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Subject: Chemistry

Class: Semester-4

Paper: C9T: Inorganic Chemistry

Topic: Coordination Chemistry

Part 3

Comments- Study the whole lesson thoroughly.Specially the topics **“chelate effect, Ionisation isomerism,Co-ordinate isomerism, linkage isomerism, ligand isomerism with examples”** are more important for preparation of examination. Also complete the given assignment.

[N.B. - Acknowledgement of indebtedness to Mr.Sibshankar Das, my respected Teacher regarding collection of study materials in Inorganic Chemistry**]**

Chelatē Effect:

The chelatēd complexes are known to be more stable than the non chelatēd complexes. This effect is known as chelatē effect.

Explanation :

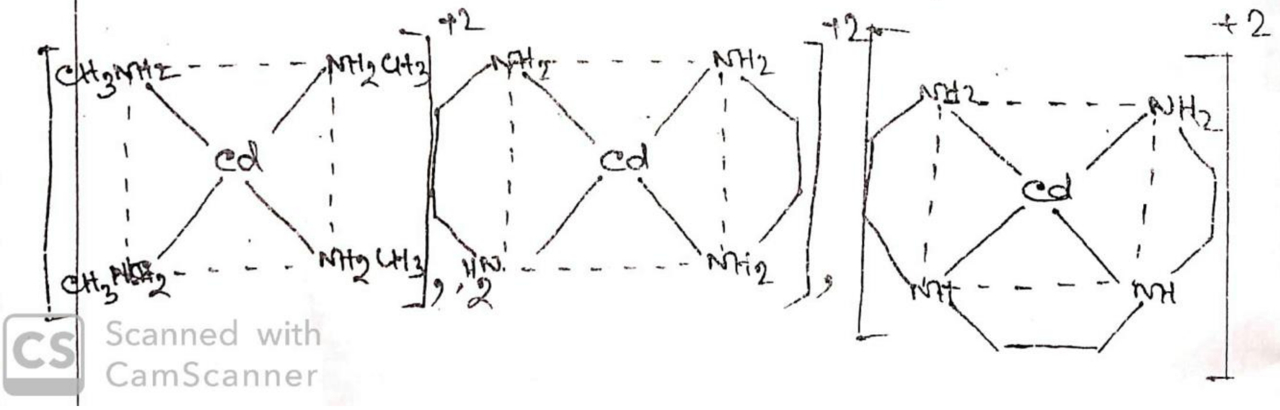
chelatē effect can be explained by considering the formation of some nonchelatēd and chelatēd complex ion of same metal. $[Cd(H_2O)_4]^{+2}$ form four coordinatēd complex ion with CH_3NH_2, en and triene which are formulatēd as $[Cd(CH_3NH_2)_4]^{+2}$, $[Cd(en)_2]^{2+}$, $[Cd(triene)]^{+2}$ resp.

$$[Cd(H_2O)_4]^{+2} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4]^{+2} + 4H_2O \quad \longrightarrow i)$$

$$[Cd(H_2O)_4]^{+2} + 2en \rightleftharpoons [Cd(en)_2]^{+2} + 4H_2O \quad \longrightarrow ii)$$

$$[Cd(H_2O)_4]^{+2} + triene \rightleftharpoons [Cd(triene)]^{+2} + 4H_2O.$$

The structure of the complex ions formed in the above reacⁿ are shown in figure below



These above str^r shows that $[Cd(CH_3NH_2)_4]^{2+}$ has no rings while $[Cd(en)_2]^{+2}$ and $[Cd(triene)]^{+2}$ ions have two and three 5-membered rings respectively including Cd^{+2} ion. In each complex ion the co-ordination no. of Cd^{+2} ion is equal to 4. Since CH_3NH_2, en, and triene are the monodentate, bidentate and tetradentate ligand respt.

Since $[Cd(en)_2]^{+2}$ and $[Cd(triene)]^{+2}$ ions are chelated ions, each of these ~~is~~ more stable than $Cd(CH_3NH_2)_4]^{+2}$ ion which is a non chelated ion. It has been found that the stability of these ions is in the order $[Cd(CH_3NH_2)_4]^{+2} <$ $Cd(en)_2]^{+2} < [Cd(triene)]^{+2}$.

The above order can be explain on the basis of ΔG° value of rea^n i), ii) iii). The value of ΔG° for a rea^n is given by the relation :

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The value of ΔH° for all the three rea^n has been found to be (−)ve. It has been found that larger is the (−)ve value of ΔG°, greater is the stability of the complex ion.

In rea^n i), since the no. of molecules on the RHS is the same as that on LHS, there is no change in the entropy in going from reactants to pdts.

ie, $\Delta G^\circ = \Delta H^\circ$ ~~$- T\Delta S$~~ $=$ (−)ve quantity

In rea^n ii), since 4 molecules of $4H_2O$ are replaced by 2en, there is an increase of two molecules on going from reactants to products and hence there is an increase in the value of ΔS° in the same direction. Thus ΔS° would have a large (+)ve value. This implies that ΔG° would be a larger (−)ve quantity than that of rea^n i)

In reac^n iii), since 4 molecules of H_2O are replaced by one molecule of triene ~~in reac^n iii~~ there is an increase of three molecule on proceeding from reactants to pdts and hence there is a greater increase of magnetude of ΔS° in the same direction. Thus ΔS° would have a larger (+)ve value. this implies that ΔG° would be a larger (-)ve quantity and it is larger than that of reac^n ii)

Therefore, magnetude of the (-)ve ΔG° value increases in the order $[Cd(CH_3NH_2)]^{2+} < Cd(en)_2]^{2+} < Cd(triene)]^{2+}$. Thus $Cd(triene)]^{2+}$ is more stable $[Cd(en)_2]^{2+}$ which is more stable than $[Cd(CH_3NH_2)_4]^{2+}$

// $[Co(en)_3]^{3+}$ is more stable than $[Co(NH_3)_6]^{3+}$ — explain.

$[Co(en)_3]^{3+}$ is more stable than $[Co(NH_3)_6]^{3+}$ It is explained with the help of chelate effect. Two factors may be considered to be responsible for such effect.

The 1st one is to consider the diff. in dissociation b/w $[Co(en)_3]^{3+}$ and $[Co(NH_3)_6]^{3+}$ If one NH_3 molecule dissociates, it has little probability or returning to its former site but if one of the $-NH_2$ gr of 'en' dissociates the ligand is retained by the other end still attached to the metal. The dissociated ~~ea~~ N-atom can move only a few picometers away and can swing back and attached to the metal ion. Thus the chelate has a smaller probability of dissociation than the non chelate complex.

The 2nd one is to consider the following eqn

$[Co(NH_3)_6]^{3+} + 3en \rightleftharpoons [Co(en)_3]^{3+} + 6NH_3$

Since the bonding of NH_3 and en is very similar, ΔH for this reaⁿ should be approximately zero. The change in entropy of this reaⁿ will be proportional to the difference in the number of particles present in the system. The reaⁿ proceed to the right with an increase in no. of particles. Hence entropy factor favours the production of the chelate complex. Therefore $[Co(en)_3]^{3+}$ complex is more stable $[Co(NH_3)_6]^{3+}$ complex.

Inner Metallic Complexes :

There are some chelating ligands which contains a neutral donor group and acidic donor group in their strʳ and they satisfy both the primary and secondary valency of the metal ion and form neutral chelate. Such chelate are known as inner metallic complex or simply inner complexes of the 1st order.

These chelate compounds are non electrolytes with very low solubility in water but high solubility in organic solvent.

Examples of ligands which form inner metallic complexes are acetyle acetone (acacH), Glycene (Gly-H) Dimethyl glyoxime (DMG-H) etc and the complexes are $[Pt(gly)_2]$, $[Ni(DMG)_2]$, $[Be(acac)_2]$ $[Co(gly)_3]$, $[Co(acac)_3]$ e

When the chelating ligand containing both a neutral and acidic donor group, can not satisfy the primary valency of the metal ion, The resulting complex itself becomes an ion and requires other ion for charge neutralisation. The complex formed is known as inner complexes of 2nd order.

eg $[Si(acac)_3]Cl$, $[B(acac)_2][\overset{III}{Fe}Cl_4]$, $K[\overset{II}{Pt}(acac)Cl_2]$ etc

Properties of Inner metallic Complex :

The properties of inner metallic complexes are given below

i) Many of them are insoluble in water but may be extracted into organic solvents

ii) There is some times pronounced colour change during the formation of inner complexes. This permits colourimetric measurements

iii) Most of the inner complexes have low melting pt. and are volatile.

Application of Inner metallic complex :

See application of chelate complex (i, ii, iii, iv, vi).

Which of the following chelating ligands have the ability to form inner metallic complex with Co^{+2} and Co^{+3}?

i) $\begin{array}{l} COOH \\ | \\ COOH \end{array}$ ii) $\begin{array}{l} COOH \\ | \\ CH_2NH_2 \end{array}$ iii) $\begin{array}{l} CH_2NH_2 \\ | \\ CH_2NH_2 \end{array}$ iv) $\begin{array}{l} CH_2-COOH \\ | \\ CH\cdot NH_2 \\ | \\ CH_2NH_2 \end{array}$ v) $\begin{array}{l} CH_2COOH \\ | \\ NH \\ | \\ CH_2COOH \end{array}$

vi) $\begin{array}{l} CH_2-COOH \\ | \\ N-CH_2COOH \\ | \\ CH_2COOH \end{array}$.

According to Werner's coordination theory, the CN of Co(II) is 4 and 6 but Co(III) is only 6. Here we shall consider the inner complexes of 1st order only in each of the complexes the CN of the metal ion and the balance of the charged must be considered. The given ligands are -

$\begin{array}{l} COOH \\ | \\ COOH \end{array}$	$\begin{array}{l} COOH \\ | \\ CH_2NH_2 \end{array}$	$\begin{array}{l} CH_2NH_2 \\ | \\ CH_2NH_2 \end{array}$	$\begin{array}{l} CH_2COOH \\ | \\ CH\cdot NH_2 \\ | \\ CH_2NH_2 \end{array}$
2-anionic sites	one anionic and 1 neutral	2-neutral sites	1-anionic and 2-neutral sites

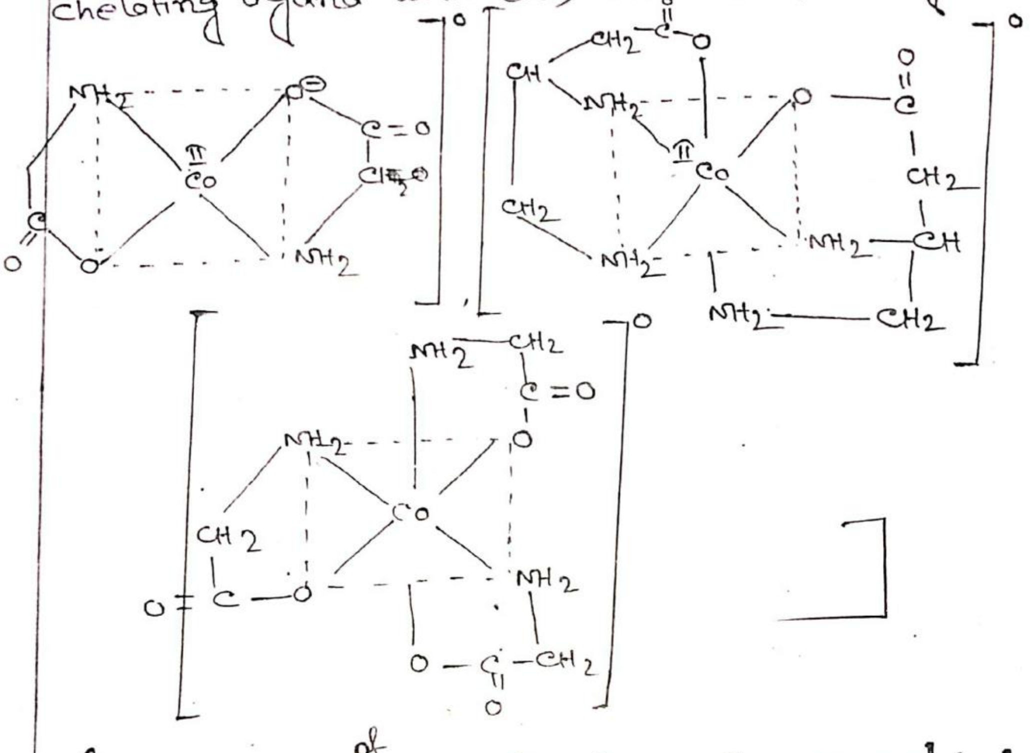
v) CH_2COOH
NH
CH_2COOH
2-anionic, 1 neutral site

vi) CH_2COOH
$N - CH_2 \cdot COOH$
CH_2COOH
3-anionic and 1-neutral site

[redacted]

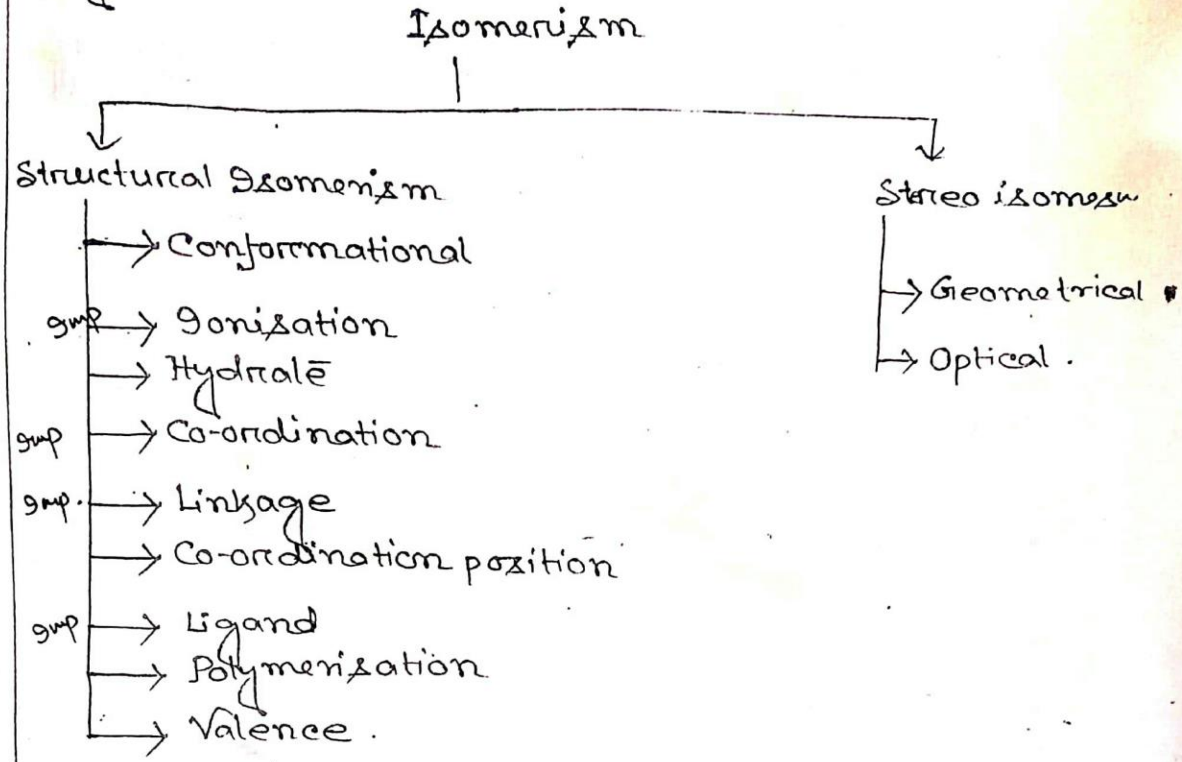
Therefore to maintain the charge and coordination no the ligand ii) and iv) have the ability to form innerr metallic complex with Co(II) ion.

In the same reason the ligand ii) has the ability to form innerr metallic complex with Co(III) ion. Hence the innerr metallic complexes formed by the cheloting ligand with Co(II) and Co(III) are given below.



Isomerism of Co-ordination Compounds :

The co-ordination compounds which have the same molecular formula but have their ligand attached to the central metal atom in diff. ways are called isomers. Isomers have diff. properties. The phenomenon that gives rise to different isomers is called isomerism different type of isomerism in complex compd may be classified as follows.



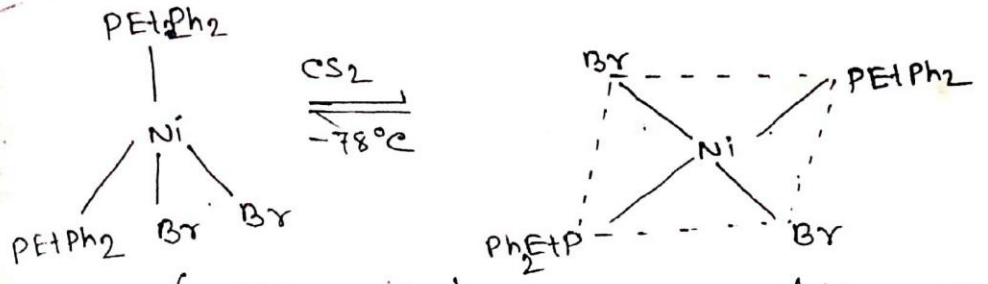
A **Structural Isomerism :**

This isomerism arises due to the diff. in the structure of complex compound. This isomeris is of the following types.

i) Conformational isomerism :-

In this isomerism two isomers have diff. geometries.

eg $[Ni(PEtPh_2)_2Br_2]$ complex gives two conformational isomers. One of these is green and paramagnetic while the other is brown and diamagnetic. The green formed is tetrahedral while the brown form is square planar. Thus these have diff. geometries but the 'cn' of Ni^{+2} ion in both the isomers is the same (cn=4). This type of isomerism is called polytopal isomerism.



green (paramagnetic)   Brown (diamagnetic)

ii) Ionisation isomerism :

Compounds having the same molecular formula but dissociate in solution to produce diff. ions, are called ionisation isomers and the phenomenon is known as ionisation isomerism.

eg:

Ionisation isomers	Mode of ionisation.
i) $[Co(NH_3)_5Br]SO_4$	$[Co(NH_3)_5Br]^{2+} + SO_4^{=}$
$[Co(NH_3)_5SO_4]Br$	$[Co(NH_3)_5SO_4]^{+} + Br^{-}$
ii) $[Co(en)(NO_2)Cl]SCN$	$[Co(en)(NO_2)Cl]^{+} + SCN^{-}$
$[Co(en)(NO_2)SCN]Cl$	$[Co(en)(NO_2)SCN]^{+}\ Cl^{-}$
$[Co(en)(SCN)(Cl)]NO_2$	$[Co(en)(SCN)(Cl)]^{+}\ NO_2^{-}$
iii) $[Co(NH_3)_4Cl(NO_2)]Cl$	$[Co(NH_3)_4Cl(NO_2)]^{+} + Cl^{-}$
$[Co(NH_3)_4Cl_2]NO_2$	$[Co(NH_3)_4Cl_2]^{+} + NO_2^{-}$.

iii) Hydrate Isomerism :

The compounds having same molecular formula but diff. no. of H_2O molecules in the 1st and 2nd co-ordination sphere are called hydrate isomers, and the phenomenon is known as hydrate isomerism. , $CrCl_3 \cdot 6H_2O$ exist in three hydrate isomer which are $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

These have diff. physical and chemical properties.

$[Cr(H_2O)_6]Cl_3$ (violet) $\rightarrow$ $\xrightarrow{\text{conc. } H_2SO_4}$ No weight loss.

$\xrightarrow{\text{Excess } AgNO_3}$ $3AgCl\downarrow$

$[Cr(H_2O)_5Cl]Cl_2$ (blue green) $\rightarrow$ $\xrightarrow{\text{conc. } H_2SO_4}$ weight loss for 1 mole H_2O.

$\xrightarrow{\text{Excess } AgNO_3}$ $2AgCl\downarrow$

$[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$ (green) $\xrightarrow{\text{conc } H_2SO_4}$ weight loss for 2 mole H_2O.

$\xrightarrow{\text{exess } AgNO_3}$ $1AgCl\downarrow$

Imp

iv) Co-ordination Isomerism :

This type of isomerism is shown by those complex compound which are composed of complex cation and complex anion. Ligands may be interchange b/w the complex cationic and anionic parts of a compound to produce co-ordination isomers and the phenomenon is known as coordination isomerism.

eg: $[Co(NH_3)_6][Cr(CN)_6]$ & $[Co(CN)_6][Cr(NH_3)_6]$

$[Pt(NH_3)_6][PtCl_6]$ & $[Pt(NH_3)_4Cl_2][PtCl_4(NH_3)_2]$.

$[Cu(NH_3)_4][PtCl_4]$ & $[Pt(NH_3)_4][CuCl_4]$.

Imp

v) Linkage Isomerism :

The ligands which have two or more donor atoms but in forming complexes only one donor atom is attached to the metal ion at a given time, such ligands are called ambidentate ligand.

Different modes of co-ordination of these ligand to the same metal ion produce linkage isomer and the phenomenan is known as linkage isomerism.

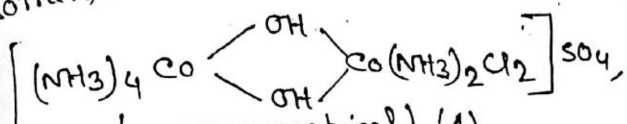
eg i) $[Co(NH_3)_5NO_2]Cl_2$, (nitro complex, yellow) and $[Co(NH_3)_5(ONO)]Cl_2$ (Nitrido complex, red)

ii) $[Co(NH_3)_5SSO_3]Cl$ and $[Co(NH_3)_5OSO_2S]Cl$.
Thiosulphato-S-complex Thiosulphato-O-complex.

Co-ordination position Isomerism :

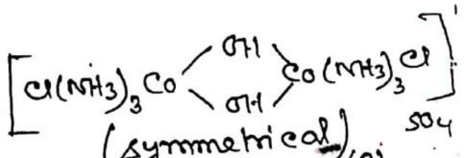
This type of isomerism is shown by those complex compound which contain bridging ligand, this arises when the non bridging ligands are differently placed around the metal ion. Thus the compounds (1) and (2) are the co-ordination position isomers to each other.

i)



$\left[(NH_3)_4Co\begin{smallmatrix}OH\\ \\OH\end{smallmatrix}Co(NH_3)_2Cl_2\right]SO_4$

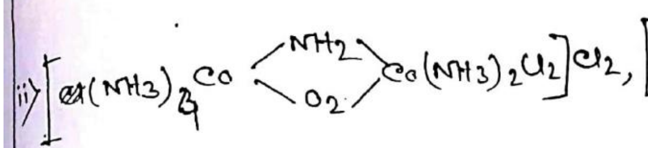
(unsymmetrical) (1)



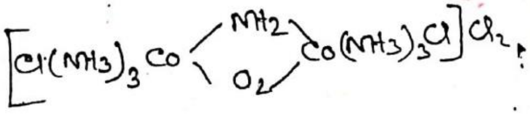
$\left[Cl(NH_3)_3Co\begin{smallmatrix}OH\\ \\OH\end{smallmatrix}Co(NH_3)_3Cl\right]SO_4$

(symmetrical) (2)

ii)



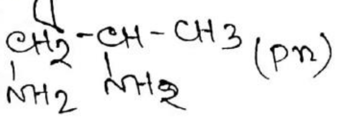
$\left[Cl(NH_3)_4Co\begin{smallmatrix}NH_2\\ \\O_2\end{smallmatrix}Co(NH_3)_2Cl_2\right]Cl_2$,



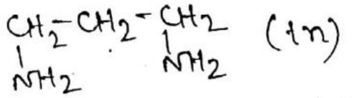
$\left[Cl(NH_3)_3Co\begin{smallmatrix}NH_2\\ \\O_2\end{smallmatrix}Co(NH_3)_3Cl\right]Cl_2$,

Ligand Isomerism :

There are certain ligands which exist as isomers eg Di-amine derivatives of propane exist in two isomeric form which are called 1,2-diamino propane or propyline diamine (pn) and 1,3-Diamino propane (tn) or trimethyline diamin (tn). The stru^r of 'tn' and 'pn' are givens below.



$\underset{NH_2}{CH_2}-\underset{NH_2}{CH}-CH_3$ (pn)



$\underset{NH_2}{CH_2}-CH_2-\underset{NH_2}{CH_2}$ (tn)

'pn' and 'tn' both are bidentate ligands when these ligand get coordinated to the metal atom two isomers are obtained these are called ligand isomers and the phenomenon is called ligand isomerism. Thus, $[Co(pn)_2Cl_2]Cl$, $[Co(tn)_2Cl_2]Cl$ are ligand isomers.

iii) Polymerisation Isomerism :

This type of isomerism is found in those complex compound whose formula appear to be polymers of some simple complex compound. All those complex compound have the same ratio of diff metal atoms and ligands in them.

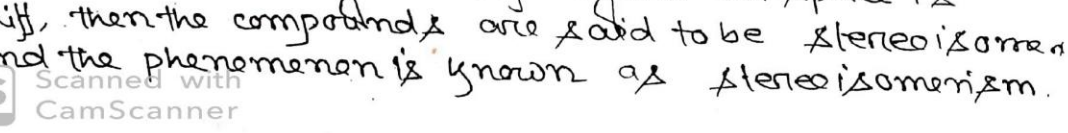
eg The following complex compounds are polymeric isomer to each other, since ii) and iii) compd appear to be dimer of i) compound and compound iv) appears to be the pentamer of compd i) The ratio $Co^{+3} : NH_3 : NO_2^-$ in all the compounds is 1:3:3.

Complex	No of Co^{+3}	NH_3	NO_2^-
i) $[Co(NH_3)_3(NO_2)_3]$	1	3	3.
ii) $[Co(NH_3)_6][Co(NO_2)_6]$	2	6	6
iii) $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$	2	6	6
iv) $[Co(NH_3)_5NO_2]_3[Co(NO_2)_6]_2$	5	15	15

x) Valency Isomerism

The term was used by Werner to complex species in which the same gr. is held in one compound by primary valency and in another compd by secondary valency.

eg



$$\left[\cancel{NH_3}(en)_2Co\left\langle\begin{matrix}NH_2\\ \underset{(-)}{O_2}\end{matrix}\right\rangle Co(en)_2\right]X_4 \text{ and } \left[(en)_2Co\left\langle\begin{matrix}\overset{\cdot HX}{NH_2}\\ \underset{(2-)}{O_2}\end{matrix}\right\rangle Co(en)_2\right]X_3$$

Stereo Isomerism :-

When two compound contain the same ligands co-ordinated to the same central metal ion but the arrangement of ligand in space is diff, then the compounds are said to be stereoisomer and the phenomenon is known as stereoisomerism.

: Assignment :

1. What is Secondary valency ?

2. $CoCl_3 \cdot 6NH_3$ - The compound contains three Cl^- ion which is precipitated immediatly on the addition of Ag^+. Draw the structure of the compound on the basis of werner's theory.

3. Write the names of the following complex compound according to IUPAC system of nomenclature.

ⓐ $[Co(en)_3]SO_4$ ⓑ $K_2[Ni(CN)_4]$

ⓒ $[Fe(NH_3)_6][Fe(CN)_6]$ ⓓ $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

4. The chelated complexes are more stable than non chelated complexes — Explain.

5. Give examples of Linkage and Ligand isomerism.