Coordination Chemistry- Structure and IUPAC nomenclature

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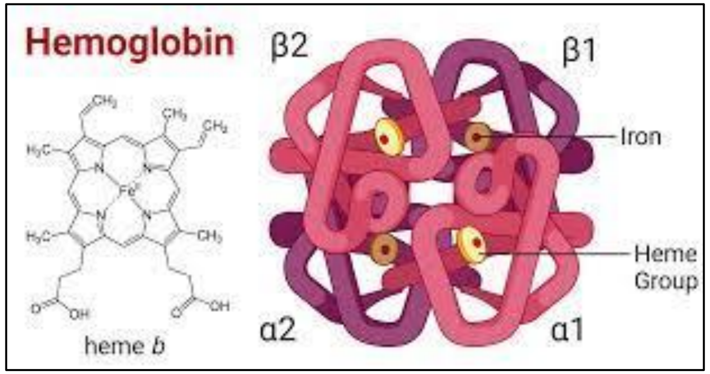
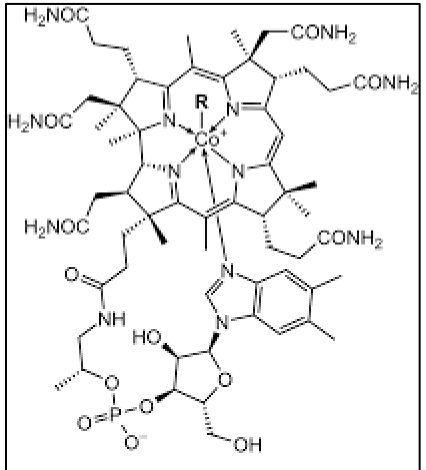
- ***The branch of chemistry which deals with the study of coordination compounds or metal complexes or complex salts is called coordination chemistry.***
- ***Alfred Warner, professor at the University of Zurich is the founder of Coordination Chemistry. He was awarded Nobel Prize of Chemistry in 1913 for his coordination theory of transition metalamine complexes.***

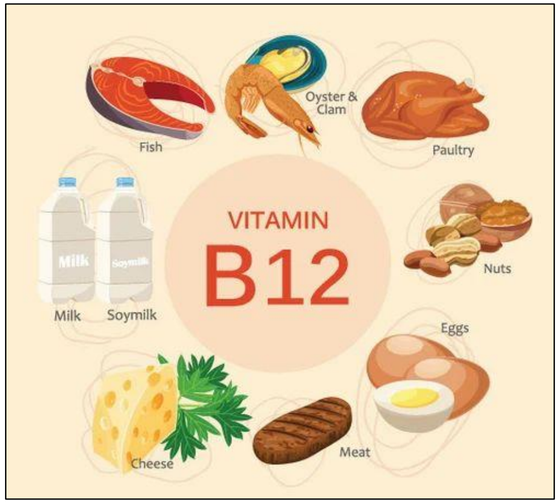
❖ *Coordination compounds or coordination complex are chemical compounds that consist of an array of anions or neutral molecules that are bound to a central atom via coordinate covalent bonds. The molecules or ions which are bonded to the central atom or ion are called ligands.*

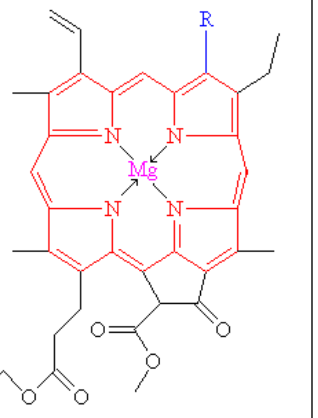
- ✓ ***Coordination compounds include such substances as vitamin B12 , hemoglobin, and chlorophyll, dyes and pigments, and catalysts used in preparing organic substances.***
- ✓ ***First coordination compound is Prussian blue, $Fe_4[Fe(CN)_6]_3$ which was accidently prepared in 1704 by a Berlin colour maker, prepared by strong heating animal waste and sodium carbonate in an iron container.***





R = 5'-deoxyadenosyl, CH_3, OH, CN





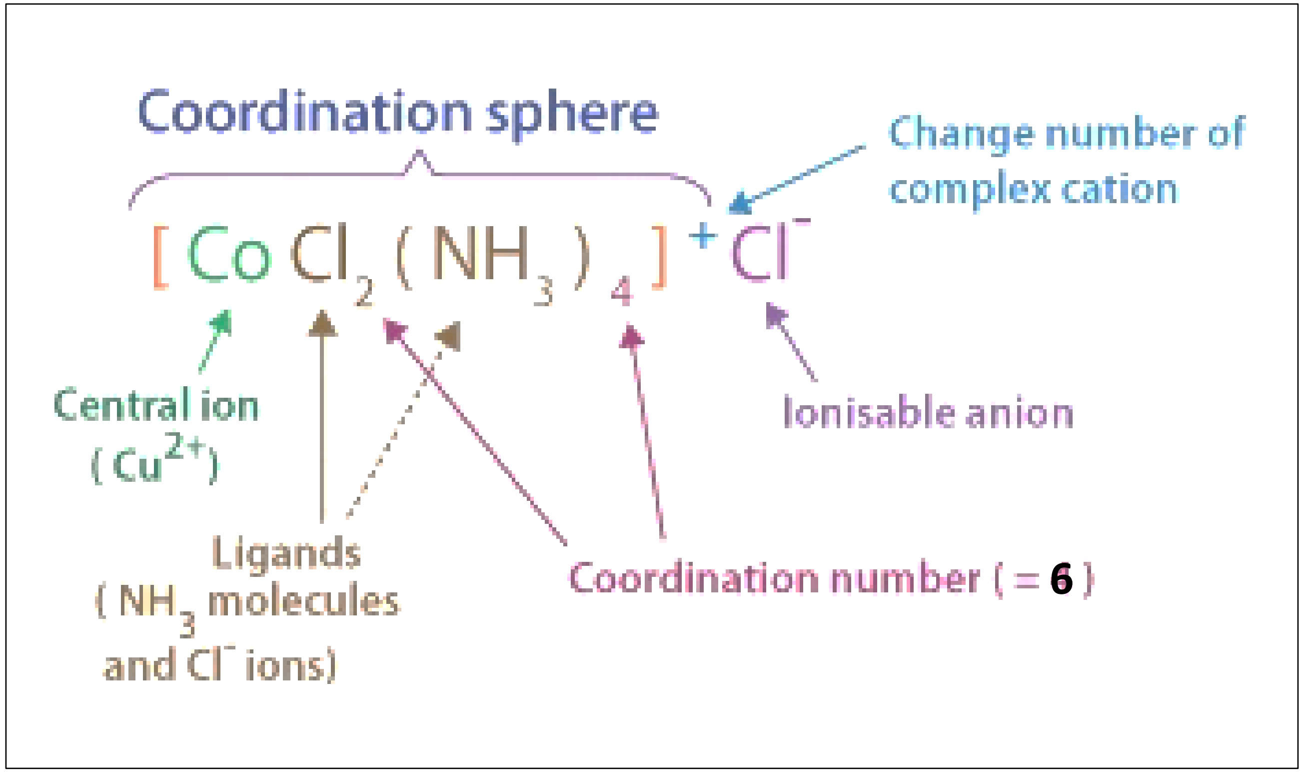
Chlorophyll *a*, R = CH_3
Chlorophyll *b*, R = CHO
The porphyrin ring is shown in Red

Definition Of Some Important Terms Pertaining To Coordination Compounds

- **Coordination entity** : *A coordination compound constitutes a central metal atom or ion bonded to a fixed number of ions or molecules, For example :* $[Fe(CN)_6]_4$.
- **Central atom/ion** : *In a coordination entity, the atom or to which a fixed number of ion/groups are bound in a definite geometrical arrangement around it, is called the central atom/ion.*
- **Coordination numbers(CN)**: *The coordination numbers (CN) of a metal ion in a complex can be defined as number of ligand donor atoms to which the metal is directly bonded.*

$$C.N = \sum \text{number of ligands} \times \text{Denticity of ligands}$$

- **Coordination Sphere** : *The central atom or ion and the ligands attached to it are enclosed in square brackets and is collectively termed as the coordination sphere.*
- **Counter ion:** *The ionizable groups are written outside the bracket and are called counter ion.*



Coordination sphere

$[\,Co\,Cl_2\,(NH_3)_4\,]^+\,Cl^-$

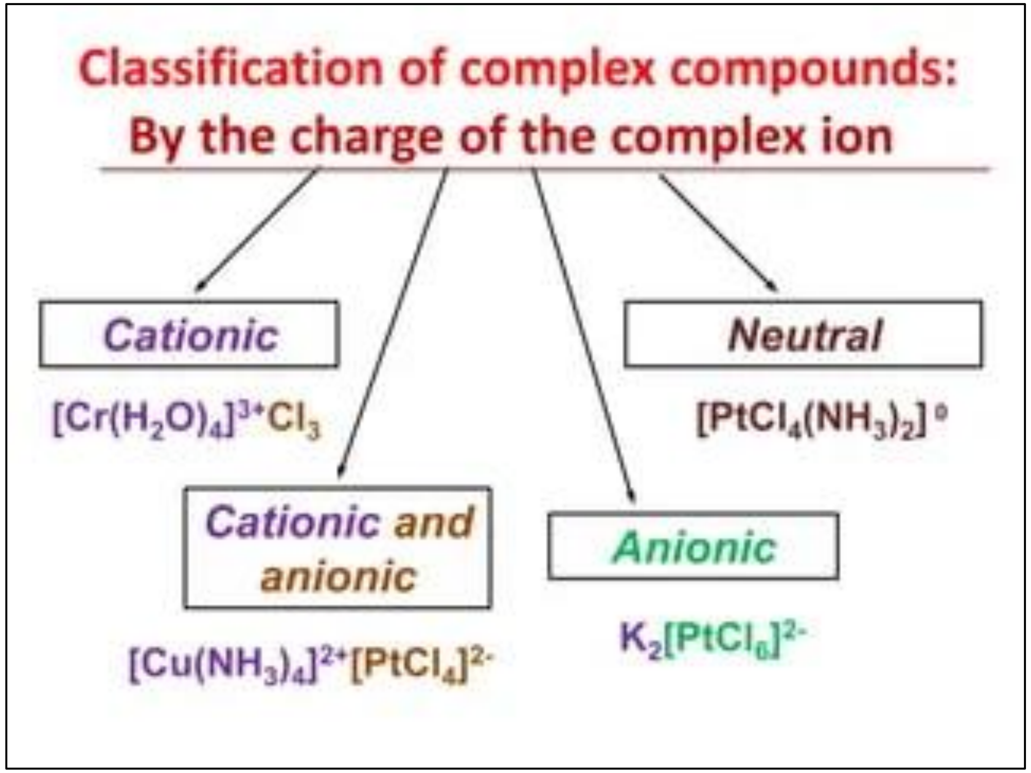
Change number of complex cation

Central ion (Cu^{2+})

Ligands (NH_3 molecules and Cl^- ions)

Coordination number (= 6)

Ionisable anion



Classification of complex compounds:
By the charge of the complex ion

Cationic

$[Cr(H_2O)_4]^{3+}Cl_3$

Cationic and anionic

$[Cu(NH_3)_4]^{2+}[PtCl_4]^{2-}$

Anionic

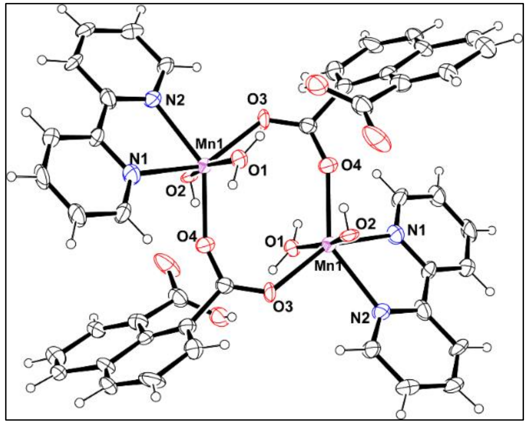
$K_2[PtCl_6]^{2-}$

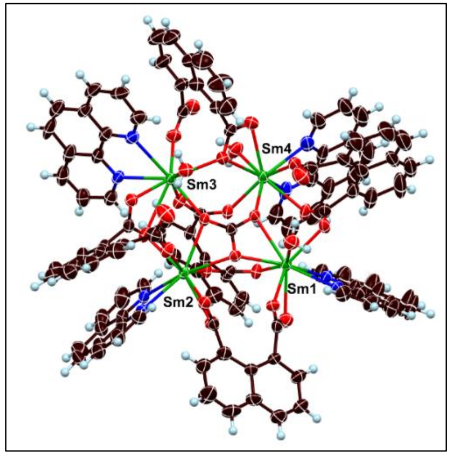
Neutral

$[PtCl_4(NH_3)_2]^{\circ}$

Types of Coordination Complexes

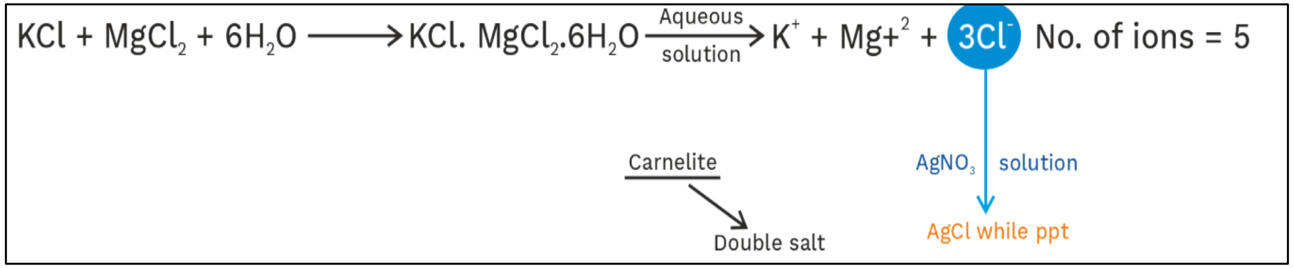
- **Cationic complexes**: In this coordination, the sphere is a cation. For example, $[Co(NH_3)_6]Cl_3$
- **Anionic complexes**: In this coordination, the sphere is Anion. For example, $K_4[Fe(CN)_6]$
- **Neutral Complexes**: In this coordination, the sphere is neither a cation nor an anion. For example, $[Ni(CO)_4]$
- **Homoleptic complex**: The complex consists of a similar type of ligands. For example, $K_4[Fe(CN)_6]$
- **Heteroleptic complexes**: These consist of different types of ligands. For example, $[Co(NH_3)_5Cl]SO_4$
- **Mononuclear complexes**: In this coordination, the sphere has a single transition metal ion. For example, K4[Fe(CN)6]
- **Polynuclear complexes**: More than one transition metal ion is present. For example,



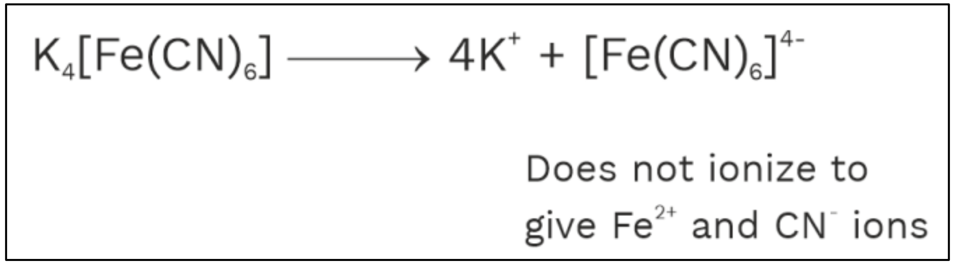


Difference between coordination complex and double salts

Double Salts	Coordination Compounds
Its aqueous solution give test of its all constitute Ions	it’s aqueous solution doesn’t give test of its all constitute ions.
Double salts lose their identity in aqueous solution.	Complex compound don’t loss their identify in aqueous solution.
Nature of bonding is ionic, weak Vander Walls forces	Usually nature of bonding is ionic, covalent and coordinate
In double salts metals show their normal valency	In complex salts metals satisfy two types of valencies, primary and secondary valencies



$$KCl + MgCl_2 + 6H_2O \longrightarrow KCl.\,MgCl_2.6H_2O \xrightarrow[\text{solution}]{\text{Aqueous}} K^+ + Mg+^2 + 3Cl^- \quad \text{No. of ions} = 5$$



$$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

LIGAND AND ITS CLASSIFICATION

Defination: A ligand is a molecule or ion that forms a coordinate bond with a central metal atom or ion by donating a pair of electrons. Ligands can be neutral molecules, anions, or cations.

- *Negatively Charged ligands are called anionic ligand. e.g* Cl^-, CN^-, $C2O4^{2-}$ *etc*
- *Positively charged ligand are called cationic ligand. e.g* NO^+, NO_2^+, $NH_2NH_3^+$
- *Neutral ligands don't contain any charge. e.g. H2O, NH3, Pyridine, Ethylenediaamine (en).*

Types of Ligand: **A ligand may contains one or more than one donor sites/atoms and it is called denticity of the ligand.**

1. **Monodentate ligand or Unidentate ligand**: ligands which donate only one pair of electrons through one donor atom is called monodentate ligand. e.g. NH_3, H_2O, Cl^-, CN^- etc.
2. **Ambidentate Ligand**: Ligands which have two different donor atoms but at time of coordination it can coordinate through only one atom to the central metal ion/atom such ligand is called ambidentate ligand. e.g. SCN^- (Thiocyanato-N), NCS^- (Isothyocyanato-S), CN^- (Cyano-N), NC^-(Cyano-C) etc.

$M^{n+} \longleftarrow C\equiv N$
Cynido (CN)
Cynido—C

$M^{n+} \longleftarrow N\equiv C^-$
Isocynido (NC)
Cynido — N

$M^{n+} \longleftarrow O^-—C\equiv N$
Cynido (OCN)
Cynido—O

$M^{n+} \longleftarrow N\equiv C—O^-$
Isocynido (NCO)
Cynido — N

3. Bidentate Ligand: Ligands which have the ability to bind to the central atom via two separate donor atoms, such as ethane-1,2-diamine, are referred to as bidentate ligands.

e.g. Oxalate ion, $C_2O_4^{2-}$, Glycinate ion, $NH_2CH_2COO^-$, Ethylenediaamine ($NH_2CH_2CH_2NH_2$)

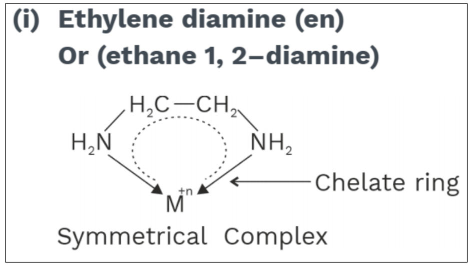
4. Polydentate ligand: Ligands which coordinate with the central metal ion through more than two donor atoms present in the molecule are called polydentate ligands.

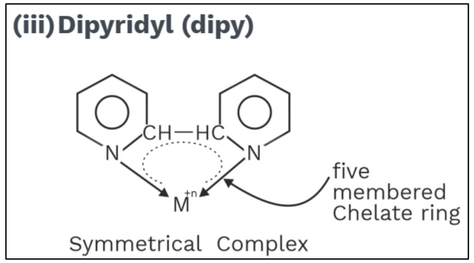
e.g. Diethylene triamine, Terpyridine……..Tridentate (denticity=3)

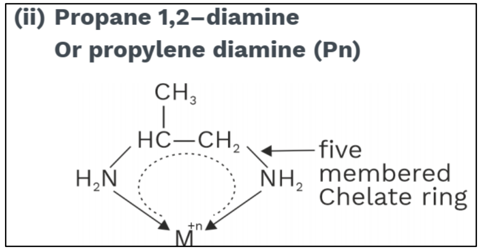
Triethylenetetrammine…………………… tetradentate (denticity = 4)

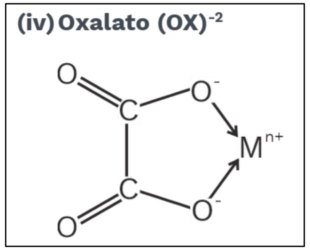
Ethylenediamminetetraacetate………. Hexadentate (denticity = 6)

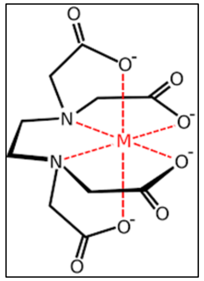
5. Chelate: When a bidentate or polydentate ligand is attached through two or more donor atoms to the same central metal ions forming a stable ring structure, the ligand is called Chelating ligand or chelate.


(i) Ethylene diamine (en)
Or (ethane 1, 2–diamine)

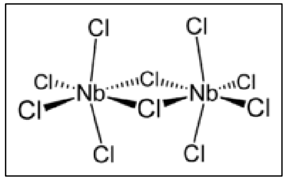

(iii) Dipyridyl (dipy)

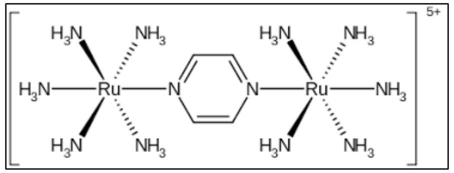

(ii) Propane 1,2–diamine
Or propylene diamine (Pn)


(iv) Oxalato (OX)$^{-2}$



6. Bridging ligand: A bridging ligand is one that can simultaneously coordinate with two or more metal atoms or ions and thus act as a bridge between metal atoms.





Werner's Theory

Werner's Theory states that :In 1823, Warner put forwarded his famous theory of coordination to explain the formation and structure of complex compounds.

1. *The metal atom exhibit two types of valency, viz. primary valence and secondary valency. The primary valence is also the oxidation number of central element . The Secondary valence is the Co-ordination Number of central element .*
2. *Every Metal tends to satisfy both , primary and secondary valency .*
3. *Every Metal has a fixed number of secondary valency .*
4. *The secondary valence is always directed towards fixed positions in space (because they form co-ordinate covalent bonds).*

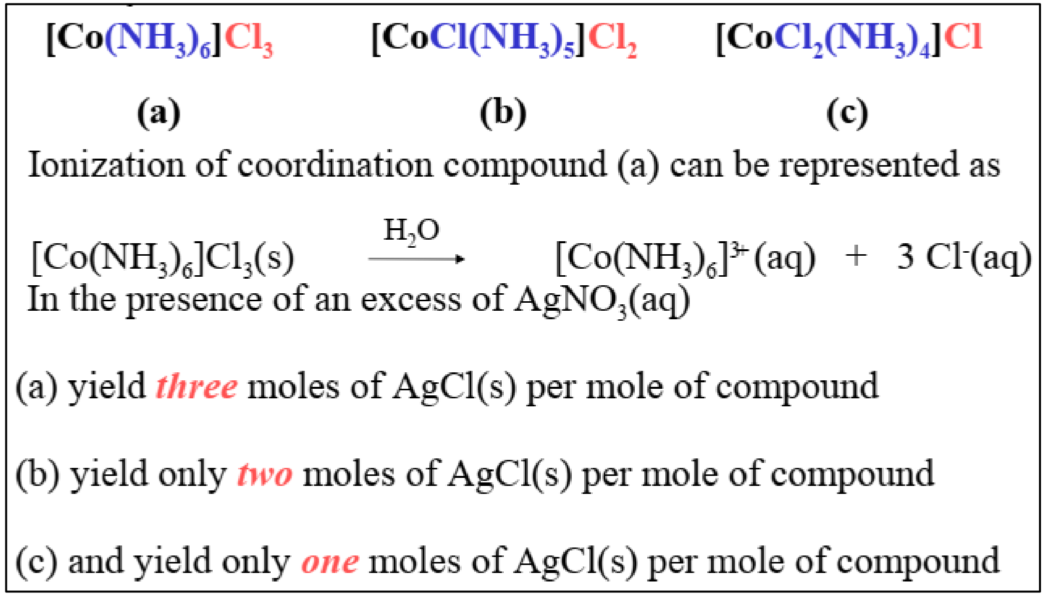
Let us try to explain the structures of various cobalt amine complexes on the Basic of Warner's theory.

- ***In all these complexes cobalt exhibits primary valency (oxidation state) of three and secondary valency (coordination number) of six.***
- ***The primary valencies are represented by broken lines and secondary valencies are represented by thick lines.***

1. $CoCl_3.6NH_3$ complex, 2. $CoCl_3.5NH_3$ complex, 3. $CoCl_3.4NH_3$ complex, 4. $CoCl_3.3NH_3$ complex

↓

No ppt.



$[Co(NH_3)_6]Cl_3$ **(a)** **$[CoCl(NH_3)_5]Cl_2$** **(b)** **$[CoCl_2(NH_3)_4]Cl$** **(c)**

Ionization of coordination compound (a) can be represented as

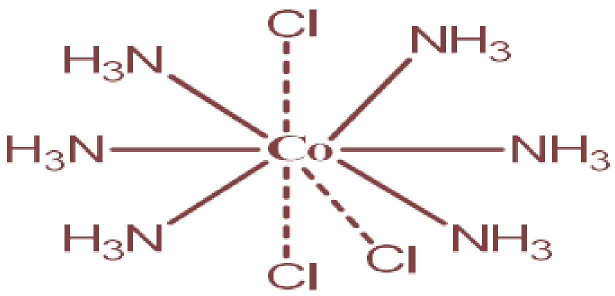
$$[Co(NH_3)_6]Cl_3(s) \xrightarrow{H_2O} [Co(NH_3)_6]^{3+}(aq) + 3\,Cl^-(aq)$$

In the presence of an excess of $AgNO_3(aq)$

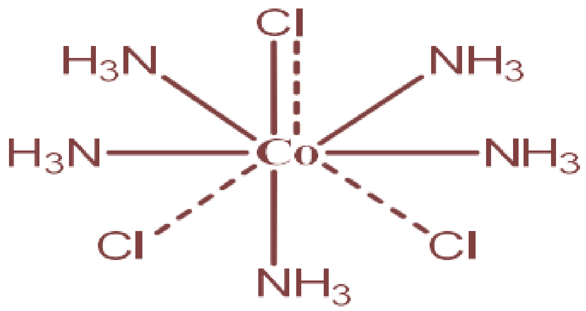
(a) yield *three* moles of AgCl(s) per mole of compound

(b) yield only *two* moles of AgCl(s) per mole of compound

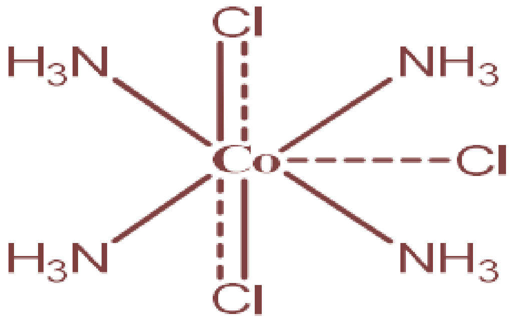
(c) and yield only *one* moles of AgCl(s) per mole of compound



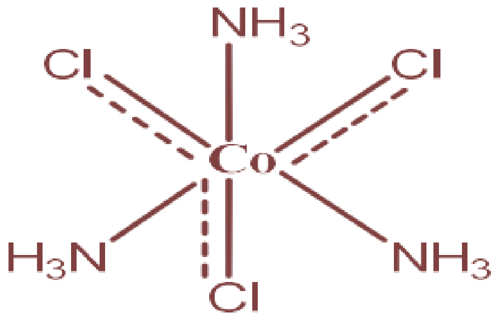
$CoCl_3.6NH_3$ complex
Total no. of ions = 4,
No. of Cl^- precipitated = 3



$CoCl_3.5NH_3$ complex
Total no. of ions = 3,
No. of Cl^- precipitated = 2



$CoCl_3.4NH_3$ complex
Total no. of ions = 2,
No. of Cl^- precipitated = 1



$CoCl_3.3NH_3$ complex
It is neutral molecule,
No. of Cl^- precipitated = 0

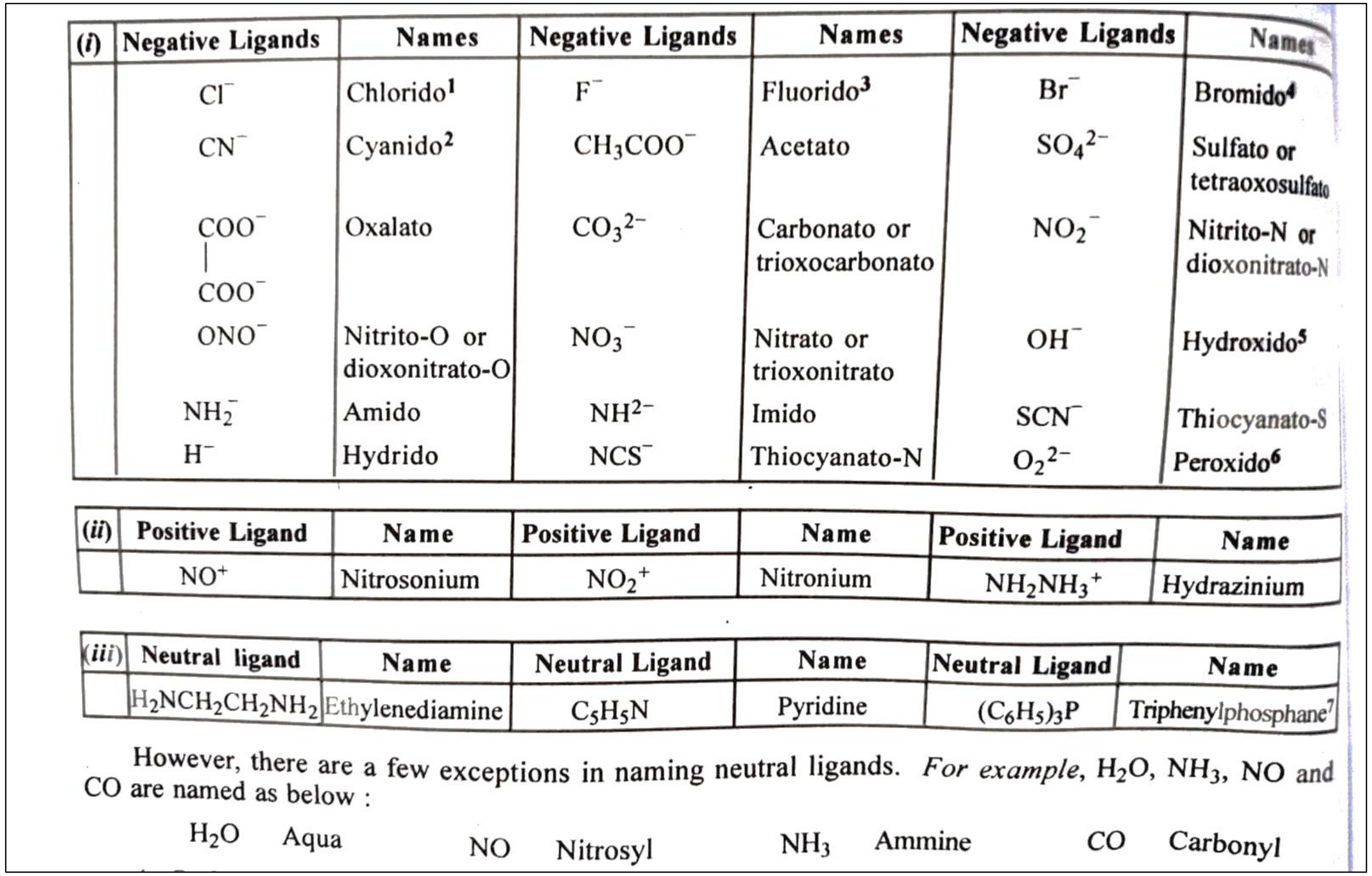
IUPAC nomenclature:

There are certain conventions for naming complex ions which need to be followed carefully.

1. **The ligands are always named before the metal ions.**
2. **If there is more than one ligand they are written in alphabetical order irrespective of their being neutral, anionic or cationic.**
3. **Monodentate ligands which occur multiple times are given a prefix according to the number of times they appear (i.e. di-, tri-, tetra- etc.). Polydentate ligands are also given prefixes, but they are bis-, tris-, and so on.**
4. **Anions are given the ending '-ido' (e.g. sulphate will become sulphato and cyanide will become cyanido).**
5. **Ligands that are neutral are usually given their normal name – there are some exceptions. These are: *ammonia becomes ammine; water becomes aqua; carbon monoxide becomes carbonyl; and nitrogen oxide becomes nitrosyl.***

6. If the entire complex is an anion, then the central metal atom’s Latin name will be used, and it will end with ‘ate’. Mercury is the only exception to this rule. e.g. Ferrate for Fe.

7. If the entire complex is a cation or neutral, then the name of the central metal atom’s is gien without any characteristic ending. e.g Iron for Fe



(i)	Negative Ligands	Names	Negative Ligands	Names	Negative Ligands	Names
	Cl^-	Chlorido[1]	F^-	Fluorido[3]	Br^-	Bromido[4]
	CN^-	Cyanido[2]	CH_3COO^-	Acetato	SO_4^{2-}	Sulfato or tetraoxosulfato
	COO^- | COO^-	Oxalato	CO_3^{2-}	Carbonato or trioxocarbonato	NO_2^-	Nitrito-N or dioxonitrato-N
	ONO^-	Nitrito-O or dioxonitrato-O	NO_3^-	Nitrato or trioxonitrato	OH^-	Hydroxido[5]
	NH_2^-	Amido	NH^{2-}	Imido	SCN^-	Thiocyanato-S
	H^-	Hydrido	NCS^-	Thiocyanato-N	O_2^{2-}	Peroxido[6]

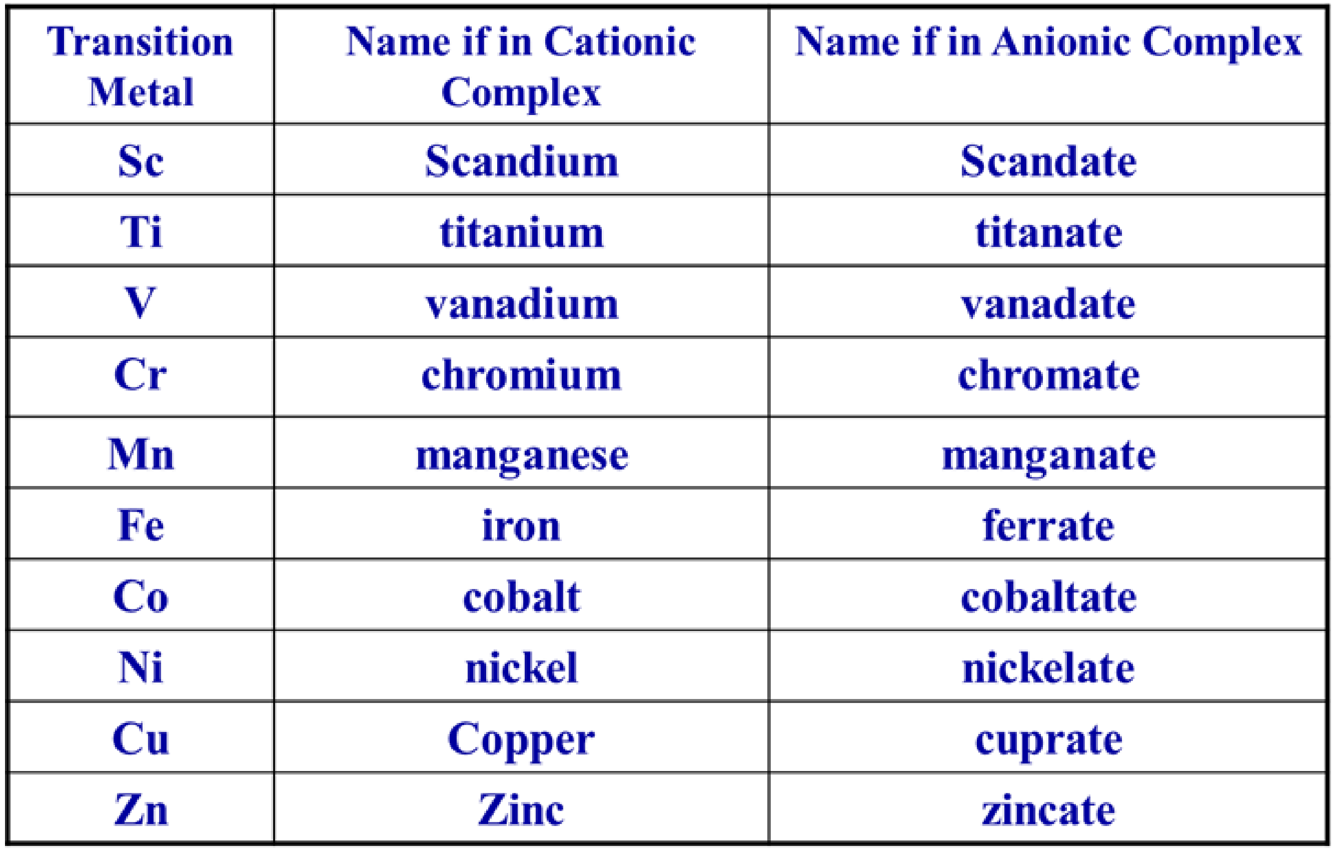
(ii)	Positive Ligand	Name	Positive Ligand	Name	Positive Ligand	Name
	NO^+	Nitrosonium	NO_2^+	Nitronium	$NH_2NH_3^+$	Hydrazinium

(iii)	Neutral ligand	Name	Neutral Ligand	Name	Neutral Ligand	Name
	$H_2NCH_2CH_2NH_2$	Ethylenediamine	C_5H_5N	Pyridine	$(C_6H_5)_3P$	Triphenylphosphane[7]

However, there are a few exceptions in naming neutral ligands. *For example*, H_2O, NH_3, NO and CO are named as below :

H_2O	Aqua	NO	Nitrosyl	NH_3	Ammine	CO	Carbonyl

Latin names is for some metal ion in anionic complex

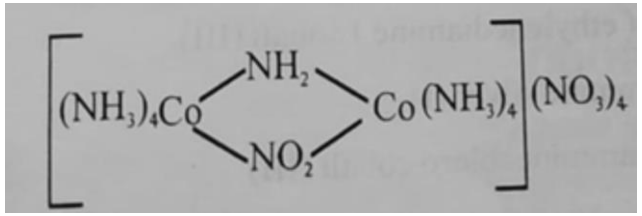


Transition Metal	Name if in Cationic Complex	Name if in Anionic Complex
Sc	Scandium	Scandate
Ti	titanium	titanate
V	vanadium	vanadate
Cr	chromium	chromate
Mn	manganese	manganate
Fe	iron	ferrate
Co	cobalt	cobaltate
Ni	nickel	nickelate
Cu	Copper	cuprate
Zn	Zinc	zincate

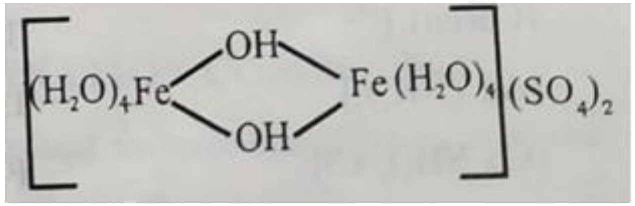
8. **Oxidation state of CMI:** The OS of the CMI is designated by a Roman numeral (such as I, II, III) in parenthesis. e.g. $[Fe(CO)_5]$ is named as Pentacarbonyl iron(0).

9. **Bridging group:** For ligands which act as bridges between two metal atoms, the Greek letter μ is written before their names. The prefix is repeated before the name of each kind of bridging ligand.

e.g.



μ-amido-μ-nitrito-N octaamminedicobalt(III) nitrate.



Di-μ-hydroxide-octaaquadiiron(III) sulphate.

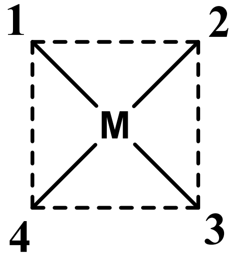
10. **Point of attachment:** If a ligand can coordinate through one or the other atoms, then the point of attachment of the ligand is indicated by putting the symbol of the atom through which coordination occurs after the name of the ligand. e.g. nitro group, thiocyanate ion.

NO_2^- (through N) is called nitrito-N; ONO^- (through O) is called nitrito-O.

SCN^-(through N) is called thiocyanato-N; NCS^- (through S) is called isothiocyanato-S.

Recently IUPAC has suggested the use of kappa (κ) convention to distinguish the actual coordinating atom/atoms in the ligand. Thus, $[Co(NH_3)_5(ONO)]^{2+}$ will be name as Pentaaminenitrito-κ-cobalt(III) ion.

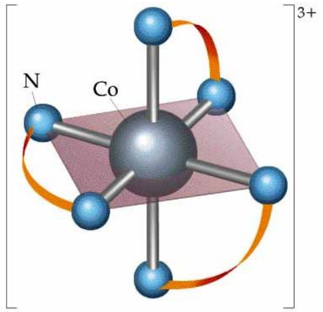
11. ***Naming of geometrical isomers***: Geometrical isomers are generally named the use of terms cis to designate adjacent positions and trans to designate opposite positions.



1,2 and 1,4 positions are cis
1,3 and 2,4 positions are trans

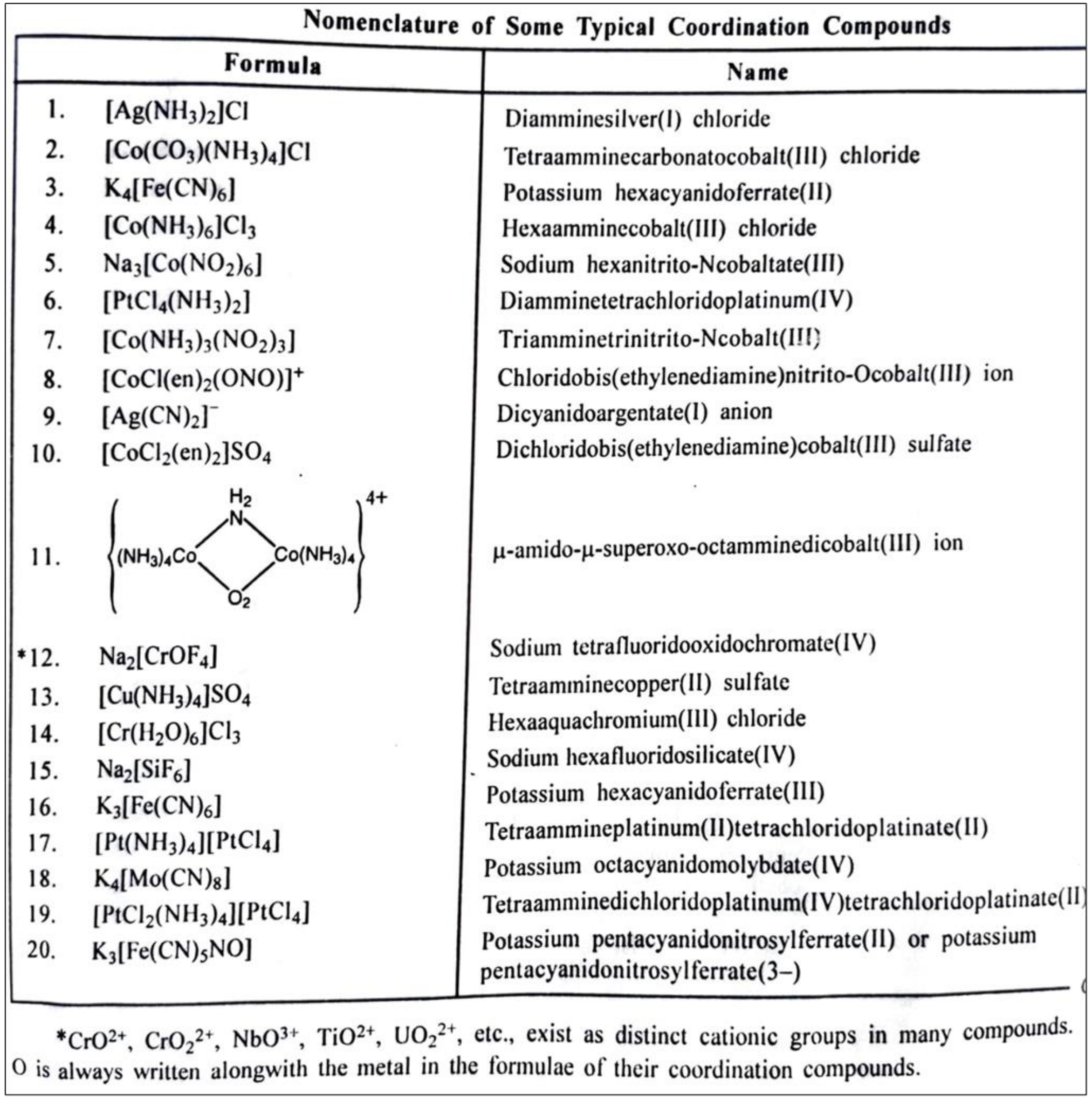
12. ***Naming of optical isomers***: Dextro and laevo rotatory optically active compounds designated by (+) and (-) or by *d* and *l.*

For example, dextrorotatory $K_3[Ir(C_2O_4)_3]$ is named as Potassium(+)trioxalatoiridate(III).



$Co(en)_3^{3+}$

13. **Abbreviation for complicated molecules**: Abbreviations are generally used for complicated molecules. For ethylenediamine is abbreviated as en; py for pyridine; acac for acetylacetonato etc.



Nomenclature of Some Typical Coordination Compounds

	Formula	Name
1.	$[Ag(NH_3)_2]Cl$	Diamminesilver(I) chloride
2.	$[Co(CO_3)(NH_3)_4]Cl$	Tetraamminecarbonatocobalt(III) chloride
3.	$K_4[Fe(CN)_6]$	Potassium hexacyanidoferrate(II)
4.	$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(III) chloride
5.	$Na_3[Co(NO_2)_6]$	Sodium hexanitrito-Ncobaltate(III)
6.	$[PtCl_4(NH_3)_2]$	Diamminetetrachloridoplatinum(IV)
7.	$[Co(NH_3)_3(NO_2)_3]$	Triamminetrinitrito-Ncobalt(III)
8.	$[CoCl(en)_2(ONO)]^+$	Chloridobis(ethylenediamine)nitrito-Ocobalt(III) ion
9.	$[Ag(CN)_2]^-$	Dicyanidoargentate(I) anion
10.	$[CoCl_2(en)_2]SO_4$	Dichloridobis(ethylenediamine)cobalt(III) sulfate
11.	H_2N $(NH_3)_4Co$ $Co(NH_3)_4$ O_2 $4+$	μ-amido-μ-superoxo-octamminedicobalt(III) ion
*12.	$Na_2[CrOF_4]$	Sodium tetrafluoridooxidochromate(IV)
13.	$[Cu(NH_3)_4]SO_4$	Tetraamminecopper(II) sulfate
14.	$[Cr(H_2O)_6]Cl_3$	Hexaaquachromium(III) chloride
15.	$Na_2[SiF_6]$	Sodium hexafluoridosilicate(IV)
16.	$K_3[Fe(CN)_6]$	Potassium hexacyanidoferrate(III)
17.	$[Pt(NH_3)_4][PtCl_4]$	Tetraammineplatinum(II)tetrachloridoplatinate(II)
18.	$K_4[Mo(CN)_8]$	Potassium octacyanidomolybdate(IV)
19.	$[PtCl_2(NH_3)_4][PtCl_4]$	Tetraamminedichloridoplatinum(IV)tetrachloridoplatinate(II
20.	$K_3[Fe(CN)_5NO]$	Potassium pentacyanidonitrosylferrate(II) or potassium pentacyanidonitrosylferrate(3–)

*CrO^{2+}, CrO_2^{2+}, NbO^{3+}, TiO^{2+}, UO_2^{2+}, etc., exist as distinct cationic groups in many compounds. O is always written alongwith the metal in the formulae of their coordination compounds.


Thank
You