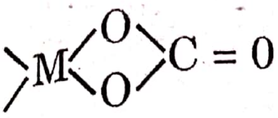
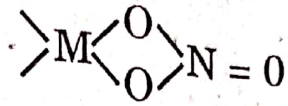
Factors influencing the stabilities of chelates

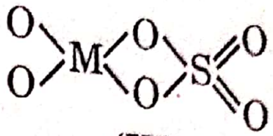
The stability of chelates is mainly due to ring formation. The chalates containing 3-membered ring including the metal are very unstable and hence are unknown. 4-membered chelate rings are rare and occur in carbonate (I), nitrate (II) and sulphate(III) chelates



(I)

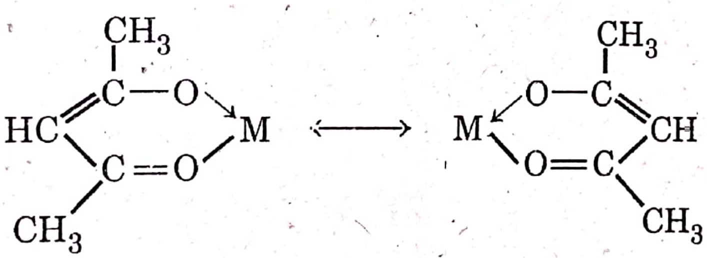


(II)



(III)

The most common and the most stable chelates are 5- and 6-membered chelates. 5-membered chelates are frequently more stable than the 6-membered chelates when the atoms in the ring are joined by single bonds only. On the other hand, 6-membered chelates are more stable than 5-membered chelates of heterocyclic ligands or of ligands involving conjugation in the chelate ring. For example, acetylacetone complexes of the metal ions which contain 6-membered conjugate chelate rings are more stable than the corresponding ethylene diamine complexes which contain only 5-membered chelate rings. In acetylacetone complexes the π-electron density gets spread up over the whole ring which increases the stability of this 6-membered ring system. The possibility of the resonace in its chelate ion is an additional factor contributing to the stability of acetylacetone complexes.



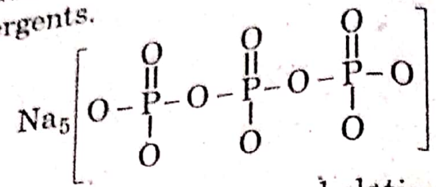
Steric effect. When a bulky group is either attached to or present near the donor atom of a ligand, mutual repulsion among the ligands occurs and consequently the metal-ligand bond is weakened. Thus large bulky ligands form less stable complexes than do the analogous smaller ligands. This effect is commonly referred to as **steric hindrance (Steric effect or Steric strain).** For example, the complexes of ethylenediamine $H_2NCH_2CH_2NH_2$ are more stable than those of the tetramethyl derivative of ethylenediamine $(H_3C)_2NCH_2CH_2N(CH_3)_2$. Thus,

$$[M(NH_2-CH_2-CH_2-NH_2)_3]^{2+} > [M(N(CH_3)_2-CH_2-CH_2-N(CH_3)_2)_3]^{2+}$$

7.7 The Stability of Chelates

In general, chelating agents form more stable complexes than do related monodentate ligands. The special stability of chelates stems from the additional entropy obtained when they are formed. This leads to a larger negative ΔG°, which is equivalent to a larger equilibrium constant for the formation of the chelate. Consider the formation of the chelate $Co(en)_3^{3+}$ from the ion $Co(NH_3)_6^{3+}$, with monodentate apart or separate).

7. Phosphates such as sodium tripolyphosphate are used to complex or sequester metal ions in hard water so these ions cannot interfere with the action of soap or detergents.



sodium tripolyphosphate

8. Mosses and lichens secrete chelating agents to capture metal ions from the rocks they inhabit.
9. Chelating agents such as EDTA are used in consumer products, including many prepared foods such as salad dressings and frozen desserts, to complex trace metal ions that catalyze decomposition reactions.
10. Chelating agents are used in dying and colouring agents.
11. Complex compounds are also widely used as catalysts in synthetic reactions. Zieglar-Natta catalyst is widely used in polymerization of ethylene to form polyethylene. Similarly, $(Ph_3P)_3$ Rh Cl acts as a catalyst for many reactions.
12. Invisible inks are mostly coordination compounds.

7.9 Nomenclature

IUPAC has adopted a set of rules formulating and naming complex coordinate compounds. These rules are listed below:

Formulas of Complexes

1. The formula of a complex shows the central atom first, followed by the ligands. Examples: $Cu(NH_3)_4^{2+}$; $CrCl_6^{3-}$.
2. When the ligands in a complex are not alike, anion ligands are written before neutral ligands. Examples: $Fe(OH)(H_2O)_5^{2+}, CrCl_2(NH_3)_4^{+}$

Naming Coordination compounds

1. **Order of listing ions.** *In naming salts, the cation* is *named* before the *name of the anion.* Thus, $[Co(NH_3)_6]Cl_3$ is named hexamminecobalt (III) chloride.

2. **Naming of coordination sphere.** (i) *In naming the coordination sphere, the ligands are named before the metal. Ligands are listed in alphabetical order, regardless of charge on the ligand. Prefixes that give the number of ligands are not considered part of the ligand name in determining alphabetical* order. Thus, in the $[Co(NH_3)_5Cl]^{2+}$ ion we name the ammonia ligand first, then the chloride, then the metal: Pentaamminechlorocobalt (III). *The name of the complex is written as one* word. Note, However, that in writing the formula, the metal is listed first.

(ii) *The prefixes di-(2); tri-(3); tetra-(4); penta-(5); hexa-(6); and so forth, are used* to specify the number of a particular kind of coordinated ligands, followed by the specific name of the ligand.

(a) **Anionic ligands** end in-o. Some examples are:

Anion Name	Ligand Name	Anion name	Ligand name
Fluoride, F^-	Fluoro	Cyanide, CN^-	Cyano
Chloride, Cl^-	Chloro	Oxalate, $C_2O_4^{2-}$	Oxalato
Bromide, Br^-	Bromo	Oxide, O^{2-}	Oxo
Iodide, I^-	Iodo	Sulphide, S^{2-}	Sulphido
Carbonate, CO_3^{2-}	Carbonato	Hydride, H^-	Hydro
Sulphate, SO_4^{2-}	Sulphato	NO_3^-	Nitrato
Hydroxide, OH^-	Hydroxo	Thiosulphate, $S_2O_3^{2-}$	Thiosulphato
Acetate, CH_3COO^-	Acetato		

(b) **Neutral Ligands** are usually given the name of molecule. There are, however several important exceptions:

Molecule	Ligand name	Molecule	Ligand name
Ammonia, NH_3	Ammine	Carbon monoxide, CO	Carbonyl
Water, H_2O	Aqua	NO	Nitrosyl

(c) **Positive ligands** end in – ium: $NH_2NH_3^+$ is named hydrazinium.

(d) **The number of complicated or chelate ligands** is denoted with *bis* (2), *tris* (3), *tetrakis* (4), and so forth. The name of the ligand follows in parentheses. For examples, the complex $[Co(en)_3]Cl_3$ is named as tris (ethylenediamine) cobalt (III) chloride.

3. **Name of the metal.** The complete metal name consists of the name of the metal, followed by-ate if the complex is an anion, followed by the oxidation number of the metal as Roman numerals in parentheses. (An oxidation state of zero is indicated by 0 in parentheses). When there is a latin name for the metal, it is used to name the anion (except for mercury). These names are:

English name	Latin name	Anion name
Copper	Cuprum	Cuprate
Gold	Aurum	Aurate
Iron	Ferrum	Ferrate
Lead	Plumbum	Plumbate
Silver	Argentum	Argenate
Tin	Stannum	Stannate

For example, the compound $K_4[Fe(CN)_6]$ is named potassium hexacyanoferrate (II), and the ion $[CoCl_4]^{2-}$ is called tetrachlorocobaltate (II) ion.

4. **Points of attachment.** Certain ligands can have more than one points of attachment. The point of attachment must be indicated while naming the complexes. For example,

- NO_2^-, nitro — $-SCN^-$, Thiocyanato
- ONO^-, nitrito — $-NCS^-$, Isothiocyanato

$Na_3[Co(NO_2)_6]$ Sodium hexanitrocobaltate (III)

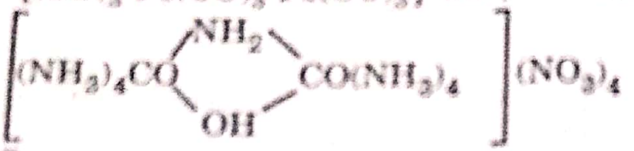
$[Co(ONO)(NH_3)_5]SO_4$ Pentaamminenitritocobalt (III) sulphate

$[Co(NCS)(NH_3)_5]Cl_2$ Pentaammineisothiocyantocobalt (III) chloride

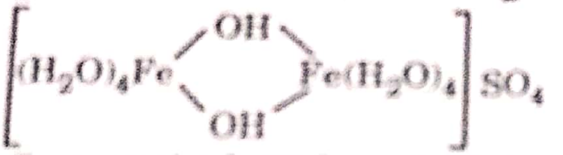
5. Bridged complexes. A bridging group present in the complexes is indicated by adding the Greek letter "μ" before its name and separating the name from the rest of the complex by hyphens. Two or more bridging groups of the same kind are indicated by di - μ - etc. If two or more kinds of bridging groups are present, they are listed in alphabetical order.

$[(NH_3)_5Cr-OH-Cr(NH_3)_5]Cl_5$ μ-hydroxobis [pentaamminechromium (III)]

$[(CO)_3 Fe(CO)_3 Fe(CO)_3]$ Tri-μ-Carbonylbis (tricarbonyliron)



μ-amide-μ-hydroxobis [tetramminecobalt (III) nitrate]



Octaaquo-μ-dihydroxodiiron (III) sulphate

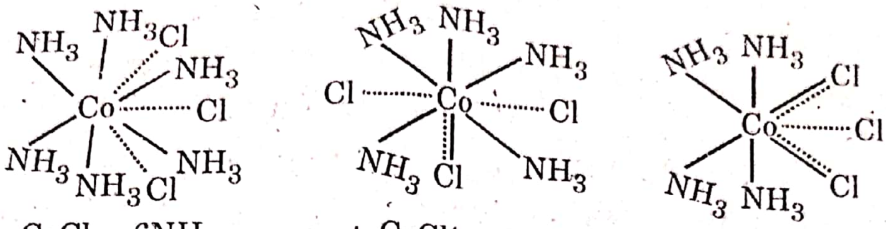
6. Geometrical and optical isomers: The isomeric forms of complexes are named by using prefixes *cis* - and *trans* - in geometrical isomerism and d - and *l* - in optical isomerism.

Some examples are given to illustrate these rules.

Formula	Name
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate (II)
$[Ni(CO)_4]$	Tetracarbonylnickel (0)
$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate (III)
$K_2[Cu(CN)_4]$	Potassium tetracyanocuprate (II)
$[Ag(NH_3)_2]Cl$	Diamminesilver chloride
$Na[Al(OH)_4]$	Sodium tetrahydroxoaluminate (III)
$[Co(NH_3)_6]Cl_3$	Hexamminecobalt (III) chloride
$[Co(NH_3)_4Cl_2]Cl$	Dichlorotetramminecobalt (III) chloride
$[Co(en)_2Br_2]Cl$	Dibromobis (ethylenediamine) Cobalt (III) chloride
$[Cr(H_2O)_6](NO_3)_3$	Hexaaquachromium (III) nitrate
$[Pt(NH_3)_4][PtCl_6]$	Tetraamineplatinum (II) hexachloroplatinate (IV)
$[Fe(H_2O)_5(NCS)]SO_4$	Pentaaquathiocyanoiron (III) sulphate
$[Cr(H_2O)_4Cl_2]Cl$	Tetraaquodichlorochromium (III) chloride
$[Cu(NH_3)(H_2O)Br_2]$	Ammineaquadibromocopper (II)
$Na[Co(CO)_4]$	Sodium tetracarbonylcobaltate (–I)
$(NH_4)_2[PtCl_6]$	Ammonium hexachloroplatinate (IV)
$Na_2[Sn(OH)_6]$	Sodium hexahydroxostannate (IV)
$Co(H_2O)_6^{2+}$	Hexaaquacobalt (II) ion

Applications of Werner's Theory to Coordination Compounds

Werner's theory has successfully been applied to explain the structures, isomerism and nature of coordination compounds. Let us apply this theory to explain the structures and nature of Co (III) complexes e.g., $CoCl_3.6NH_3$, $CoCl_3.5NH_3$ and $CoCl_3.4NH_3$ complexes. On the basis of this theory, the structure of these complexes can be shown as follow:



$CoCl_3 . 6NH_3$ $CoCl_3 . 5NH_3$ $CoCl_3 . 4NH_3$

The solid lines (–) between Co and other atoms or molecules represent the secondary valencies and dotted lines (---) represent primary valencies. We see that the number of secondary valencies remain fixed in the above three structural representations of Co (III) complexes in accordance with Werner's theory, and is six in all the three cases. However, the number of primary valencies is three in $CoCl_3. 6NH_3$, two in $CoCl_3.5NH_3$ and one in $CoCl_3.4NH_3$ as shown by dotted lines in the above structures.

According to Werner's theory, the primary valencies are ionizable. In $CoCl_3. 6NH_3$ the number of ionizable primary valencies is three because all the three Cl^- ions are loosely bound and are immediately precipitated as Ag Cl by the addition of $AgNO_3$ solution. In the complex $CoCl_3.5NH_3$ one of the Cl^- ions gets attached through secondary valency and becomes unionizable. But the other two Cl^- ions remain attached through primary valencies, are ionizable and are precipitated as AgCl by $AgNO_3$ solution. In the complex $CoCl_3. 4NH_3$ two Cl^- ions are attached through secondary valencies to the central metal atom and are unionizable. Only one Cl^- ion possesses primary valency, is ionizable and is precipitated as Ag Cl by $AgNO_3$ solution.

Note that square brackets are used in modern formulas to separate the metal and its associated groups from the rest of the formula. In terms of Werner's modern formulas, the formulas of the above complexes can be written as

$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_4Cl_2]Cl$
$(CoCl_3.6NH_3)$	$(CoCl_3.5NH_3)$	$(CoCl_3.4NH_3)$

7.11 Sidgwick's Electronic Interpretation of Coordination compounds - Nature of coordinate bond.

In 1927, **Sidgwick** introduced the idea of a coordinate covalent bond, according