# INORGANIC CHEMISTRY

**Topic: 5**

## LANTHANIDES

**LONG ANSWER QUESTIONS**

**1. What are the general characteristics of Lanthanides..**

**Ans: F – BLOCK ELEMENTS**

The elements in which the differentiating electron enters the anti penultimate energy level i.e. (n – 2)f, are called f – block elements. These are often called as inner transition elements or rare earth elements. The differentiating electron in transition elements may enter either 4f or 5f orbitals based upon which they are differentiated into lanthanides and actinides.

**Lanthanides**

In lanthanides the differentiating electron enters 4f orbital. These are cerium to lutetium. The name lanthanide is because they come immediately after lanthanum.

**Actinides** In actinides the differentiating electron enters 5f orbitals. These are thorium to lawrencium. These elements come immediately after actinium.

**Electronic configuration:**

General electronic configuration of f – block elements is $(n–2)f^{l–14}(n–1)d^{0–1}ns^2$

Lanthanides $[Xe]4f^{l–14}5d^{0–1}6s^2$

Actinides $[Rn]5f^{l–14}6d^{0–1}7s^2$

**CHARACTERISTICS OF LANTHANIDES**

**1. Oxidation states**

Lanthanides show only one stable oxidation state, which is not in the case of actinides. The typical oxidation state of lanthanides is +3. Some elements show +2 and +4 also, when they lead to

(a) a noble gas configuration e.g. $Ce^{4+}(f^0)$

(b) a half filled f shell e.g. $Eu^{2+}(f^7)$

(c) a completely filled f shell e.g. $YB^{22+}(f^{14})$

**2. Lanthanide contraction**
In lanthanide series with increasing atomic number there is a progressive decrease in the atomic as well as ionic radii. This regular decrease is known as lanthanide contraction. This is due to the poor shielding of f orbitals, which are unable to counter balance the effect of increasing nuclear charge. Net result is contraction in size.

**Consequences of lanthanide contraction**
Since the change in ionic radii in lanthanides is very small (only 15 pm from $Ce^{3+}$ to $Cu^{3+}$), their chemical properties are similar. This makes the separation of the elements in pure state very difficult.

Due to lanthanide contraction, the difference in size between second (4d) and third (5d) is very small.

As the size of the lanthanide ions decreases from $La^{+3}$ to $Lu^{+3}$, the covalent character of the hydroxides increases and hence the basic strength decreases. Thus $La(OH)_3$ is most basic whereas $Lu(OH)_3$ is least basic.

**3. Complex formation**

The lanthanides do not have much tendency to form complexes due to low charge density because of their size. However, the tendency to form complex and their stability increases with increasing atomic number.

**4. Chemical Behaviour**
The first few members of the series are quite reactive like calcium. However with increasing atomic number, their behaviour becomes similar to that of aluminum.

(a) They combine with $H_2$ on gentle heating. When heated with carbon, they form carbides. On burning in the presence of halogens, they form halides.

(b) They react with dilute acids to liberate $H_2$.

(c) They form oxides and hydroxides of the type $N_2O_3$ and $M(OH)_3$ which are basic alkaline earth metal oxides and hydroxides.

**2. What are the oxidation states exhibited by the Lanthanide elements? Write a note with at least one example each.**

Ans: **Oxidation states**
Lanthanides exhibit different oxidation states like +2, +3 and +4. Among these +3 is the most stable oxidation state. The elements that attain stable electronic configuration by losing 2 or 4 electrons exhibit +2 and +4 oxidation states.

**Example:** Europium and ytterbium exhibits +2 and +3 oxidation states - cerium exhibits +4 oxidation state.

Most stable oxidation state of lanthanides is +3. Oxidation states + 2 and + 4 also exist but they revert to +3 e.g. $Sm^{2}$+, $Eu^{2+}$, $Yb^{2+}$ lose electron to become +3 and hence are good reducing agents, where as $Ce^{4+}$, $Pr^{4+}$, $Tb^{4+}$ in aqueous solution gain electron to become + 3 and hence are good oxidizing agents. There is a large gap in energy of 4 f and 5 d sub shells and thus the number of oxidation states is limited.

3. **What is meant by Lanthanide contraction? Explain in brief.**

**Ans: Lanthanide contraction**: The regular decrease in the size of lanthanide ions from atomic number 58, Cerium to 71, Lutetium to is known as lanthanide contraction. It is due to greater effect of the increased nuclear charge than that of the screening effect. In lanthanide series with increasing atomic number there is a progressive decrease in the atomic as well as ionic radii. This regular decrease is known as lanthanide contraction. This is due to the poor shielding of f orbitals, which are unable to counter balance the effect of increasing nuclear charge. Net result is contraction in size.

**Consequences of lanthanide contraction**

(a) It results in slight variation in their chemical properties which helps in their separation by ion exchange

(b) Each element beyond lanthanum has same atomic radius as that of the element lying above it in the group
(e.g. Zr 145 pm, Hf 144 pm); Nb 134 pm, Ta 134 pm ; Mo 129 pm, W 130 pm).

(c) The covalent character of hydroxides of lanthanides increases as the size decreases from $La^{3+}$ to $Lu^{3+}$ . However basic strength decreases. La $(OH)_3$Thus is most basic whereas Lu $(OH)_3$ is least basic. Similarly, the basicity of oxides also decreases in the order from $La^{3+}$ to $Lu^{3+}$.

(d) Tendency to form stable complexes from $La^{3+}$ to $Lu^{3+}$ increases as the size decreases in that order.

(e) There is a slight increase in electronegativity of the trivalent ions from La to Lu.

(f) Since the radius of $Yb^{3+}$ ion (86 pm) is comparable to the heavier lanthanides Tb, Dy, Ho and Er, therefore they occur together in natural minerals.

## SHORT ANSWER QUESTIONS

1. **Write any two methods of obtaining Lanthanide metals.**

**Ans:** Lanthanides are separated from monazite and are converted in to chlorides or oxides.

Then the metals are obtained either by the electrolysis of molten chlorides or by the reduction of the anhydrous halides with strong electropositive metals as Na, Mg etc.

2. **Mention the chemical properties of Lanthanides.**

**Ans:** Lanthanum exhibits two oxidation states, +3 and +2, the former being much more stable. For example, $LaH_3$ is more stable than $LaH_2$.Lanthanum burns readily at 150 °C to form lanthanum (III) oxide:

$$4\ La + 3\ O_2 \rightarrow 2\ La_2O_3$$

However, when exposed to moist air at room temperature, lanthanum oxide forms a hydrated oxide with a large volume increase.

Lanthanum is quite electropositive and reacts slowly with cold water and quite quickly with hot water to form lanthanum hydroxide:

$$2\ La\ (s) + 6\ H_2O\ (l) \rightarrow 2\ La(OH)_3\ (aq) + 3\ H_2\ (g)$$

Lanthanum metal reacts with all the halogens. The reaction is vigorous if conducted at above 200 °C:

$$2\ La\ (s) + 3\ F_2\ (g) \rightarrow 2\ LaF_3\ (s)$$
$$2\ La\ (s) + 3\ Cl_2\ (g) \rightarrow 2\ LaCl_3\ (s)$$
$$2\ La\ (s) + 3\ Br_2\ (g) \rightarrow 2\ LaBr_3\ (s)$$
$$2\ La\ (s) + 3\ I_2\ (g) \rightarrow 2\ LaI_3\ (s)$$

Lanthanum dissolves readily in dilute sulfuric acid to form solutions containing the La(III) ions, which exist as $[La(OH_2)_9]^{3+}$ complexes:

3. **Explain Lanthanide contraction.**

**Ans: Lanthanide contraction**
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**Consequences of lanthanide contraction**

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4. **Why Lanthanides exhibit variable valency?**

**Ans:** Lanthanides exhibit different oxidation states like +2, +3 and +4. Among these +3 is the most stable oxidation state. The elements that attain stable electronic configuration by losing 2 or 4 electrons exhibit +2 and +4 oxidation states.

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# TRANSITION ELEMENTS

**Topic: 6**

# CO-ORDINATION COMPOUNDS

**LONG ANSWER QUESTIONS**

**1. Explain the Werner's theory of co-ordination compounds with examples.**

**Introduction to Werner's theory**

**Alfred Werner** is considered to be the father of coordination chemistry. His explanation formation is based on the following postulates.

1) Every complex compound has a central metal atom or ion.

2) The central metal shows two types of valencies; namely

a) Primary valency b) Secondary valency

**A. Primary valency**:

Normally primary valency is numerically equal to the oxidation state of the metal . The valencies are non directional and are represented by discontinuous lines (-------) . Species or groups bound by primary valencies undergo complete ionization. Primary valency applies equally to metals in simple salts as well as those in complex compounds. These valencies are identical with ionic bonds. In $CoCl_3$, ($Co^{+3}$ and $3Cl^-$ are present). There are three primary valencies i.e. three ionic bonds present .

**B. Secondary valency:**

The secondary valencies are directed in space around the central metal in a symmetric order . Each metal has a characteristic number of secondary valencies .

Ex : 1 In $CoCl_3 . 6NH_3$ complex, 3 chlorides are held by primary valencies . $6NH_3$ molecules are held by secondary valencies .

2 In $CuSO_4 . 4NH_3$ complex, $SO_4^{-2}$ is held by two valencies of Cu. Four $NH_3$ groups are held by secondary valencies.

Since the secondary valencies are directional in nature, a complex has a specific shape.

**Coordination Numbers and Shapes (Werner's Rule)**

| S.No | No of secondary valencies or coordination number | Shape of the corresponding complex species |
|---|---|---|
| 1 | 2 | Linear |
| 2 | 3 | Trigonal planar |
| 3 | 4 | Tetrahedral |
| | 4 | Square planar |
| 4 | 5 | Square pyramidal |
| | 5 | Trigonal bipyramidal |
| 5 | 6 | Octahedral |
| 6 | 7 | Pentagonal bipyramidal |

**Table: Coordination numbers and shapes of complex species**

**C . <u>Ligands</u>:**

The molecules or ions bonded to the central metal through secondary valencies are now called as **Ligands** . The ligands amy be neutral molecules ( Eg : $NH_3$ , $H_2O$ ) or negatively charged ions . ( $Cl^-$ ; $CN^-$ ; $NO_2^-$ ) or positively charged ions (Eg : $NO^+$ ) Some negative ligands , depending upon the complex , may satisfy both primary and secondary valencies . Such ligands

which satisfy both primary and secondary valencies .It follows the werner's theory ligands which satisfy both primary and secondayr valencies do not ionise . It follows the werner's theory.

2. **Discuss the colour of transition metal complexes with suitable example.**

3. **Explain the structures of the following examples in terms of Werner's theory**
   **a) $CoCl_3$. $6NH_3$ b) $CoCl_3$. $5NH_3$ c) ) $CoCl_3$. $4NH_3$ d) ) $CoCl_3$. $3NH_3$**

**Ans:**

**Primary valency**:

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**Complex Structure using Werner's Theory**

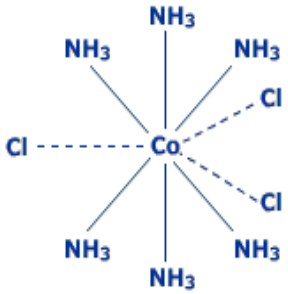
Example: In the complex between $CoCl_3$ and $NH_3$ the ionizable chloride ions are found by precipitation with $AgNO_3$. The remaining Cl and $NH_3$ are present around the central Co in such directions so as to minimize repulsion and are linked by secondary valencies.

a) Primary valencies - represented by dotted lines.

b) Secondary valencies - by solid lines.

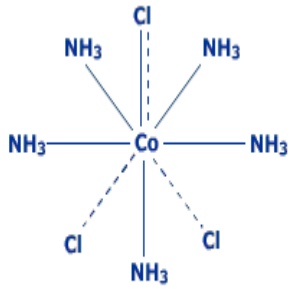
c) Groups satisfying both primary and secondary valency - by solid and dotted lines.

1)



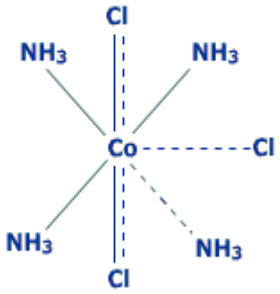

$[Co(NH_3)_6]Cl_3$

2)



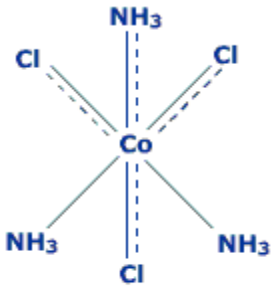

$[CoCl(NH_3)_5]Cl_2$

3)




$[CoCl_2(NH_3)_4]Cl$

4)




$[CoCl_3(NH_3)_3]$

Werner was given the Nobel Prize in 1913 for his work in complexes.

**4. Write the postulates of Valence Bond Theory.**

**Valence Bond (VB) Theory**

I) The metal ligand bond arises by donation of pair of electrons by ligands to the central metal atom.

II) To accommodate these electrons the metal ion must possess requisite number of vacant orbitals of equal energy. These orbitals of the metal atom undergo hybridisation to give hybrid orbitals.

III) Sometimes the unpaired (n-1)d orbitals pair up before bond formation making (n-1)d orbitals vacant. The central metal atom makes available number of d-orbitals equal to its co-ordination number.

iv) The metal ligand bonds are thus formed by donation of electron pairs by the ligands to the empty hybridized orbitals. These bonds are equal in strength and directional in nature.

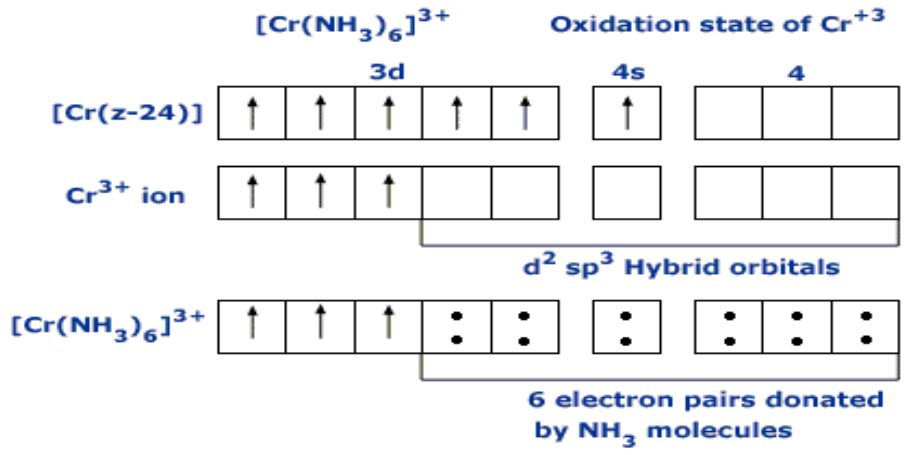
v) Octahadral, square planar and tetrahedral complexes are formed as a result of $d^2sp^3$ (or $sp^3 d^2$), $dsp^2$ and $sp^3$ hybridization respectively

**5. Discuss the complex on the basis of Valence bond theory.**

**Octahedral Complexes**

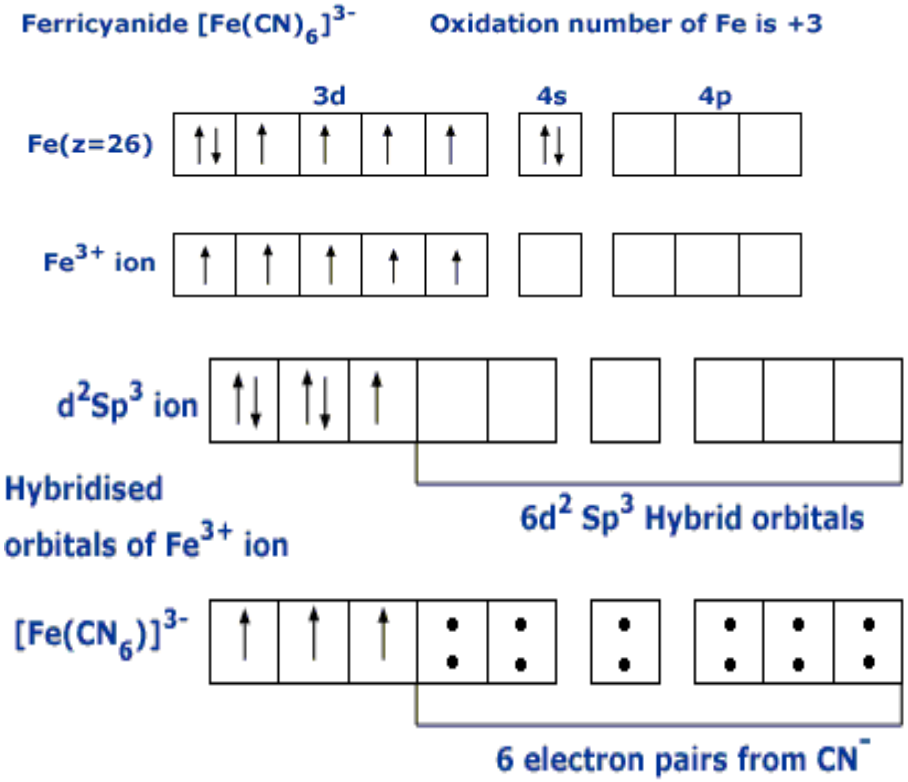
1) Shape - Octahedral $d^2sp^3$

Magnetic behavior - Paramagnetic because it has unpaired electrons.



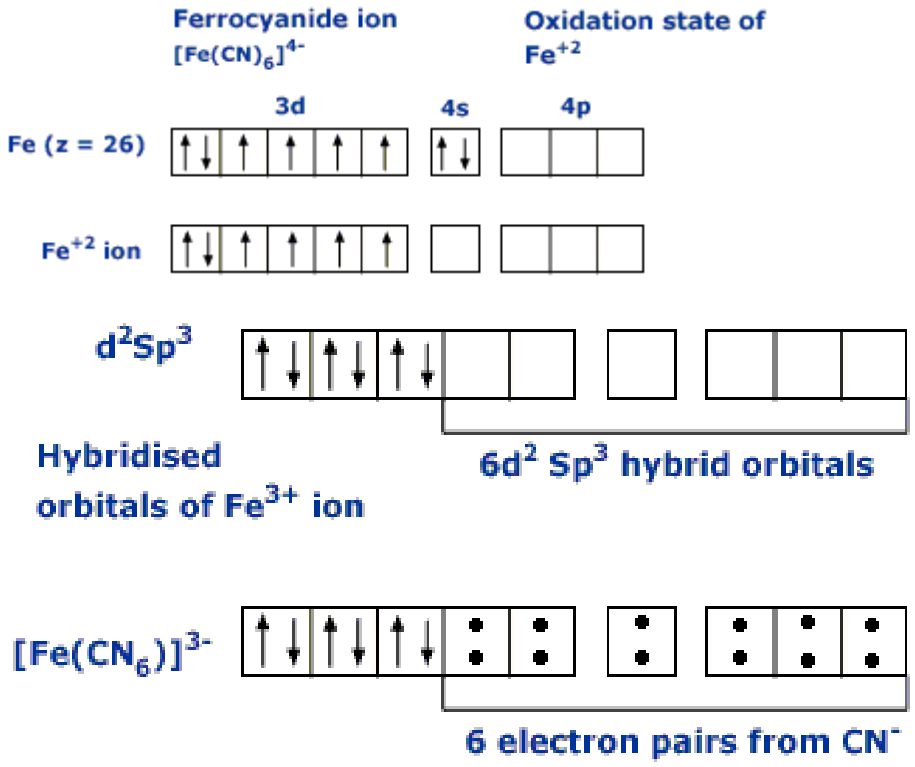

2) Shape - Octahedral

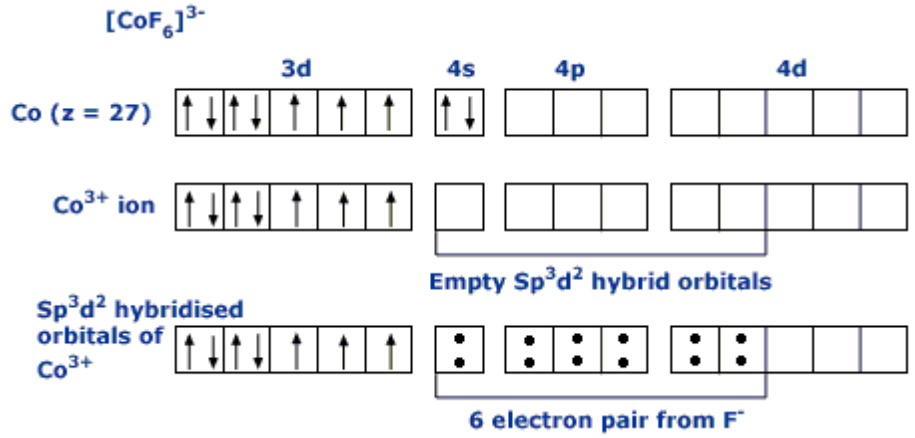
Paramagnetic - One unpaired electron




3) Shape - Octahedral

Diamagnetic - No unpaired electrons



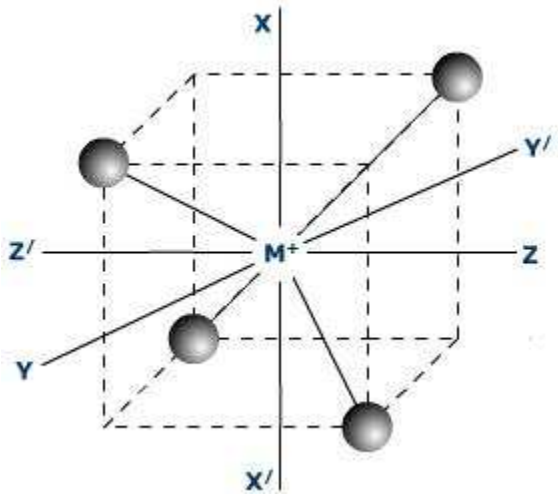

$F^-$ ion is a weak ligand, it is unable to pair up the unpaired electrons.

Shape - Octahedral

Magnetic behavior - Highly paramagnetic.

**Crystal Field Splitting in Tetrahedral Complexes**

The tetrahedral arrangement of four ligands surrounding the metal ions is as shown in the figure.

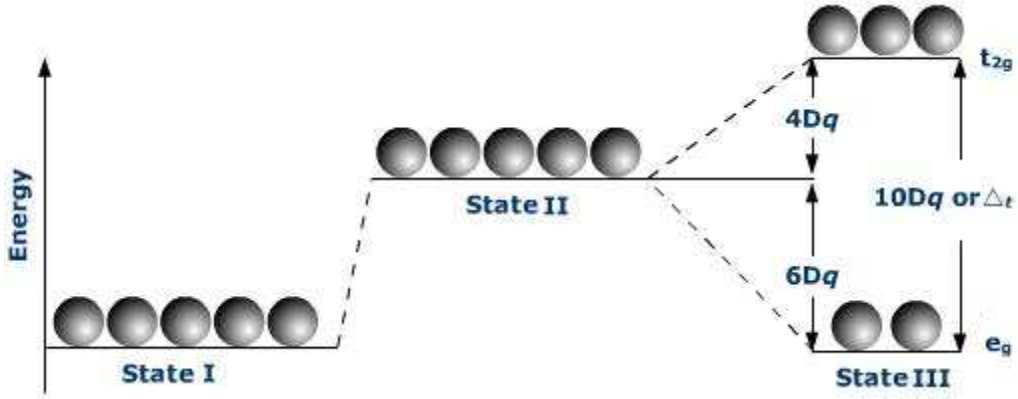



**Tetrahedral arrangement of four ligands surrounding the metal ions**

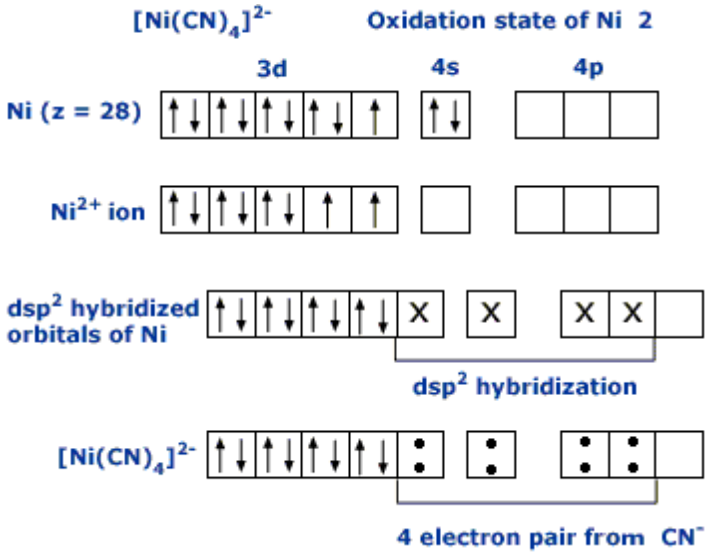
It is clear from the figure that none of the d-orbitals point exactly towards the ligands. The three d-orbitals $d_{xy}$, $d_{yz}$ and $d_{zx}$ are pointing close to the direction in which ligands are approaching.

As a result of this, the energy of these three orbitals increases much more than the other two d-orbitals ($dx^2$ - $y^2$ and $dz^2$).

The d-orbitals will thus split as shown below:

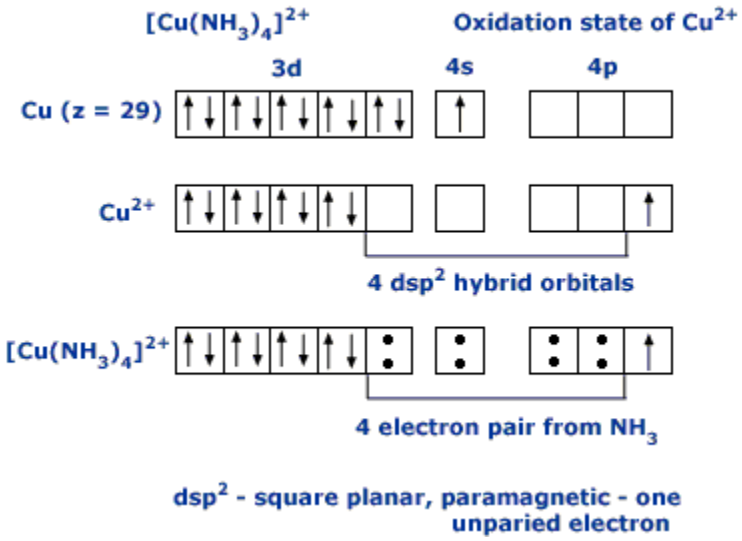


**Square Planar Complexes**




**$dsp^2$ hybridization - square planar**

**Diamagnetic - No unpaired electrons.**




**Inner and Outer Orbital Complexes**

In the octahedral structure the central metal atom uses inner

(n -1) d - orbitals or outer (n)d-orbitals for hybridization. This results in

**Inner orbital complex**

- involving (n-1)d orbitals for $d^2sp^3$ hybridization.

The electrons in the metal pair, so the complex is either diamagnetic or will have lesser number of unpaired electrons.

**Example**: $[V(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$

**Outer orbital complex**

When the complex formed involves use of outer nd - orbitals $sp^3d^2$. It is called outer orbital complex. It has a large number of unpaired electrons.

**Example**: $[CoF_6]^{3-}$, $[MnF_6]^{3-}$, $[Fe\ F_6]^{3-}$ because $F^-$ is a weak ligand, it cannot cause force pairing.

**6. Define EAN. Calculate the EAN of the following metals in the respective complexes.**

**Effective Atomic Number (EAN) :**

- The sum of the number of electrons, donated by all ligands and those present on the central metal ion or atom in complex is called as effective atomic number (EAN).
- Generally EAN of central metal ion will be equal to the number of electrons in the nearest noble gas.
- If the EAN of the central metal is equal to the number of electrons in the nearest noble gas then the complex possess greater stability.

  **EAN** = [(atomic number of central metal) – (the oxidation state of the metal) + (the number of electrons gained by the metal from the ligands through co-ordination)] = [Z metal – (ox.state of the metal) + 2(coordination number of the metal)].

Ex: 1) $[Fe(CN)_6]^{4-}$ EAN = [26 – (2) + 2(6)] = 36
2) $[Co(NH_3)_6]^{3+}$ EAN = [27 – 3 + 2(6)] = 36
3) $[Ni(CO)_4]$ EAN = [28 – 0 + 2(4)] = 36
4) $[Fe(CN)_6]^{3-}$ EAN = [26 – 3 + 2(6)] = 35
5) $[Ni\ (CN)_4]^{2-}$ EAN = [28 – 2+ 2(4)] = 36
6) $[Cu(NH_3)_4]^{2+}$ EAN = [29 – 2 + 4(2)] = 35
7) $[Ag(NH_3)_2]^{+}$ EAN = [47 – 1 + 2(2)] = 42

**7. What do you understand by Ligand?**

**Ligand :** An ion or a molecule that can have an independent existence and can donate a pair of electrons.

Ligand can be negative, neutral or positive.

**Formula and names of some ligands.**

| Neutral ligands | Negative ligands | Positive Ligands |
|---|---|---|
| $H_2O$ aqua | $OH^-$ hydroxo | $NO_2^{\oplus}$ nitronium |
| CO carbonyl | $F^-$ Fluoro | $NO^{\oplus}$ Nitrosonium |
| $NH_3$ ammine | $Br^-$ Bromo | $(NH_2NH_3)^+$ hydrazinium |
| NO Nitrosyl | $CN^-$ Cyano | |
| $C_6H_5$ Phenyl | $NCS^-$ Isothiocyanato | |
| $C_6H_5N$ Pyridine | $SO_4^{2-}$ Sulphato | |
| $PH_3$ Phosphine | $NO_2^-$ Nitro | |
| $P(C_6H_5)_3$ Triphenyl phosphine | $CO_3^{2-}$ Carbanato | |
| $H_2N.CS.NH_2$ Thiourea | $O^{2-}$ Oxo | |
| $H_2N.CH_2.CH_2.NH_2$ Ethylene diammine | $Cl^-$ Chloro | |
| | $I^-$ Iodo | |
| | $O_2^{2-}$ Peroxo | |
| | $C_2O_4^{2-}$ Oxalato | |
| | $CH_3COO^-$ Acetato | |

**Coordination number:** Number of electron pairs arising from ligand donor atoms to which the metal is directly bonded (or) the number of coordinate bonds around the central metal atom in a complex compound is called as co-ordination number of the metal. Coordination number range from 1 to 12. (For some f –block elements it is greater than 12 also).

**Types of ligands:**

**a) <u>Unidentate</u>:** Ligand which binds to a metal through a single point of attachment.
Ex : $NH_3, H_2O,\ X^-\left(Cl^-, Br^-, I^-\right), O_2^{2-}$ etc.

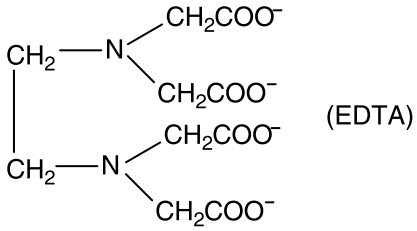
**b) <u>Bidentate:</u>** Ligand which binds to a metal through two points.

Ex: : Ethylene diammine $(H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2)$

$C_2O_4^{2-}$ (oxalato) etc.

**c) <u>Polydentate</u>:** Several donor atoms are present in one molecule.

Ex :




(EDTA)

Ethylene diamminetetra acetate

**8. Explain the concept of isomerism in coordination complexes.**

**Isomerism:** Two or more compounds having the same molecular formula but different properties are called isomers and the phenomenon is called isomerism.

**Structural isomerism:** the isomers which have same molecular formula but different structural arrangement of atoms or groups of atoms around the central metal ion are called structural isomers.

1) **Ionisation isomerism**: The compounds which have same molecular formula but give different ions in solution are called ionisation isomers.

- In this type of isomerism the interchange of groups within or outside the co-ordination entity.
- The counter ion itself is a ligand in such type of isomers.

Ex: 1. $[Co(NH_3)_4ClBr]Cl$ and $[Co(NH_3)_4Cl_2]Br$

$[Co(NH_3)_4ClBr]Cl \rightarrow$

Tetramminebromochloro cobalt (III) chloride $[Co(NH_3)_4Cl_2]Br \rightarrow$

Cobalt tetrammine dichloro (III) bromide

2. $[CoBr(NH_3)_5]SO_4$ and $[CoSO_4(NH_3)_5]Br$

$[CoBr(NH_3)_5]SO_4 \rightarrow$

Pentamminebromo Cobalt (III) sulphate

$[CoSO_4(NH_3)_5]Br \rightarrow$

Pentamminesulphato Cobalt(III)bromide

2) **Hydrate isomerism:**

The compounds which have the similar molecular formula but differ in the number of water molecules present as ligands or as molecules of hydration are called hydrate isomers.

- This isomerism is similar to that of ionisation isomerism.
  Ex : $[CrCl_3(H_2O)_3]$, $[CrCl(H_2O)_5]Cl_2.H_2O$ and
  $[CrCl_2(H_2O)_4]Cl.2H_2O$

**3) Co-ordination isomerism:**

- The type of isomerism occurs in compounds containing both cationic and anionic entities and the isomers differ in the distribution of ligands in the co-ordination entity of cationic and anionic parts.

Ex: i) $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $[Cr(NH_3)_6]$ $[Co(CN)_6]$
ii) $[Cu(NH_3)_4]$ $[PtCl_4]$ and $[Pt(NH_3)_4]$ $[CuCl_4]$

**4) Linkage isomerism:**

The compounds which have the same molecular formula but differ in the mode of attachment of a ligand to the metal atom or ion are called linkage isomers.

Ex: $[Co(ONO)(NH_3)_5]Cl_2$ and $[Co(NO_2)(NH_3)_5]Cl_2$

| Pentaamminenitrito cobalt (III) chloride | Pentaamminenitro cobalt (III) chloride |
|---|---|

- In complex 'A' oxygen atom of $NO_2^-$ is the electron pair donar and in B nitrogen atom of $NO_2^-$ is the electronpair donar $NO_2^-$ is ambidentate ligand.
- **Ambidentate liands :** The unidentate ligands which can bind to the central atom through two donor atoms are called as ambidentate ligands.
  Ex : – CN (cyano), –NC (iso cyano)
  – SCN (thiocyanato), –NCS (isothiocyanato).

**5) Stereoisomers:**

The isomers which have the same position of atoms or groups but they differ in the spatial arrangements around the central atom. Stereoisomerism is of tow types (a) Geometrical isomerism and (b) Optical isomerism.

**i) Geometrical isomerism:**

This kind of isomerism gives rise to two kinds of isomers, namely cis and trans isomer.

**Cis isomer:**

- When two ligands of same type occupy adjacent positions in co-ordination sphere of the central atom then it is called as cis isomer.

**Trans isomer:**

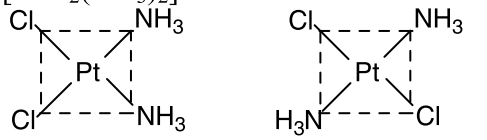
- When two ligands of same type occupy opposite positions to each other in co-ordination sphere of the central atom then it is called as trans isomer.
- Geometrical isomerism is important in complexes of co-ordination number 4 or 6.

**Geometrical isomerism in complexes of co-ordination number 4:**

- Complexes having co-ordination number 4 adopt tetrahedral or square planar geometry.
- Geometrical isomerism is not possible in tetrahedral complexes.
- Square planar complexes of the type $MA_2X_2$, $MA_2XY$, $MABX_2$, MABXY can exist as geometrical isomers.

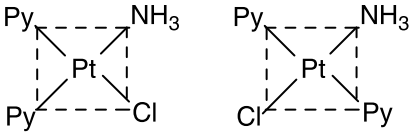
(Here A and B are neutral ligands such as $H_2O$, $NH_3$, CO, NO, $C_2H_5N$ whereas X and Y are anionic ligands such as $Cl^-$, $NO_2^-$, $CN^-$, $SCN^{-1}$ etc.)

1) $[PtCl_2(NH_3)_2]$



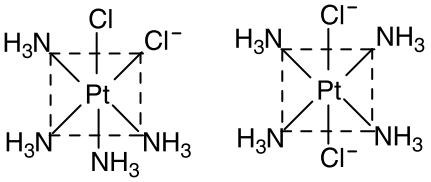

Cis-(Pale yellow) Trans (Dark yellow)

2) $[PtCl(C_5H_5N)_2(NH_3)]$



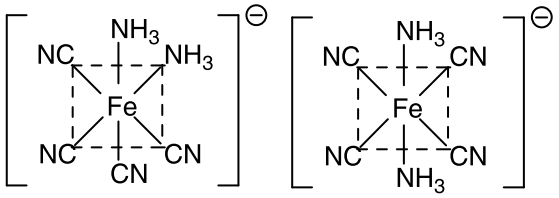

Cis Trans

- Geometrical isomerism is also shown by octahedron complexes in which the co-ordination number of the central metal atom is 6.
- $MA_2X_4$, $MA_4X_2$, $MA_4XY$ etc. types of complexes exhibit geometrical isomerism. Ex: $[CoCl_2(NH_3)_4]^+$




Cis-(Violet) Trans(Green)

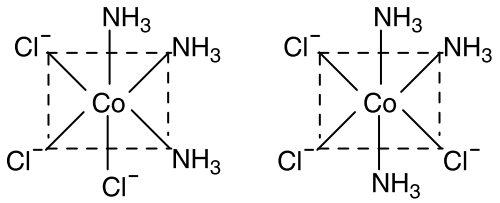
2) $[Fe(CN)_4(NH_3)_2]^-$




**Cis** **Trans**

- Octahedral complexes of the type $[MA_3B_3]$ like $[Co(NO_2)_3(NH_3)_3]$ also exist in two geometrical isomers.
- When the three ligands (with same donor atoms) are on the same triangular face of the octahedron, the isomer is called facial or fac isomer.
- When the three ligands are on the same equatorial plane of the octahedron i.e. around the meridian of the octahedron, the isomer is called meridional or merisomer.

  Ex : $[CoCl_3(NH_3)_3]$




**Fac isomer** **Meridional isomer**

- In facial isomer, the three ligands are at the corners of a triangular face while in meridional isomer, the three ligands are at the three corners of a square plane.

**Optical isomerism:**

- The isomerism which arises due to the rotation of the plane of a polarised light in a polarimeter is called as optical isomerism.
- The isomer which rotates plane polarised light towards right side is called dextro rotatory substance denoted by d – or ( +).
- The isomer which rotates plane polarised light towards left side is called laevorotatory substance denoted by l – or (–).
- Optical isomers are called as enantiomorphs or enantiomers.

**Enantiomers:**

- A pair of substances with same molecular formula but differ in the rotation of plane polarised light are called as enantiomers.
- Enantiomers are non –super imposable.

**Racemic mixture:**

- A 1 : 1 equilibrium mixture of d – and l – forms which gives a net zero rotation of plane polarised light is called as racemic mixture.

## SHORT ANSWER QUESTIONS

**1. Write an example for double salt?**

**Ans:** Those compounds which loose their identity in solution are called double salts. They exist in crystalline state.

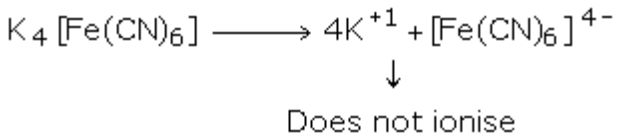
**Double salt**: Ionizes completely in solution.

Example:

$$FeSO_4(NH_4)_2SO_4 6H_2O \longrightarrow Fe^{2+} + 2NH_4^+ + 2SO_4^{2-} + 6H_2O$$

The complex ion: The complex ion does not dissociate.

Example:




2. **Write the difference between double salt and complex compound. ?**
   Even though, both double and complex salts contain two metal ions and may be large salts with have many anions attached to them. They differ in one basic way, when dissolved double salts break down to give it constituent ions, whereas complex salts does not break down in the same manner. Rather when dissolved complex salts give the cation and a complex ion. Also, when double salts are tested for presence of their constituent ions, for example KClMgCl.6H2O when tested for presence of K, will give a positive result, whereas a complex ion would not.

3. **Define ligand.**

**Ligand:** An ion or a molecule that can have an independent existence and can donate a pair of electrons. Ligand can be negative, neutral or positive.

**Formula and names of some ligands**

| **Neutral ligands** | **Negative ligands** | **Positive Ligands** |
|---|---|---|
| $H_2O$ aqua | $OH^-$ hydroxo | $NO_2^{\oplus}$ nitronium |
| CO carbonyl | $F^-$ Fluoro | $NO^{\oplus}$ Nitrosonium |
| $NH_3$ ammine | $Br^-$ Bromo | $(NH_2NH_3)^+$ hydrazinium |

4. **Write two postulates of Werner' theory.**

**<u>Primary valency</u> :**

Normally primary valency is numerically equal to the oxidation state of the metal. The valencies are non directional and are represented by discontinuous lines (-------). Species or groups bound by primary valencies undergo complete ionisation . Primary valency applies equally to metals in simple salts as well as those in complex compounds. These valencies are identical with ionic bonds. In $CoCl_3$ , ( $Co^{+3}$ and $3Cl^-$ are present ) . There are three primary valencies i.e. three ionic bonds present .

**<u>Secondary valency</u>:**

The secondary valencies are directed in space around the central metal in a symmetric order . Each metal has a characteristic number of secondary valencies .

**5. Give the draw backs of Werner's theory.**

- Werner's theory does not correlate electronic configuration of the central metal with the formation of the complex compounds.
- Postulates of Werner do not offer any explanation to the colour and magnetic behaviour of complex compounds.

**6. Write the formula to calculate the EAN of a central metal atom.**

**Ans:**

If the EAN of the central metal is equal to the number of electrons in the nearest noble gas then the complex possess greater stability.

**EAN** = [(atomic number of central metal) – (the oxidation state of the metal) + (the number of electrons gained by the metal from the ligands through co- ordination)]

= [Z metal – (ox.state of the metal) + 2(coordination number of the metal)].

**7. Give an example for the ionization isomerism.**

**Ionisation isomerism**: The compounds which have same molecular formula but give different ions in solution are called ionisation isomers.

- In this type of isomerism the interchange of groups within or outside the co-ordination entity.
- The counter ion itself is a ligand in such type of isomers.
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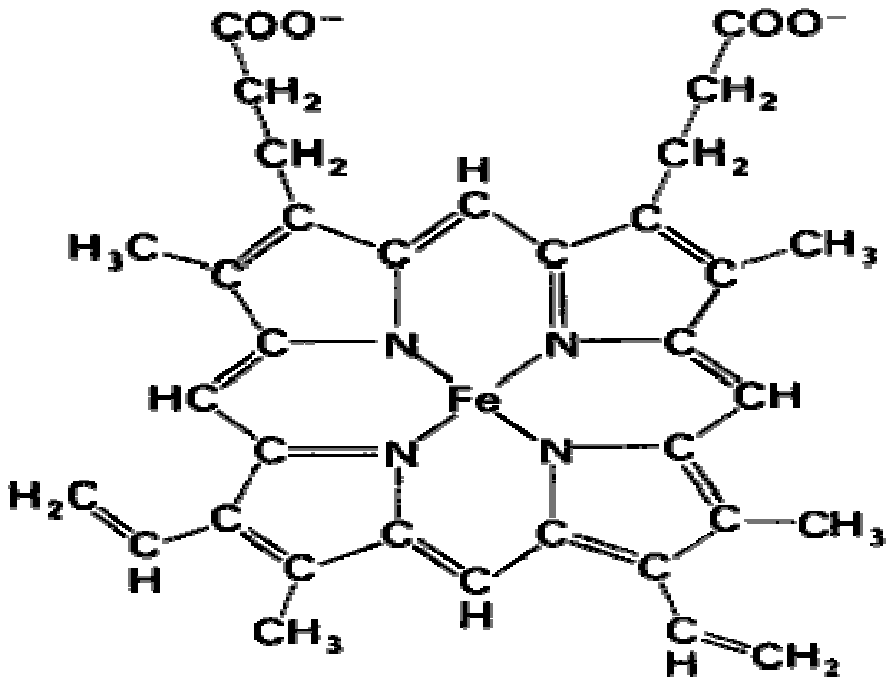
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Pentamminebromo Cobalt (III) sulphate

$[CoSO_4(NH_3)_5]Br \rightarrow$

Pentamminesulphato Cobalt(III)bromide

**8. Mention a complex that is present in biological systems.**




**Heme**
**(Fe-protoporphyrin IX)**

## VERY SHORT ANSWER QUESTIONS

**1. What double salt?**

**Ans: Double salts:** Double salts are those compounds which exist only in crystal lattice and lose their identity when dissolved in water. Ex: Mohr's salt $FeSO_4$. $(NH_4)_2SO_4.6H_2O$.

2. **Define co-ordination compound.**

**Ans: Coordination or Complex compounds:**

Coordination compounds are those molecular compounds which retain their identities when dissolved in water or any other solvent and their properties are different from those of the constituents. Ex: $K_4[Fe(CN)_6]$.

$Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + Fe(CN)_6^{4-}$

**3. What is complex ion?**

**Ans: Complex ion (or) Coordination entity :**

It may be defined as an electrically charged (cationic or anionic) or even a neutral species which is formed by the combination of a simple cation with more than one neutral molecule or negative ion.

Ex: $[Ag(NH_3)_2]^+$

**4. What is co-ordination number?**

**Ans: Coordination number:** Number of electron pairs arising from ligand donor atoms to which the metal is directly bonded (or) the number of coordinate bonds around the central metal atom in a complex compound is called as co-ordination number of the metal. Coordination number range from 1 to 12. (For some f –block elements it is greater than 12 also).

**5. Define EAN.**

**Ans: Effective Atomic Number (EAN):**

The sum of the number of electrons, donated by all ligands and those present on the central metal ion or atom in complex is called as effective atomic number (EAN).

**6. Write a short note on primary valency**

**Primary valency :** Normally primary valency is numerically equal to the oxidation state of the metal . The valencies are non directional and are represented by discontinuous lines (-------) . Species or groups bound by primary valencies undergo complete ionisation . Primary valency applies equally to metals in simple salts as well as those in complex compounds. These valencies are identical with ionic bonds. In $CoCl_3$, ( $Co^{+3}$ and $3Cl^-$ are present ). There are three primary valencies i.e. three ionic bonds present