\left[\begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \text{ } \\ \text{:}\ddot{\text{O}}-\text{P}-\ddot{\text{O}}-\text{P}-\ddot{\text{O}}-\text{P}-\ddot{\text{O}}\text{:} \\ \text{ } \quad \text{ } \quad \text{ } \\ \text{:}\ddot{\text{O}}\text{:} \quad \text{:}\ddot{\text{O}}\text{:} \quad \text{:}\ddot{\text{O}}\text{:} \end{array} \right]^{5-}$ triphosphate ion $\left[\begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \text{ } \\ \text{:}\ddot{\text{O}}-\text{C}-\text{CH}_2 \\ \text{ } \\ \text{:}\ddot{\text{O}}\text{:} \end{array} - \text{CH}_2 - \text{CH}_2 - \begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \text{ } \\ \text{CH}_2-\text{C}-\ddot{\text{O}}\text{:} \\ \text{ } \\ \text{:}\ddot{\text{O}}\text{:} \end{array} \right]^{4-}$ ethylenediaminetetraacetate ion (EDTA ⁴⁻)

Chelates

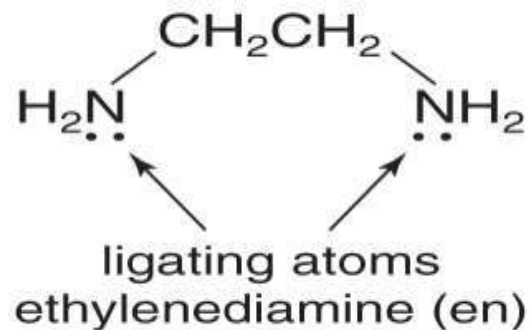
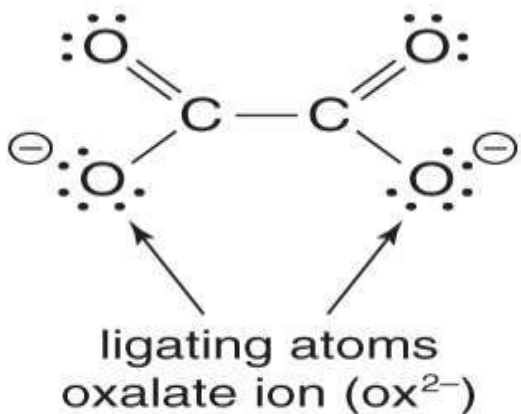
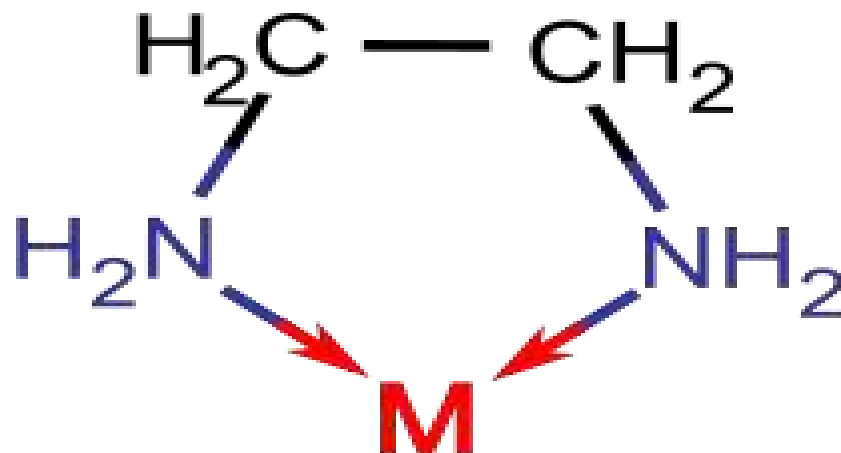
Bidentate and polydentate ligands give rise to rings in the complex ion.

A complex ion containing this type of structure is called a **chelate because the ligand seems to grab the metal ion like claws.**

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When a **bidentate ligand** binds to a metal.



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NOTE: Chelate effect

metal complexes of polydentate ligands are **more stable** than complexes of chemically similar **monodentate ligands**.

22. The most stable ion is:



Example

Write the formulas for the following coordination compounds:

- (a) Tetraammineaquachloridocobalt(III) chloride
- (b) Potassium tetrahydroxidozincate(II)
- (c) Potassium trioxalatoaluminate(III)
- (d) Dichloridobis(ethane-1,2-diamine)cobalt(III)
- (e) Tetracarbonylnickel(0)

Solution

- (a) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$
- (b) $\text{K}_2[\text{Zn}(\text{OH})_4]$
- (c) $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$
- (d) $[\text{CoCl}_2(\text{en})_2]^+$
- (e) $[\text{Ni}(\text{CO})_4]$

Example

Write the IUPAC names of the following coordination compounds:

- (a) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$
- (b) $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$
- (c) $[\text{CoCl}_2(\text{en})_2]\text{Cl}$
- (d) $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$
- (e) $\text{Hg}[\text{Co}(\text{SCN})_4]$

Solution

- (a) Diamminechloridonitrito-N-platinum(II)
- (b) Potassium trioxalatochromate(III)
- (c) Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
- (d) Pentaamminecarbonatocobalt(III) chloride
- (e) Mercury (I) tetrathiocyanatocobaltate(III)

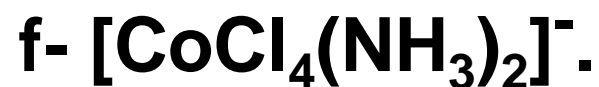
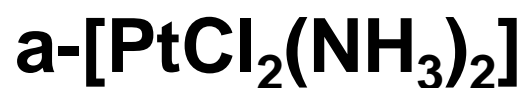
Problems:

- (a) What is the systematic name of $\text{Na}_3[\text{AlF}_6]$?
- (b) What is the systematic name of $[\text{CoCl}_2(\text{en})_2]\text{NO}_3$?
- (c) What is the formula of tetraammine bromo chloroplatinum(IV) chloride?
- (d) What is the formula of hexaamminecobalt(III) hexachloroferrate(III)?
- (e) What is the systematic name of $\text{Li}[\text{AlH}_4]$?
- (f) What is the systematic name of $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$?

1-Give the chemical formula for Hexaaquanickel(II) aquapentabromochromate(III).

2-Give the name for $[\text{Co}(\text{NH}_3)_6][\text{CoCl}_6]$.

3-Practice naming some complex compounds:



Practice writing the complex compound formulas:

1-Hexaaquochromium(III) chloride.

2-Ammonium diaquatetrachloroaurate(III).

3-Potassium hexacyanoferrate(II).

4-Potassium hexacyanoferrate(III).

5-Lithium tetrahydrido aluminate(III).

6-Sodium hexanitrito Cobaltate(III).

7-Potassium tetracyanoaurate(II) ion .

Clicker Qstn:

the correct name for the complex $\text{Na}_2[\text{Ni}(\text{CN})_4]$

- A. Disodium tetranickelcyanide.
- B. Sodium tetracyanidenickel(I).
- C. Disodium tetracyanonickelo(IV).
- D. Natrium tetranickel(VI)cyanide.
- E. Sodium tetracyanonickelate(II).



In these compounds,
silver is _____.

NH_3 is _____.

and Cl^- or NO_3^- is _____.

C.N. is _____.

Ligands are attached by _____ bonds.

Counterions are attached by _____ bonds.

36. In which of the following compounds, transition metal may have zero oxidation state?



16. Which of the following is a tridentate ligand?



(b) Oxalate ion

(c) Glycinate ion

(d) Dien

34. Which has maximum coordinating (donor) points?

(a) DMG

(b) EDTA

(c) en

(d) py

53. Coordination number of Ni in $[\text{Ni}(\text{C}_2\text{O}_4)_3]^{4-}$ is:

(a) 3

(b) 6

(c) 4

(d) 5

1. Ligand with two or more points of attachment to single metal atoms are called:
- (a) Monodentate ligand
 - (b) Chelating ligand
 - (c) Ambidentate ligand
 - (d) None of these
3. Select the correct I.U.P.A.C. name for $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$:
- (a) Tetraamminecopper(II) tetrachloridoplatinum(II)
 - (b) Tetraamminecopper(II) tetrachloridoplatinum(IV)
 - (c) Tetraamminecopper(II) tetrachloridoplatinate(II)
 - (d) Tetraamminecuprate(II) tetrachloridoplatinate(II)
2. Select the correct I.U.P.A.C. name for $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$ complex:
- (a) Triamminetrichloridochromate(III)
 - (b) Triamminetrichloridochromium(III)
 - (c) Trichloridotriamminechromium(III)
 - (d) Trichloridotriamminechromate(III)

Three theories were used to describe the nature of the bonding in metal complexes, these are :

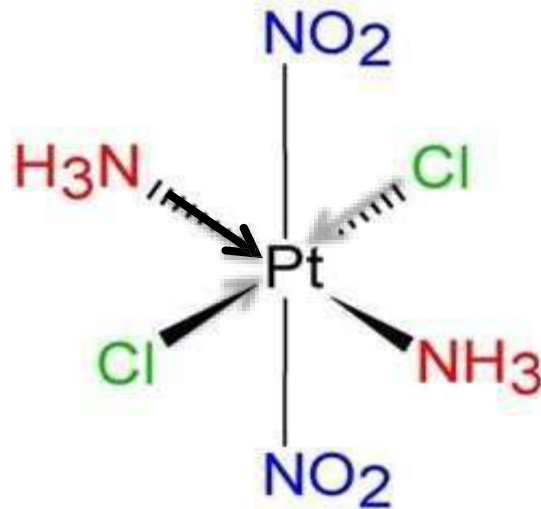
- **Valence Bond Theory (VBT).**
- **Crystal Field Theory (CFT).**
- **Molecular Orbital Theory (MOT).**

Firstly we shall describe the contribution of G.N. Lewis and N.V.Sidgwick to the theory of chemical bonding.

- Sidgwick in 1927 extended the Lewis theory of electron pair bond formation to explain the bonding in coordination compounds.
- He suggested that metal ion accepts electron pairs from the ligands until it achieves the next noble gas configuration.
- This is called EFFECTIVE ATOMIC NUMBER RULE. The total number of electrons possessed by the central metal ion and the electrons gained by it from ligands is called the EFFECTIVE ATOMIC NUMBER (EAN).

Sidgwick's electronic theory

- **The ligand donate the electron pair to the central metal ion and thus form a number of coordinate bond.**



EAN rule (Effective Atomic Number)

Sidgwick postulated that the central metal would surround itself with sufficient ligands that the total number of electrons around the metal would be the same as that in a rare gases:

He	Ne	Ar	Kr	Xe	Rn
2	10	18	36	54	86

$\text{EAN} = \text{No. of electrons on the metal} + \text{No. of electrons donated by surrounding ligands.}$

Effective atomic number (EAN)

- $EAN = Z - X + Y$

Where,

Z = atomic no. of the metal.

X = no. of electron lost during the formation of the metal ion from its atom.

Y = no. of electrons donated by the ligands.

**Eg. $[\text{Fe}(\text{CN})_6]^{4-}$, Fe oxidation = 2+ & Z = 26
= 26 - 2 + 6(2) = 36 it is similar to Kr.**

- The effective atomic number is derived from valence bond theory, where ligand coordination allows the metal center to reach a noble gas configuration through covalent bond formation.
- Complexes of the transition metals with π -acid ligands, as well as their organometallic complexes, generally obey the EAN rule.
 - The nd , $(n+1)s$ and $(n+1)p$ orbitals are all valence orbitals, and all their bonding capacity is used when the 18 electron configuration is reached.

Number of electrons donated to a Transition metal by some typical ligands:

1-Each ligand **donates 2 electrons** such as F^- , NO_2^- , CN^- , CH_3^- , Pph_3 ----- etc.

2-Free radical **donates only one electron**: **Ex.** $\text{R}\cdot$, $\text{Cl}\cdot$, $\text{C}_5\text{H}_5\cdot$

3- Each double bond **donates 2 electrons**
Ex. Carbenes $\text{R}_2\text{C}=\text{}$ **donates 2 electrons** , dienes **donate 4** and benzene **donates 6 electrons**.

4- Nitrosyl NO^+ and carbynes **donate 3 electrons**.

• Application of EAN rule :

- Ex¹: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ Calculated EAN of this complex
 - Atomic number of Co = 27 (Ar) $4s^2 3d^7$
 - $\text{Co}^{+3} = 27 - 3 = 24$
 - $6\text{NH}_3 = 2 \times 6 = 12$
- Then EAN = 36 This is similar to Kr = 36

Ex₂ : $[\text{Ag}(\text{NH}_3)_4]\text{Cl}$

Ag = 47

Ag⁺ = 47 - 1 = 46

- $4\text{NH}_3 = 2 \times 4 = 8$ EAN = 54 similar to Xe, This obey the rule.

Unfortunately this rule can not be applied on all complexes, Otherwise we could determine coordination number of the complexes by knowing (EAN) of the complex.

- however There are many exceptions to this rule :
- Only metal carbonyls and their derivatives are frequently does obey the EAN rule (some times Nitrosyl).
- For example :
- $[\text{Ni}(\text{CO})_4]$, $[\text{Fe}(\text{CO})_5]$, $[\text{Fe}(\text{CO})_4\text{Cl}_2]$ EAN for these complexes = 36
- For metals having odd number of electrons as Mn =25 and Co = 27
- $[\text{Mn}(\text{CO})_5]$ Mn =25 + 10 = 35 not obey the EAN rule.

Then it is possible to obey the rule by one of the following methods:

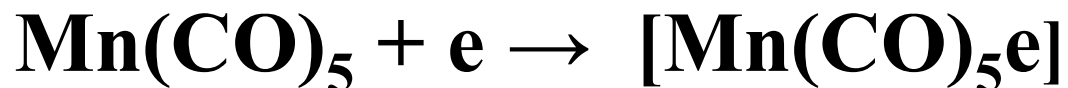
1-Dimerization:



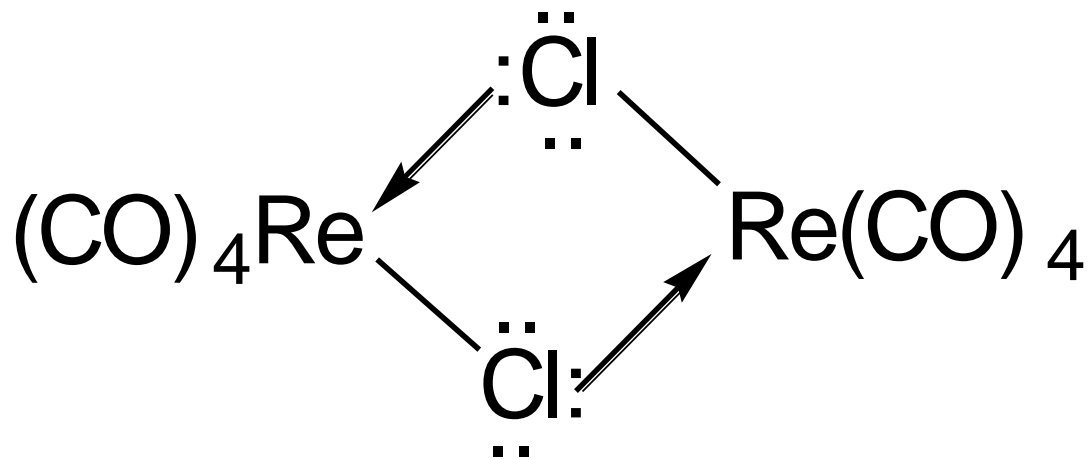
2-Addition of free radical such as $\text{Cl}\cdot$, $\text{CH}_3\cdot$:



3-Reduction :addition of an electron:



Ex3: Calculate EAN for the following complex.



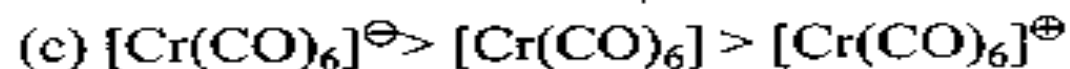
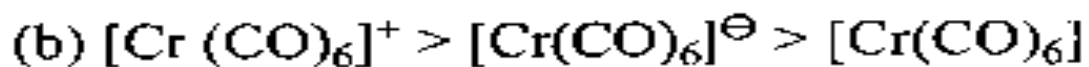
Re (75) (Xe) $4f^{14} 5d^5 6s^2$

For each Re atom:

Re⁺	6 electrons
4CO	8 electrons
2Cl	4electrons

EAN = 18 electrons

6. Select the correct order of E.A.N:



12. The number of ions produced by the complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ is:

(a) 2

(b) 3

(c) 4

(d) 6

13. The I.U.P.A.C. name for $[\text{Ni}(\text{CN})_4]^{2-}$ is:

(a) Tetracyanonickel (II) ion

(b) Tetracyanonickel (0) ion

(c) Tetracyanonickelate (II) ion

(d) Tetracyanonickelate (0) ion

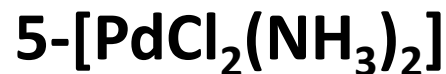
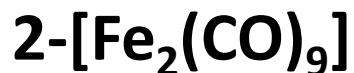
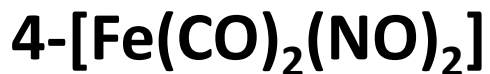
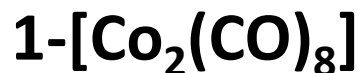
14. The I.U.P.A.C. name for $K_3[Co(NO_2)_6]$ is:
- (a) Potassium(I) hexanitrocobaltate (II)
 - (b) Potassium(I) hexanitrocobaltate (IV)
 - (c) Potassium hexanitrocobalt (0)
 - (d) Potassium hexanitrocobaltate (III)

62. The effective atomic number of cobalt in the complex $[Co(NH_3)_6]^{3+}$ is:

- (a) 36
- (b) 33
- (c) 24
- (d) 30

Calculate EAN for the following :

Which one obey the EAN rule ?



Limitations of Sedgwick theory

- ❑ Many complexes are stable but do not follow EAN rule.
- ❑ Theory doesn't predict the geometry of the complexes.
- ❑ Theory doesn't predict the magnetic behavior of the complexes.

Bonding in coordination compound

- 1. Valence bond theory(VBT).**
- 2. Crystal field theory(CFT).**
- 3. Ligand field theory(LFT).**
- 4. Molecular orbital theory(MOT).**

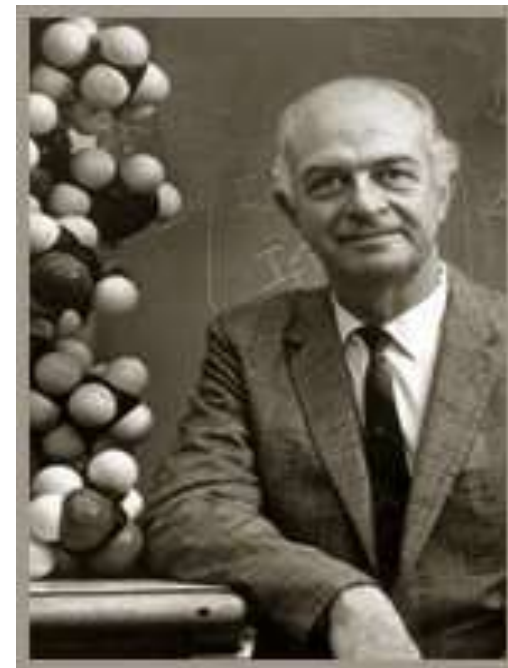
Valence Bond Theory

Basic Principles

1-Central metal provides number of vacant (empty) orbitals equal to its coordination number.

2-The coordinate covalent bond (σ -bond) between metal and ligand is results of overlap between empty orbitals of the metal and the filled (σ -orbital) of the ligand .

3- π -bond usually results from overlap between t_{2g} orbitals of the metal (d-orbital) and (p-orbital) of the ligand.



Linus Carl Pauling
(1901-1994)

Nobel prizes: 1954, 1962
Chemistry , Peace

1. Valence bond theory(VBT)

- **Linus Pauling 1931.**
- **The valence bond theory satisfactorily explains the structure and magnetic properties of a large number of coordination compounds.**

Salient features of the theory:

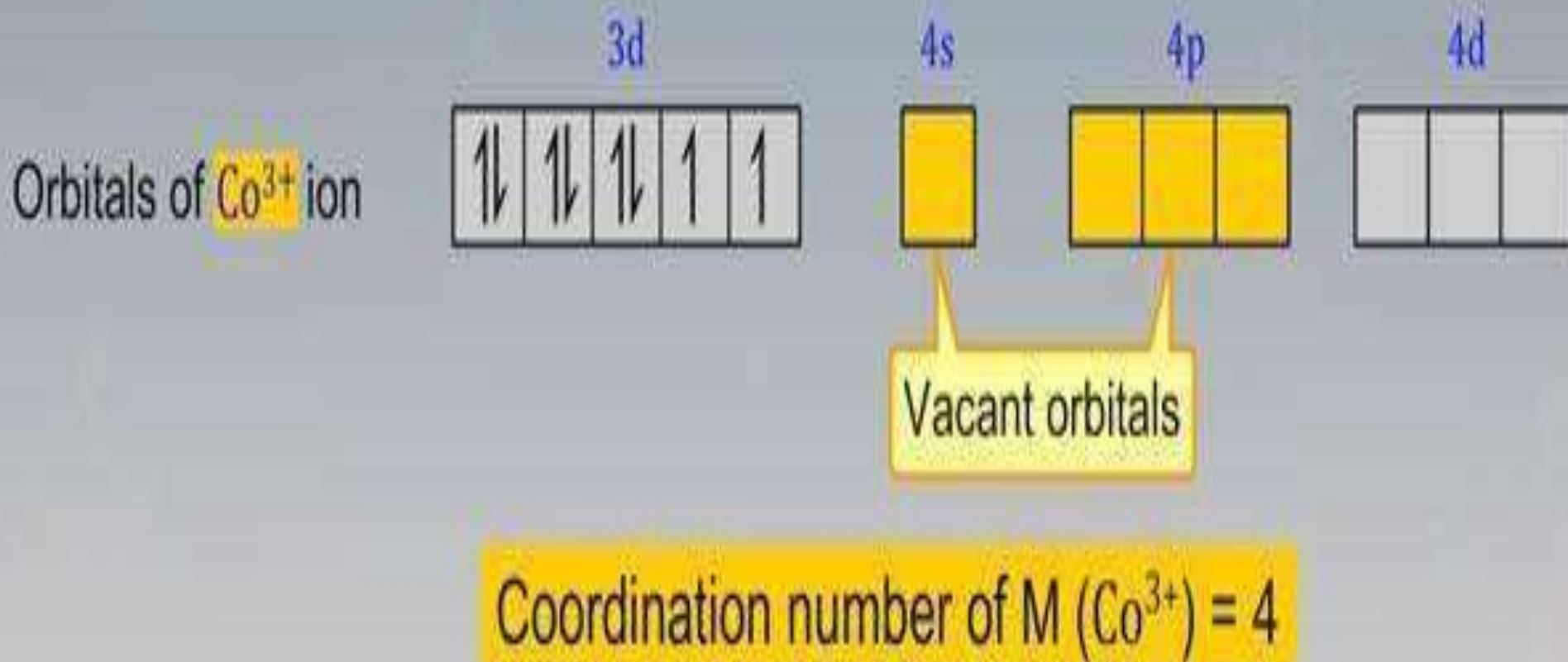
- **The central metal atom(or) ion has the required number of vacant orbitals for accommodating the electrons donated by the ligands. The number of vacant orbitals is equal to the coordination number of the metal ion for a particular complex.**

Vacant orbital s, p, d, f.

Salient features of the VBT theory

- This vacant orbital goes hybridization to form same no. of hybrid orbitals.
- Each ligand has at least one orbital containing lone pair of electrons.
- Vacant hybrid orbital filled with ligand to form coordination bond.
- Coordinate bond is stronger if the overlapping between the orbitals is greater.

- The vacant orbitals of the metal atom (or) ion undergo suitable hybridization to yield a set of equivalent hybrid orbitals of definite geometry.



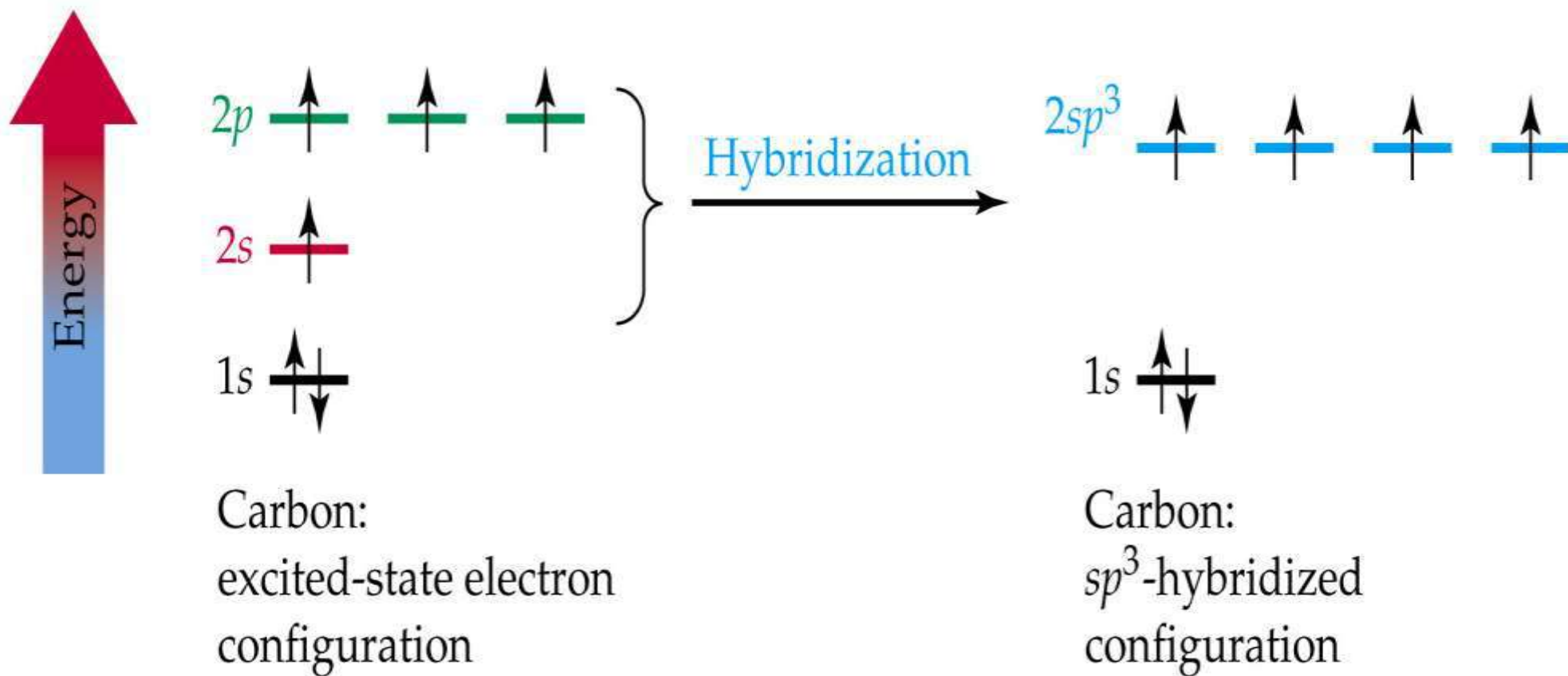
Hybridization

In 1931, Linus Pauling proposed that the wave functions for the s and p atomic orbitals can be mathematically combined to form a new set of equivalent wave functions called hybrid orbitals.

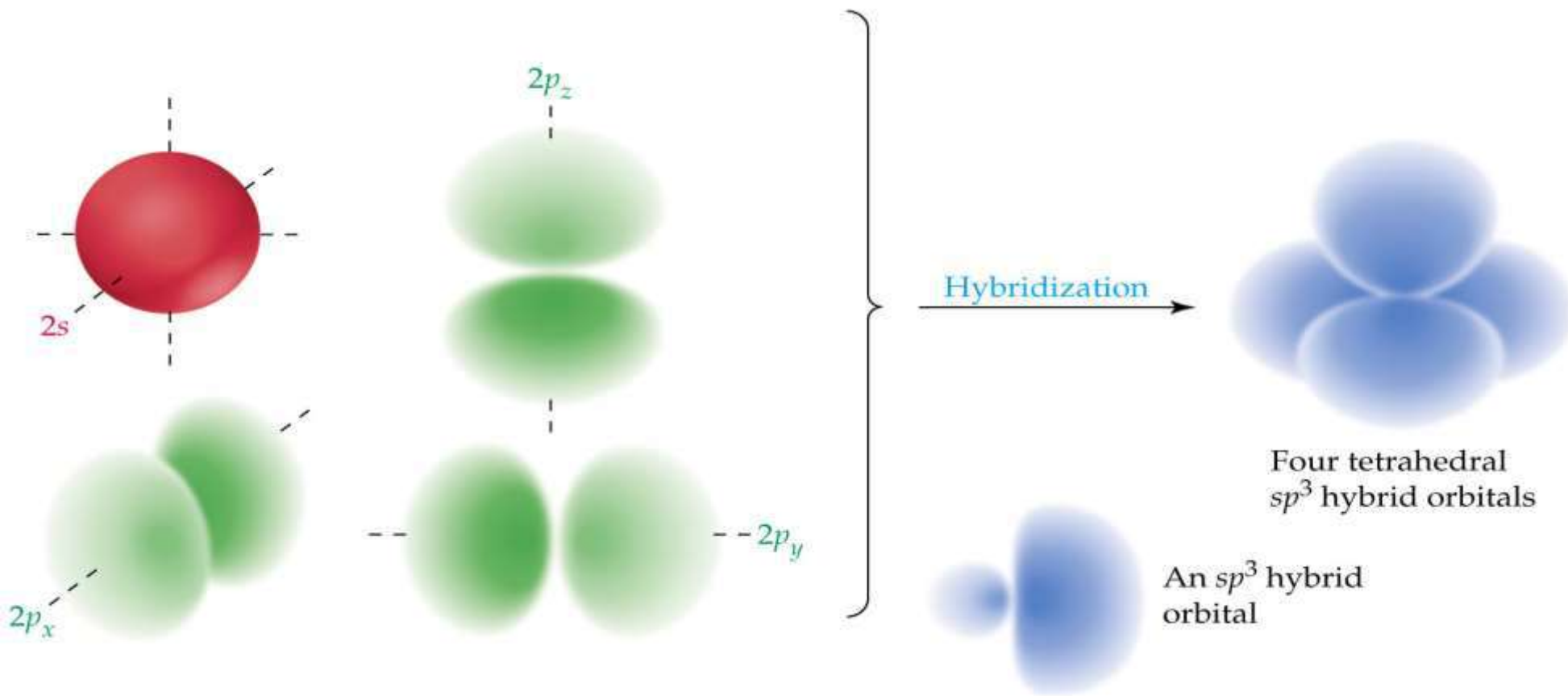
The mathematical process of replacing pure atomic orbitals with reformulated atomic orbitals for bonded atoms is called hybridization.

In a hybridization scheme, the number of hybrid orbitals equals to the total number of atomic orbitals that are combined. The symbols identify the numbers and kinds orbitals involved.

E.g. sp^3 signifies one s and three p orbitals are combined.



Mixing one s orbital with three p orbitals yields four equivalent sp^3 hybrid orbitals.



The formation of four sp^3 hybrid orbitals by combination of an atomic s orbital with three atomic p orbitals. Each sp^3 hybrid orbital has two lobes, one of which is larger than the other. The four large lobes are oriented toward the corners of a tetrahedron at angles of 109.5° .

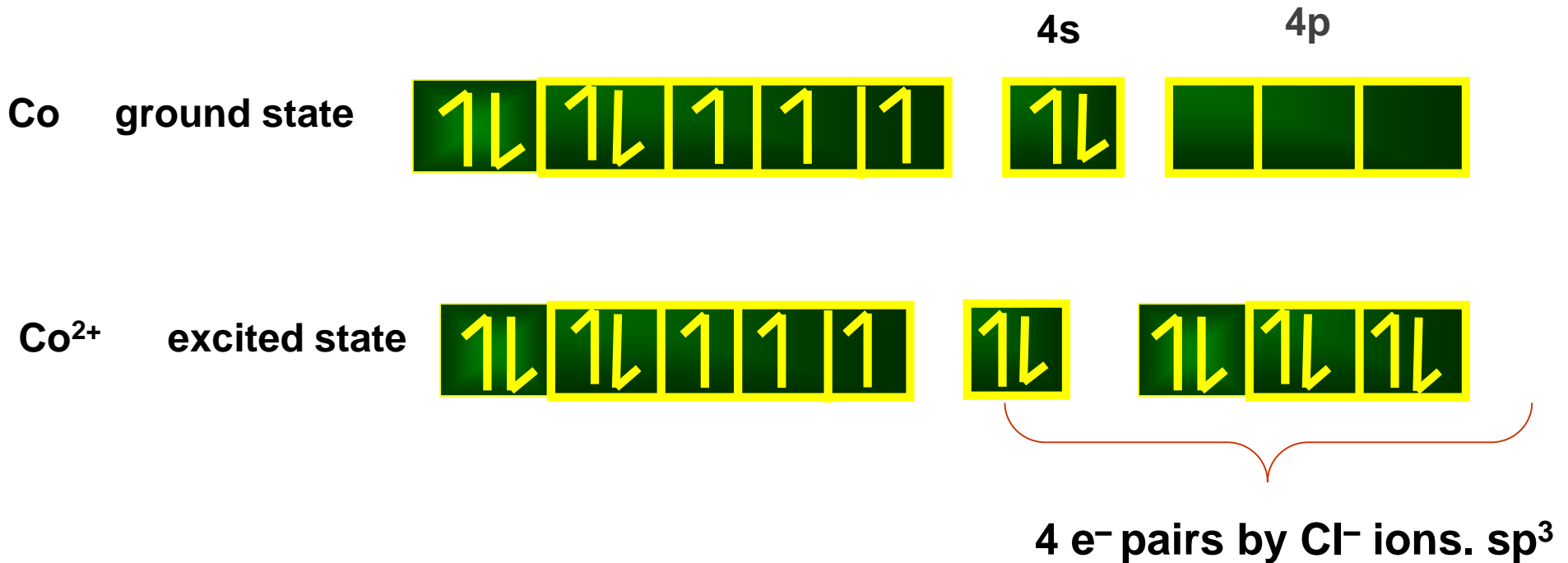
The overlap between s, p and d orbitals produce hybridization.

Coordination number	Geometry	Hybrid orbitals	Example
2	Linear	sp	$[\text{Ag}(\text{NH}_3)_2]^+$
3	Triangle	sp ²	$[\text{HgI}_3]^-$
4	Tetrahedral	sp ³	$[\text{CoCl}_4]^{2-}$
4	Square planar	dsp ²	$[\text{Ni}(\text{CN})_4]^{2-}$
5	Sq.pyramid or (TBP)	dsp ³	$[\text{Fe}(\text{CO})_5]$
6	Octahedral	d ² sp ³ or sp ³ d ²	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}, [\text{Co}(\text{H}_2\text{O})_6]^{2+}$

Tetrahedral complex

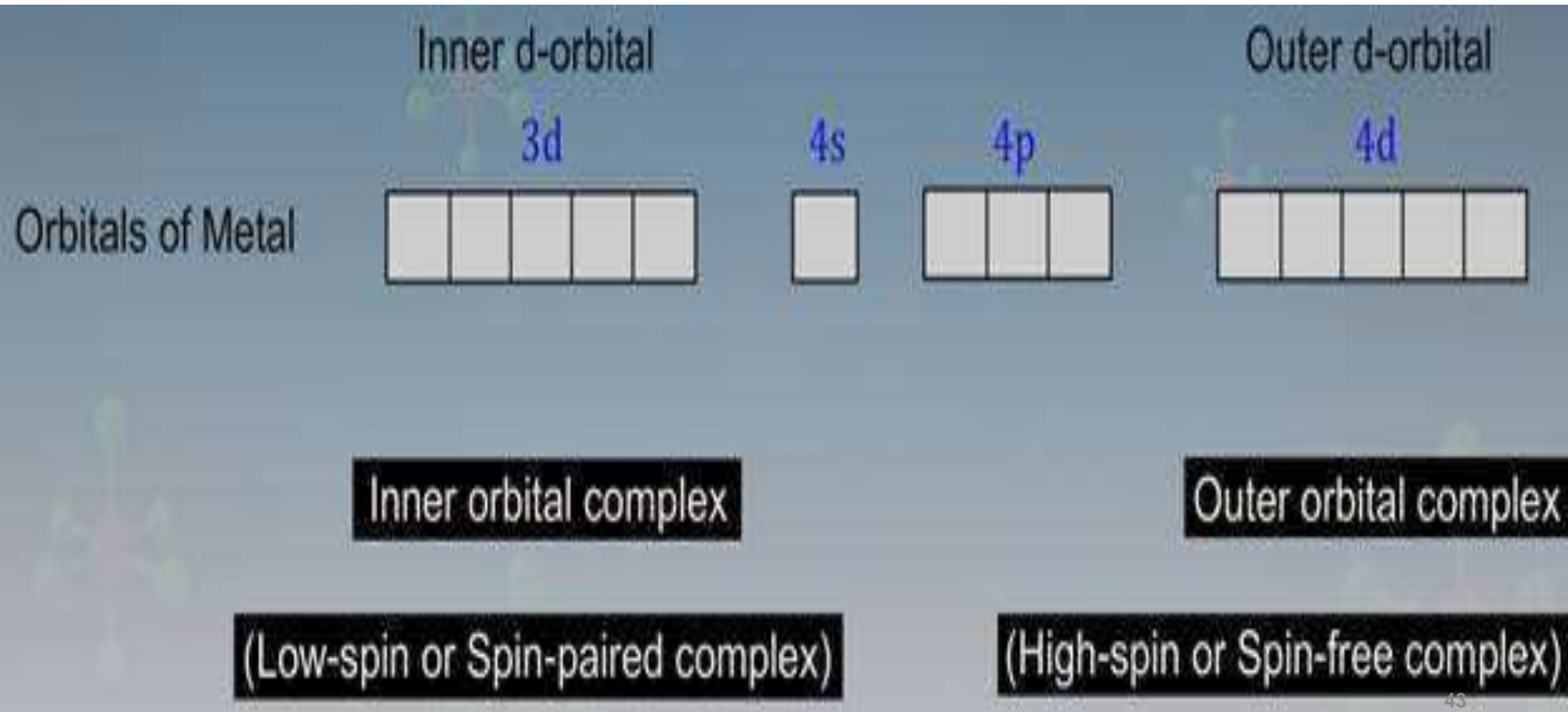


Tetrahedral geometry



Gives $[\text{CoCl}_4]^{2-}$ **three unpaired electrons**, which makes it **paramagnetic** and attracted by magnets.

If (n-1)d orbitals are used for hybridization, the complexes are called inner complexes and nd called outer complexes.



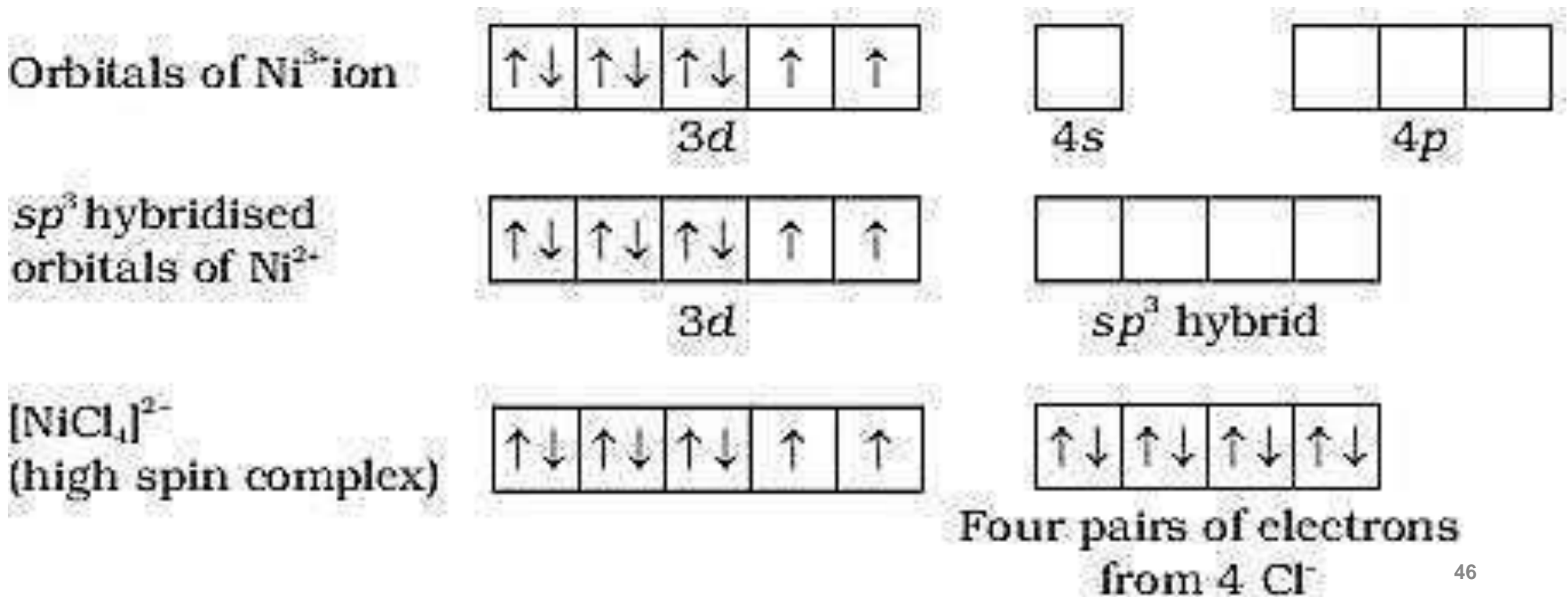
- ❖ When strong field ligands like NH_3 and CN^- are involved in the formation of complexes, they cause pairing of electrons present in metal ions. This process is called as spin pairing.**
- ❖ When weak field ligands like Halogens are involved in the formation of complexes, they cause single electrons present in metal ions. This process is called as spin free.**

Structure of complex compounds based on VBT

1. **Structure of nickel tetracarbonyl $[\text{Ni}(\text{CO})_4]$.**
2. **Formation of $[\text{NiCl}_4]^{2-}$**
3. **Structure of $[\text{Ni}(\text{CN})_4]^{2-}$.**
4. **Structure of $[\text{CoF}_6]^{3-}$.**
5. **Structure of $[\text{Co}(\text{NH}_3)_6]^{3+}$.**

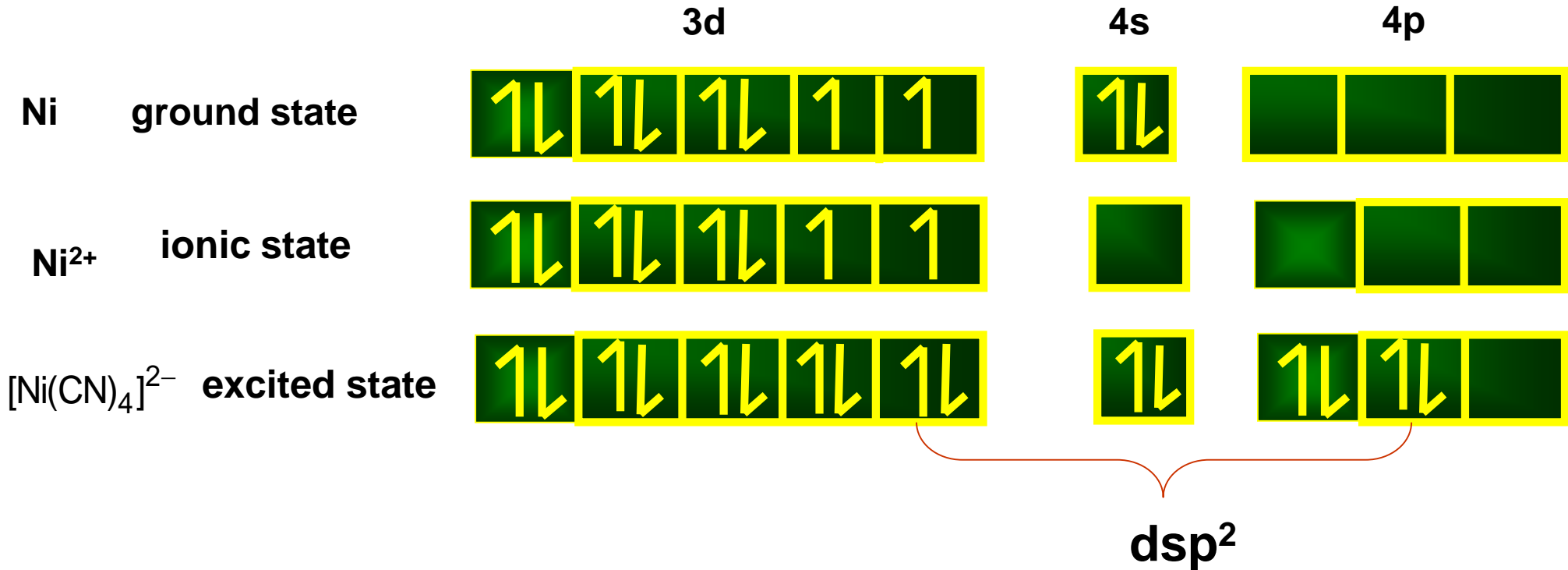
Formation of $[\text{NiCl}_4]^{2-}$

- Oxidation is 2+. each chlorine ion donate 2 electron. Ni = $3d^8 4s^2$.
- Paramagnetic contain 2 unpaired electron.



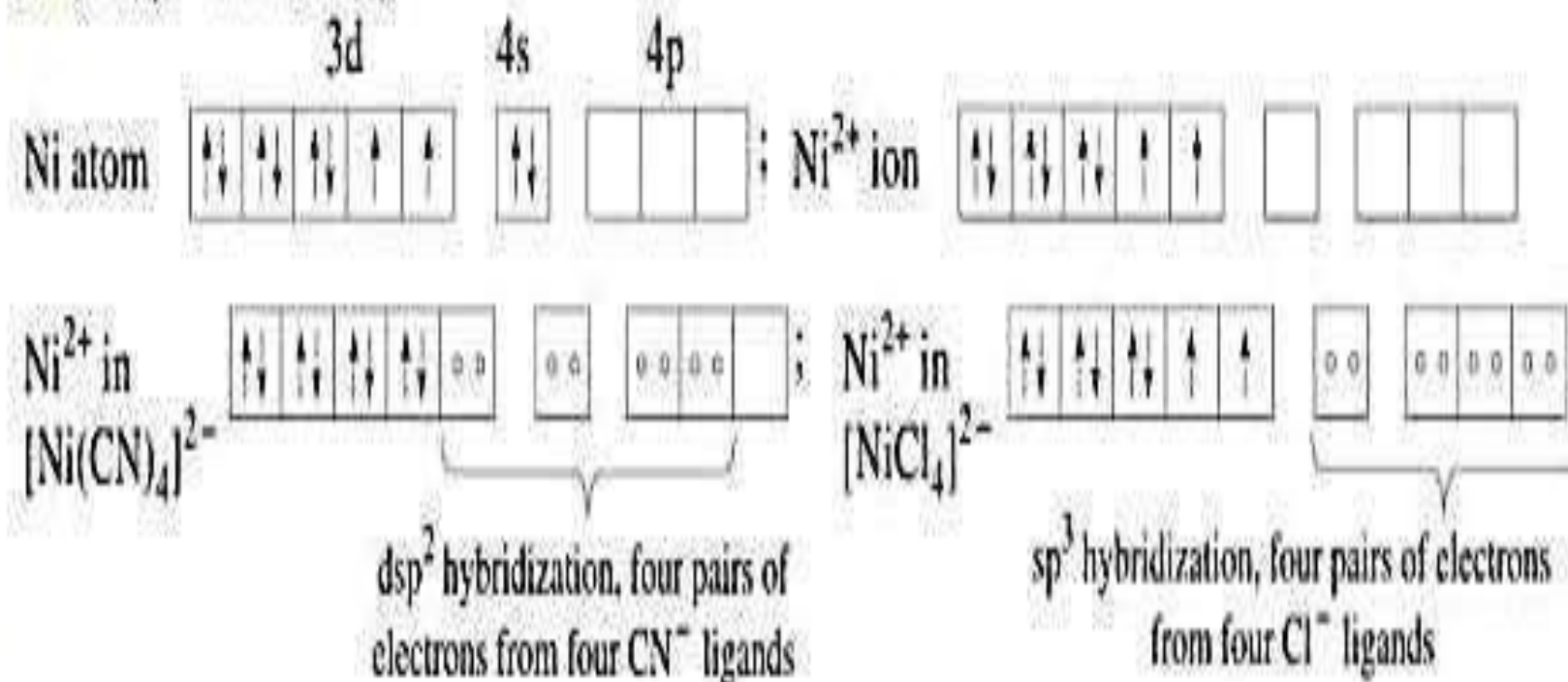


Square Planar Geometry



Gives [Ni(CN)₄]²⁻ all paired electrons, which makes it diamagnetic and weakly repelled by magnets.

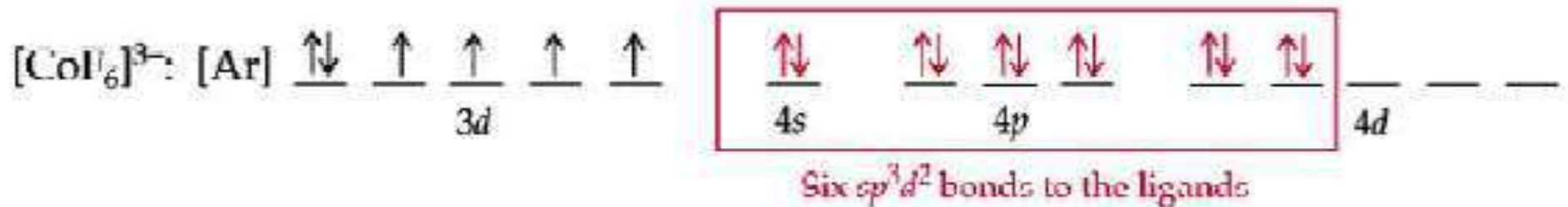
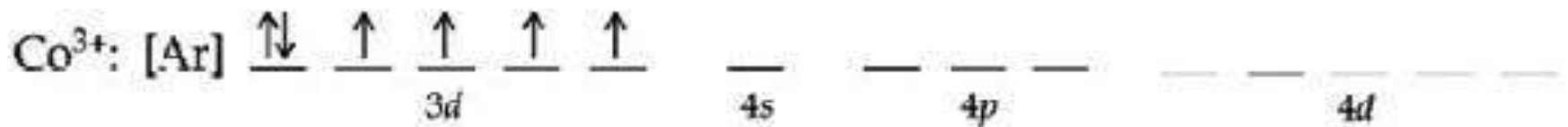
$[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{NiCl}_4]^{2-}$



$[\text{Ni}(\text{CN})_4]^{2-}$ is a square planar (dsp^2 hybridization) and diamagnetic (no unpaired electrons) while $[\text{NiCl}_4]^{2-}$ is tetrahedron (sp^3 hybridization) and paramagnetic (two unpaired electrons). The CN^- ligand is strong and it forces the two unpaired electrons to pair up.

Octahedral sp^3d^2 Geometry

Gives $[\text{CoF}_6]^{3-}$ **four unpaired electrons**, which makes it **paramagnetic** and is called a **high-spin complex**.



Octahedral d^2sp^3 Geometry



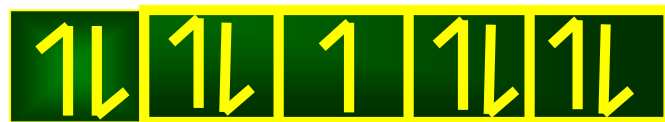
3d



4s



4p



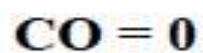
$\text{CN}^- \rightarrow$ Strong ligand

d^2sp^3

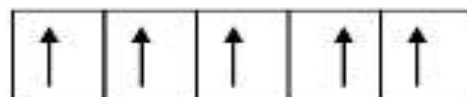
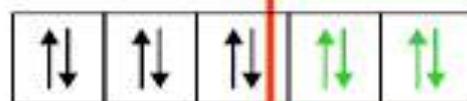
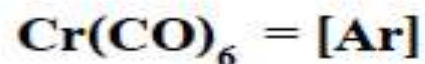
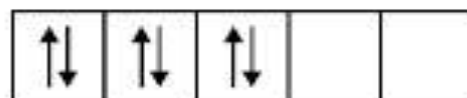
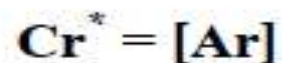
(Inner orbital complex)

High-Spin and Low-Spin

- The difference between sp^3d^2 and d^2sp^3 hybrids lies in the principal quantum number of the d orbital.
- In sp^3d^2 hybrids, the s, p, and d orbitals have the same principal quantum number—**High Spin**.
- In d^2sp^3 hybrids, the principal quantum number of the d orbitals is one less than s and p orbitals—**Low Spin**.
- A complex's magnetic properties determine which hybrid is being used.



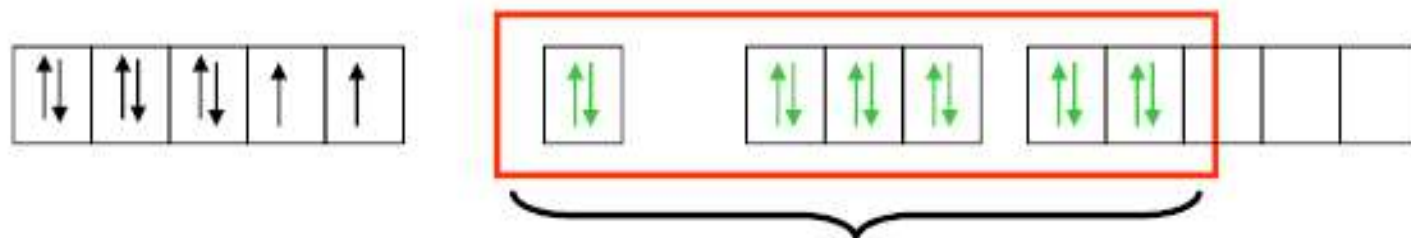
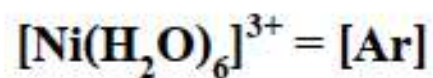
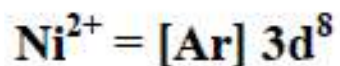
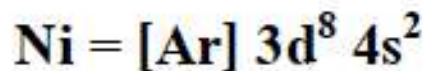
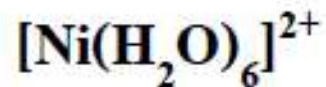
Diamagnetic

 $3d^5$ $4s^1$ $4p^0$  $3d^6$ $4s^0$ $4p^0$ 

d^2sp^3 hybrid
Octahedral



d^2sp^3 hybrid
Octahedral
Inner
paramagnetic



sp^3d^2 hybrid
 Octahedral
 Outer
 paramagnetic

18. A complex involving dsp^2 -hybridization has:
- (a) A square planar geometry
 - (b) A tetrahedral geometry
 - (c) An octahedral geometry
 - (d) Trigonal planar geometry
19. A complex involving d^2sp^3 -hybridization is:
- (a) A square planar geometry
 - (b) A tetrahedral geometry
 - (c) An octahedral geometry
 - (d) Trigonal planar geometry
22. Which of the following complex ion possesses dsp^2 hybridization?
- | | |
|-------------------------------------|----------------------------------|
| (a) $[\text{Ni}(\text{CN})_4]^{2-}$ | (b) $[\text{Ni}(\text{CO})_4]$ |
| (c) $[\text{NiCl}_4]^{2-}$ | (d) $[\text{Ni}(\text{PF}_3)_4]$ |

21. Which of the following complex ion possesses d^2sp^3 hybridization?



23. Which of the following complex ion possesses sp^3d^2 hybridization?



Origin of Magnetic behavior

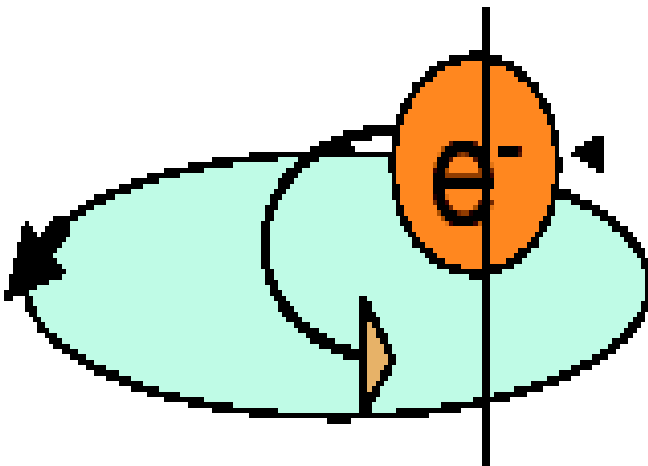
- A wave mechanics images an electron as a small ball bearing a negative charge and it is spin around itself producing a spin magnetic moment μ_s . It is rotates in a close way around the nucleus giving an orbital magnetic moment μ_l .
- Total mag.moment = $\mu_s + \mu_l$ (Bohr Magnton units (B.M))

Magnetism

Each electron has a magnetic moment owing to its:

spin angular momentum

orbital angular momentum



Orbital motion of e generates current and magnetic field

Spin motion of e about its own Axis also generates a magnetic field

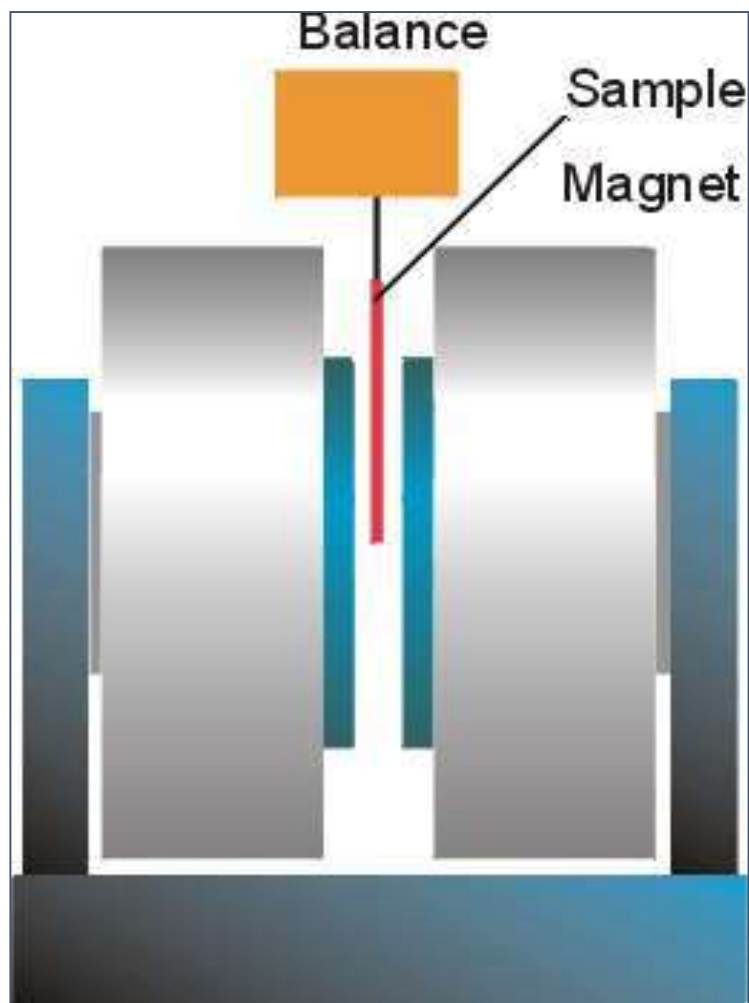
- The magnetic moment μ of a complex with total spin quantum number S is:
- $\mu_s = 2\{S(S+1)\}^{1/2}$ B.M (B.M is the Bohr magneton).
- $B.M = eh/4\pi m_e = 9.274 \times 10^{-24} \text{ J T}^{-1}$
- Since each unpaired electron has a spin $1/2$,
- $S = (1/2)n$, where $n = \text{no. of unpaired electrons}$
- $\mu = \{n(n+2)\}^{1/2}$ B.M .
- **For measuring** magnetic susceptibility we use Gouy method, using Gouy balance:

n = no. of unpaired electrons

$$\mu = \{n(n+2)\}^{1/2} \text{ B.M}$$

Ion	n	S	μ/μ_B Calculate d	Experimental
Ti³⁺	1	1/2	1.73	1.7 – 1.8
V³⁺	2	1	2.83	2.7 – 2.9
Cr³⁺	3	3/2	3.87	3.8
Mn³⁺	4	2	4.90	4.8 – 4.9
Fe³⁺	5	5/2	5.92	5.3

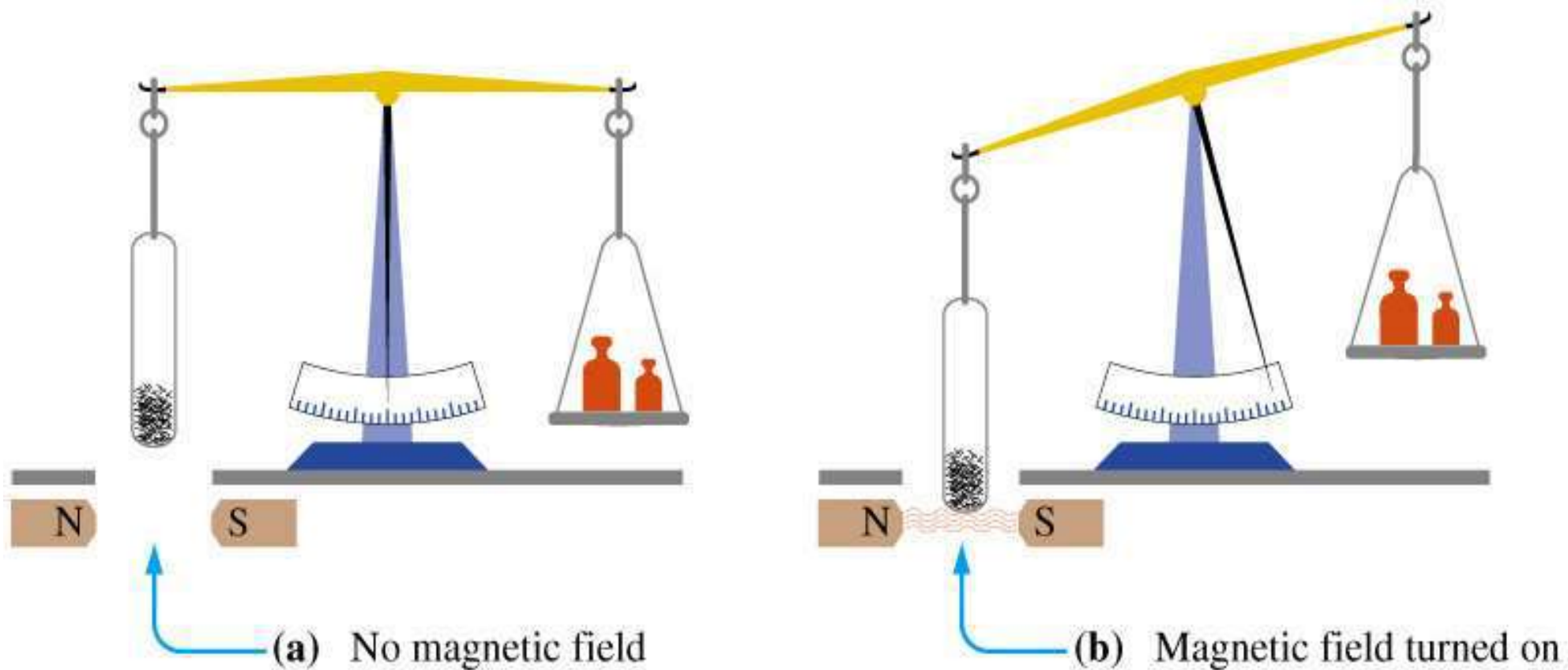
**Similar Calculation can be done
for Low-spin Complex**



Gouy balance to measure the magnetic susceptibilities

- We can measure the magnetic properties of a sample by hanging a vial of material from a balance so that it sits partly in a magnetic field
 - The sample will be pulled down into the magnet if it contains unpaired electrons (said to be paramagnetic)
 - It will tend to be pushed out of the field if it contains no unpaired electrons (diamagnetic)
- The amount of material in the vial along with the extent to which the sample is pulled into the magnet allows us to calculate the magnetic susceptibility of the sample
 - Sample with a high magnetic susceptibility is strongly pulled into the magnetic field

Magnetic behavior



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

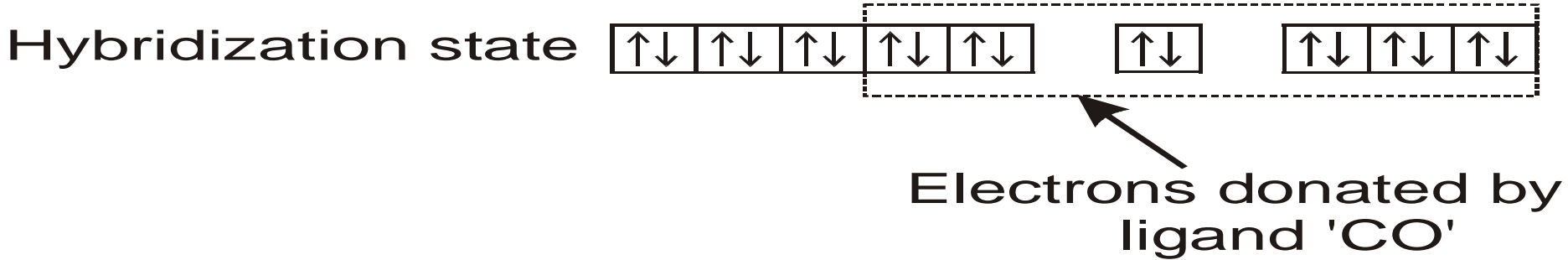
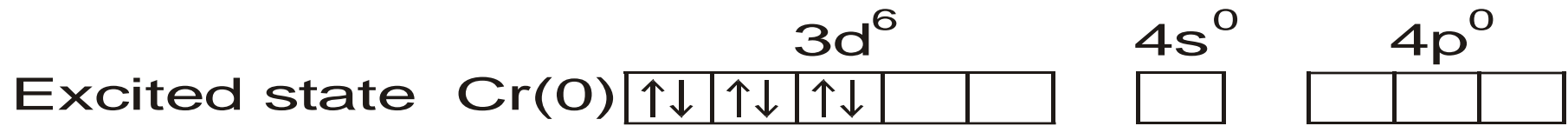
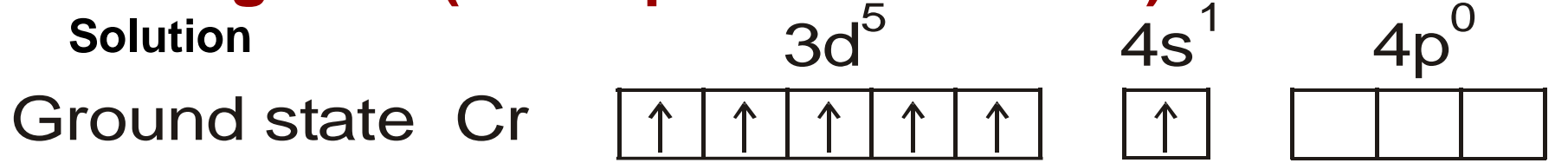
Where n is the number of unpaired electrons

Illustrative Example

Discuss the geometry of the compound $[\text{Cr}(\text{CO})_6]$.

Diamagnetic (No unpaired electrons).

Solution

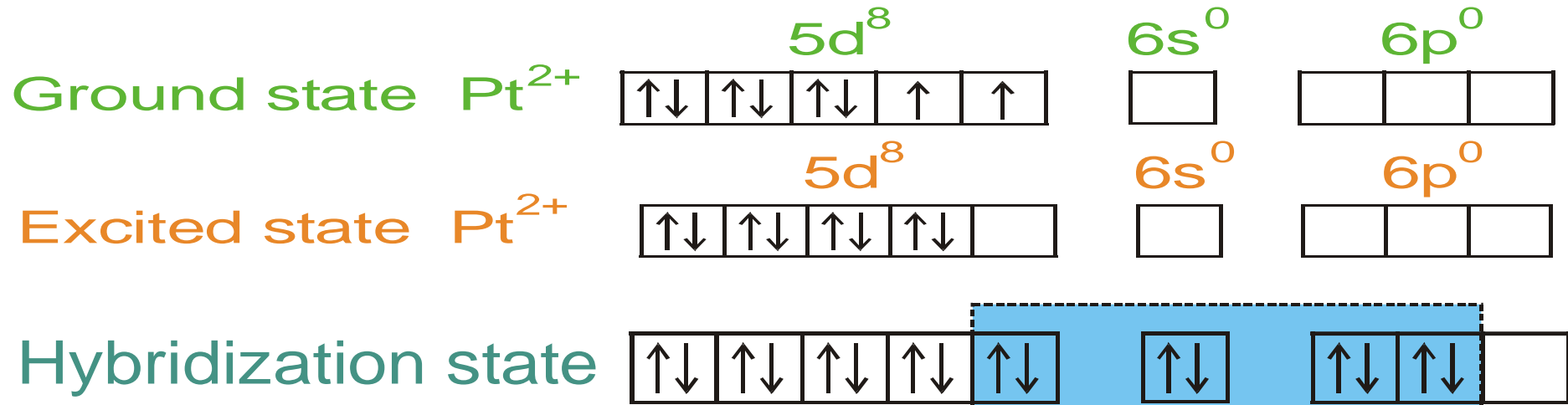


d^2sp^3 hybridization = octahedral geometry

Illustrative Example

Discuss the geometry of $[\text{PtCl}_4]^{2-}$ and $[\text{NiCl}_4]^{2-}$.

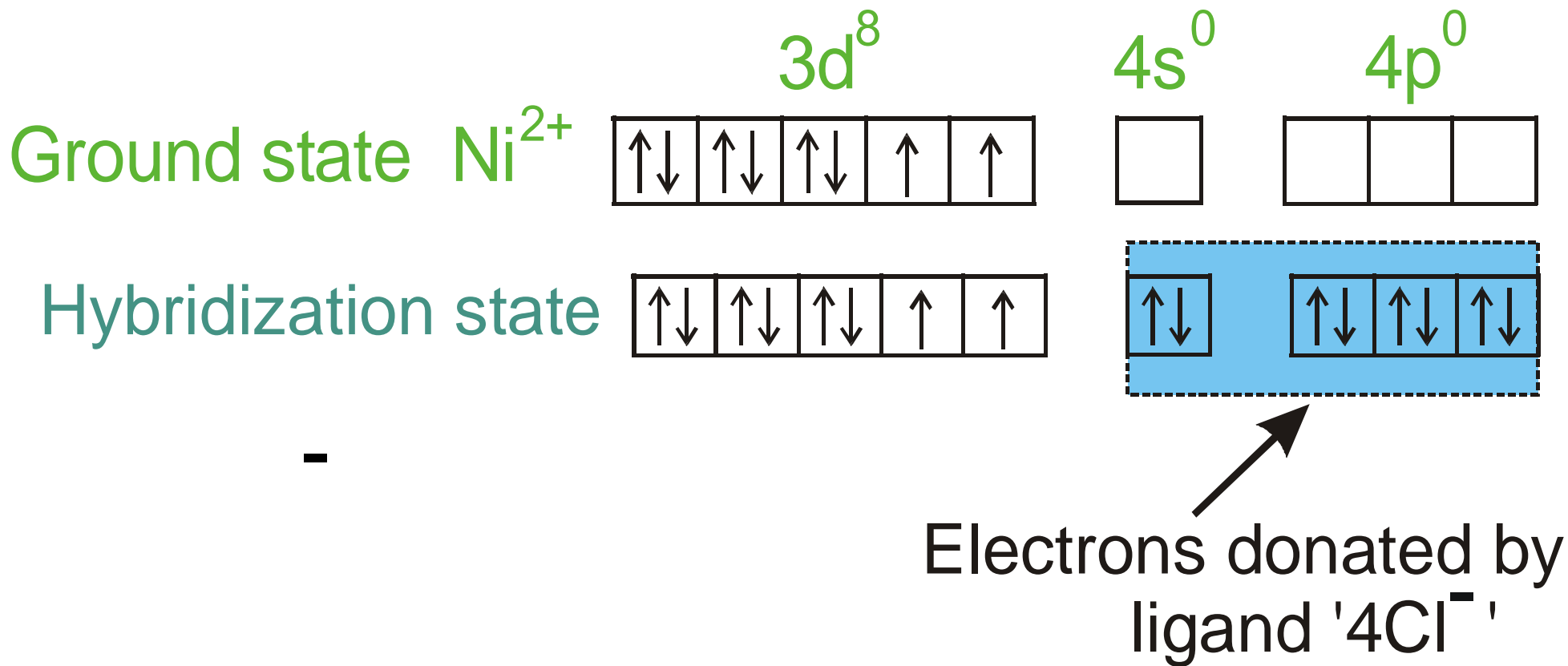
Solution: Geometry of $[\text{PtCl}_4]^{2-}$



Electrons donated by ligand ' 4Cl^- '

dsp^2 hybrid = square planar.

Geometry of $[\text{NiCl}_4]^{2-}$



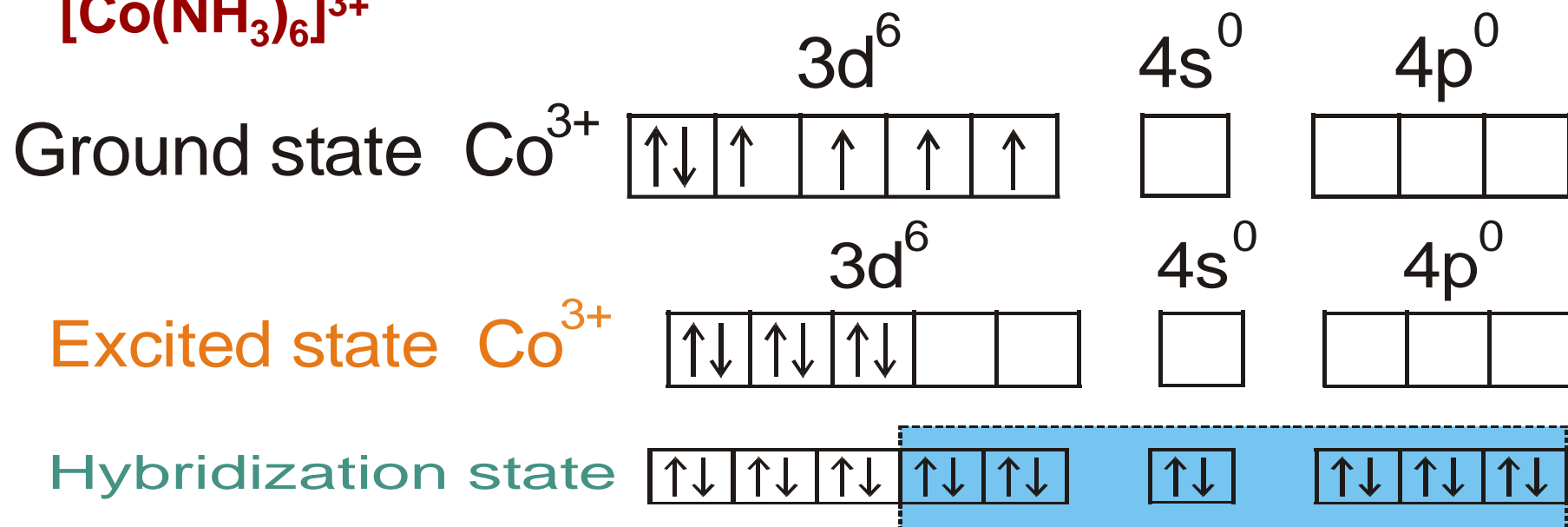
sp^3 hybrid = tetrahedral.

$n=2$ unpaired electrons, paramagnetic

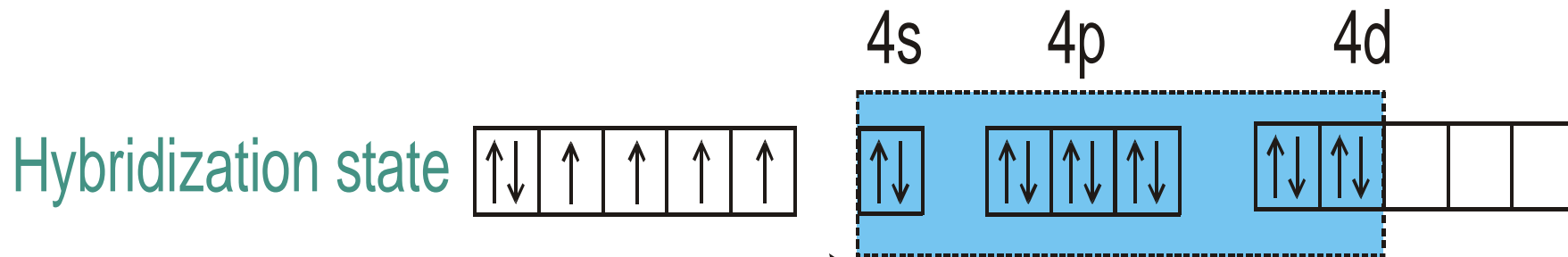
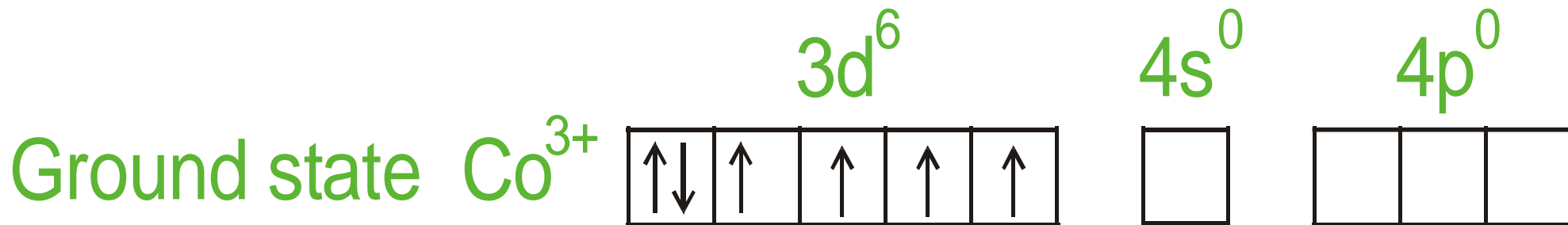
$[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic and $[\text{CoF}_6]^{3-}$ is paramagnetic. Explain with the help of valence bond theory.

Solution

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



Electrons donated by ligand '6NH₃'



Electrons donated by
ligand '6F⁻'

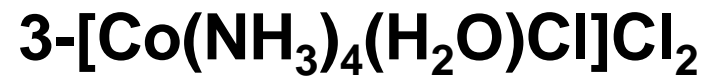
65. Assign the hybridization, shape, and magnetic moment of $K_2[Cu(CN)_4]$ are:

- (a) sp^3 , tetrahedral, 1.73 B.M.
- (b) dsp^2 , square planar, 1.73 B.M.
- (c) sp^3 , tetrahedral, 2.44 B.M.
- (d) dsp^2 , square planar, 2.44 B.M.

69. Hybridization, shape, and magnetic moment of $K_3[Co(CO_3)_3]$ are:

- (a) d^2sp^3 , octahedral, 4.9 B.M.
- (b) sp^3d^2 , octahedral, 4.9 B.M.
- (c) dsp^2 , square planar, 4.9 B.M.
- (d) sp^3 , tetrahedral, 4.9 B.M.

Q/ Draw the electron box diagram, geometrical structure, hybridization and calculate magnetic moment for the following coordination compounds according VBT:



Drawbacks (Weakness points) of the valence bond theory

- a) Does not explain the colour of coordination compound.**
- b) Cannot explain magnetic behavior based on geometry.**
- c) Does not explain why some called inner and outer complex same metal ion in the same oxidation state.**
- d) Fails to predict the exact geometry of the complexes with the coordination number four.**
- e) Does not distinguish weak field and strong field of ligand.**
- f) It cannot predict exactly the tetrahedral and square planar structure of 4-coordinate bond or coordination No.4 complexes.
Ex. $[\text{Cu}(\text{NH}_3)_4]^{+2}$ is dsp^2 sq. plane not sp^3 T.H.**
- g) Whether O.h complexes are high-spin or low-spin, also failed in exterminating distorted O.h complexes.**