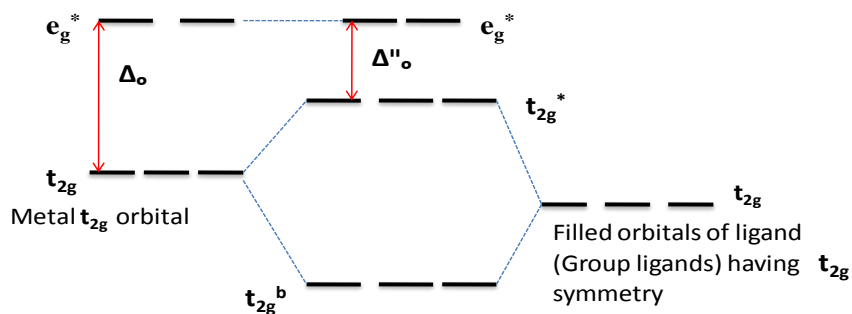


2. Filled π orbital ligand (π -donor): Examples Cl^- , Br^- , F^- , I^- , SCN^- etc

Here t_{2g} of ligand is having filled electrons and having lower energy than the metal t_{2g} orbital because of more electronegative nature of ligand than the metal atom. When π bond is formed by the sideways overlapping of these two orbitals, the electron is donated from from ligand t_{2g} orbital to metal t_{2g} orbital. As the ligand t_{2g} orbital is lower in energy the bonding molecular orbital is more resemble to ligand orbital ie the ligand orbitals are more stabilized whereas the antibonding molecular orbital (t_{2g}^*) is more resemble to metal t_{2g} orbital ie the metal t_{2g} orbital is destabilized. However the metal e_g^* is not disturbed by the formation of π bond since they take part in the σ bond formation due to their lobes are directed along the axes. Therefore the d-splitting is decreased due to the formation of π bond. Therefore this type of ligands is kept at the low end of spectrochemical series. In this type of complex is the metal atom is in high oxidation state otherwise due to the increase of electron density around the central atom the stability decreases.

Effect of π donor ligand on the d-splitting of metal atom (Examples: F^- , Cl^- , RO^- , O^{2-} etc)



Δ_o = d splitting after σ bonding

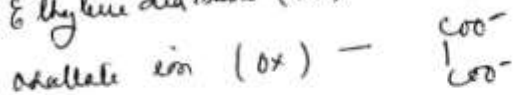
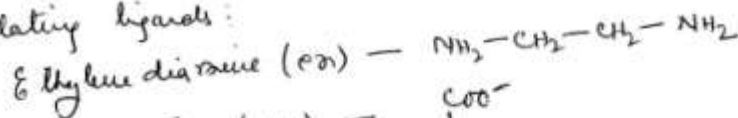
Δ''_o = d splitting after π bonding (d-splitting decreases due to the formation of π bond)

As ligand is more electronegative and have filled pi orbitals, the energy levels of ligand orbital is lower than metal orbital and hence π bonding MO is more resemble to ligand orbital and the π antibonding MO is to metal orbital. Therefore the d-splitting is decreased due to the formation of this type of pi bond. Therefore those ligands which can form π bond of this type are weak ligand since the d-splitting decreases due to formation of π bond.

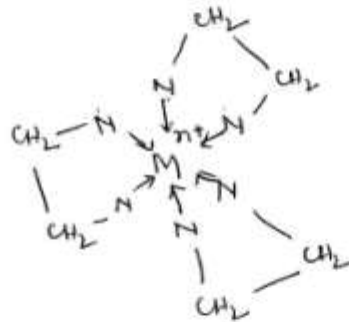
Chelation →

Some of the Polydentate ligands (ligands having two or more donor atoms) can form complex by attaching through all or some of their donor atoms to the metal atom and form one or more rings. This type of complex is called chelate complex and these ligands are called chelating ligands. However it is not necessary that all polydentate ligands should be chelating ligand, there are some other polydentate ligands also that can't form chelate complex. Let us take examples of chelating & non chelating polydentate ligand.

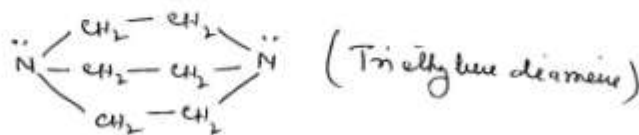
Chelating ligands:



They are chelating ligand because they can form five member ring.



The oxalate ion also can form 5 member ring. However triethylenediamine is not a chelating ligand although it is polydentate ligand.



The stability of a chelate complex is ~~increased~~ some times depends on the no of atoms present in the ring. Generally 5 or 6 membered rings are more stable than the 3 or 4 membered rings. This is because of the increase of strain in the 3 or 4 membered ring.

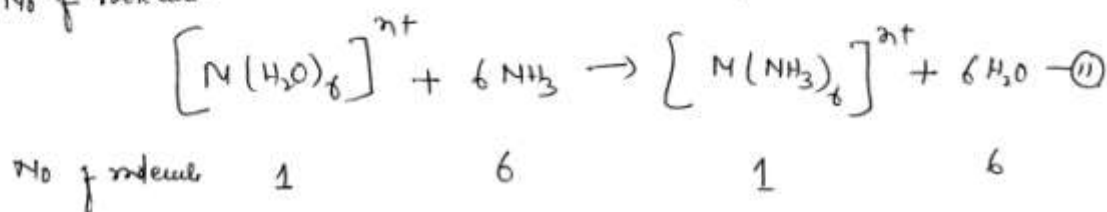
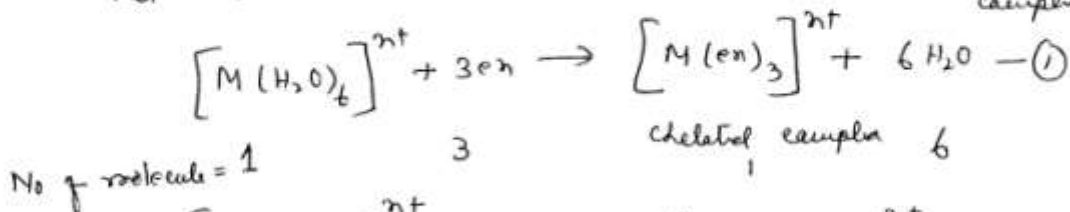
Chelate complex are more stable than the non-chelated complex. This can be explained as the following.

(1) In a chelated complex, the ligands are attached to the central metal atom at least through two donor atoms. So ^{although} if one of the M-L bond is broken, still the other bond is remains attached to the metal atom, therefore the broken bond can be easily re-established. However in case of non-chelated ligand like $[M(H_2O)_6]^{n+}$, if one M-L bond is broken, the ligand leave away from the vicinity of the metal atom, therefore the bond can't be re-established. Thus chelated complex are more stable than the non-chelated complex.

(2) This is very important explanation.

In the chelated complex, due to the increase of entropy the complex is more stable than the non-chelated complex.

Let us take ~~one~~ examples for the formation of chelated and non-chelated complex.



In the first reaction (formation of chelate complex), there is an increase of no of molecules from 4 to 6 where chelate complex is form. In the second reaction, there is no ~~change~~ net change in the no of molecules.

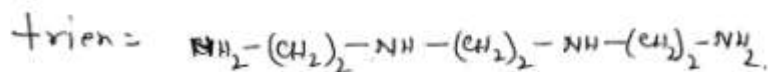
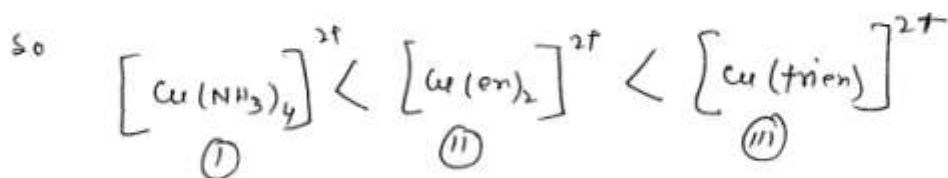
The increase in the no of particles or molecules indicates the increase in the no of disorder & hence entropy. Therefore the entropy increases in the first & no change in the 2nd reaction.

From the thermodynamic, we know that for an spontaneous reaction ΔG should be $-ve$, means the stability increases with the $-ve$ value of ΔG .

$$-RT \ln \beta = \Delta G = \Delta H - T\Delta S$$

β - Stability const. R = Gas const.
 ΔG = Gibbs free energy T = absolute Temp
 ΔH = change of enthalpy ΔS = change of entropy

In both the above reactions, as the donor atom is same, there is no large difference in the ΔH value. Temp is also same. So the stability is due to entropy value. If entropy value is increased, then the value of ΔG becomes more $-ve$, so the complex becomes more stable. In the above two reactions, as there is increase in the entropy value (ΔS) in chelate formation the ΔG value becomes more negative. Therefore the complex is more stable.



Change of entropy ΔS increases in the order.



Isomerism in co-ordination compounds:

⊙ Isomers: Isomers are the compounds which have the same composition but have the different structural arrangements of atoms and the phenomenon of giving isomers is called isomerism.

In co-ordination compounds, isomerism can be discussed into two types.

- ① Structural isomerism.
- ② Stereoisomerism or space isomerism.

Structural isomerism:

Structural isomerism is one of the isomerism types of co-ordination compounds which is arisen due to the difference in the structures of co-ordination comp. Structural isomerism of co-ordination compounds can be classified into the following types

- ① Ionisation isomerism
- ② Hydrate isomerism
- ③ Linkage isomerism
- ④ Ligand isomerism
- ⑤ Co-ordination isomerism
- ⑥ Co-ordination Position isomerism.

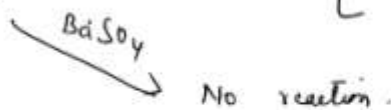
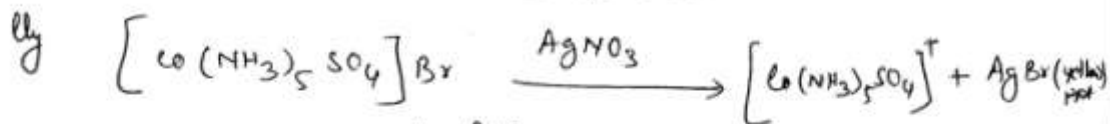
① Ionisation isomerism:

In this type of isomerism, the complex produces different ions in solution. For example $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ + $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$.

Although both complexes ① & ② exhibited same empirical formula, giving different ions in solution.



As different ions are produced in solⁿ, they give precipitate of different compounds on reacting with suitable reagent.



Thus this types of complexes are called ionisation ^{isomers} ~~isomerism~~.

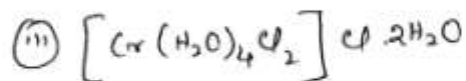
② Hydrate isomerism:

In this type of isomerism, the no of H_2O molecules present in primary sphere is different although they have the same empirical formula. Similarly the no of water molecules present in secondary sphere is also different.

Examples:

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ complex.

which can have three hydrate isomers, they are



Therefore when they are reacted with AgNO_3

Complex ① Produced 3 molecules of AgCl

Complex ② Produced 2 molecules of AgCl

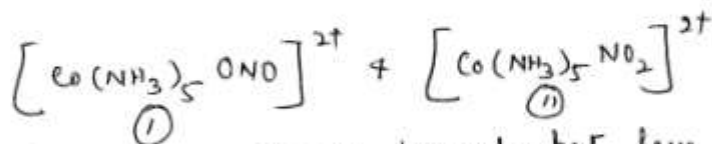
Complex ③ Produced 1 molecule of AgCl .

Note Complex of the type $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$ is logically possible, however still the complex is not found. Therefore for the $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, there is only three hydrate isomers exist.

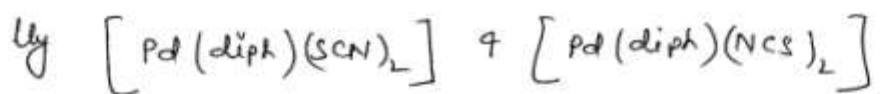
③ Linkage isomerism:

This type of isomerism is shown by those complexes which have ambidentate ligand. Ambidentate ligands are those ligands which have two or more than two donor atoms, but in forming complex only one donor atom is used.

Examples



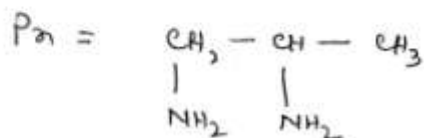
They have the same molecular formula, but have different attachment of ligand to metal atom. In complex no 1 ONO is attached to central atom through O whereas in complex ② NO_2 is attached through N.



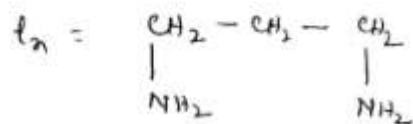
They are linkage isomerism.

(iv) Ligand isomerism is

In this type of isomerism, the ligand itself exists as isomers. For example $[\text{Co}(\text{Pn})_2\text{Cl}_2]^+$ & $[\text{Co}(\text{tn})_2\text{Cl}_2]^+$
Here the ligand Pn & tn have same empirical formula but have different positions for the substituent NH_2 group



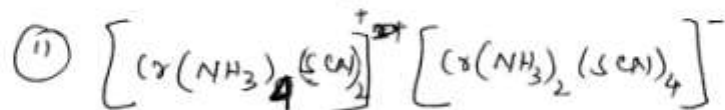
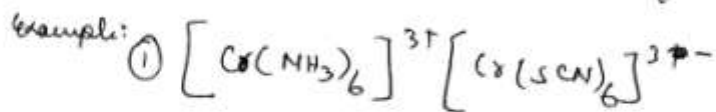
(1, 2, diamino Propane or
Propylenediamine)



(1, 3 diamino Propane)
(trimethylenediamine)

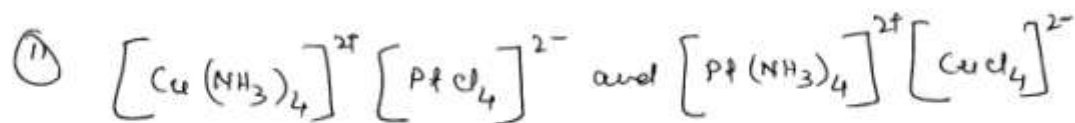
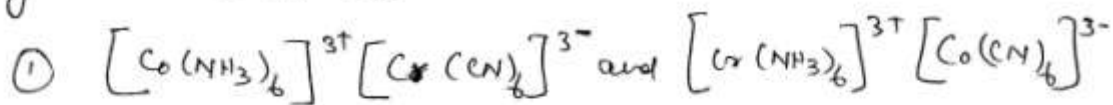
(v) co-ordination isomerism is

This type of isomerism is shown by those complexes which have complex in both cation and anion parts of complex.



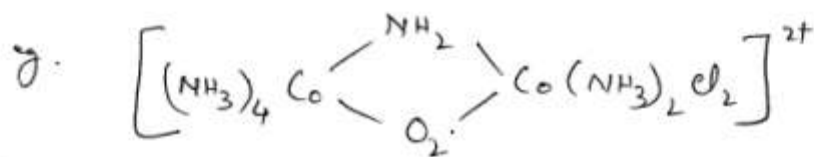
These two complexes have same empirical formula but have different arrangement of ligands. They are formed by exchanging the ligands in cation and anion parts of complex. Because of this exchange of ligands the arrangement of ligand is different.

ly we can have

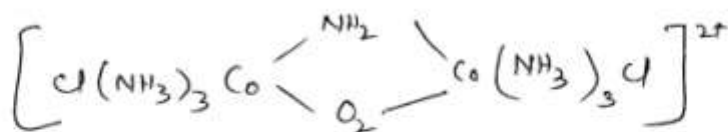


(VI) Co-oxidative Position isomerism:

This type of isomerism is found in polynuclear complexes. In this isomerism there is an interchange of ligands between the metal nuclei.



and



Here there is an interchange of 4 NH_3 ligands in between the two cobalt atoms.