

10

Coordination Chemistry

10.1. INTRODUCTION

Tassaert made the beginning in 1798 with an orange coloured compound, $\text{CoCl}_3 \cdot 6\text{NH}_3$, obtained on standing an ammoniacal solution of cobalt(II) chloride. This same compound is now easily obtained in a pure state and in high yield by air-oxidation of ammoniacal cobalt(II) chloride in the presence of active charcoal as a catalyst. The structures of such compounds were the subject of prolonged controversies between two famous adversaries of the late nineteenth century, Jorgensen and Werner. Werner finally solved the mysteries and brought order into the area by announcing his famous coordination theory.

In his coordination theory Werner introduced two great ideas : (1) In a coordination complex a metal ion is engaged in strong binding with a certain number of neutral and/or anionic groups in the first sphere of attraction, now called the *coordination zone* or *sphere* ; (2) The metal ion is surrounded by the neutral and/or anionic groups in the coordination zone in a definite geometrical arrangement.

Werner argued that ions possessed two kinds of valence : a *primary valence* and a *secondary valence*. Primary valence was satisfied by requisite number of anions or negative groups being present inside and/or outside the coordination sphere. Secondary valence indicated the capacity of the metal ion to accommodate certain number of groups around itself in the first sphere of attraction. *Primary valence is now equated with the oxidation state and the secondary valence with the coordination number of the metal ion.*

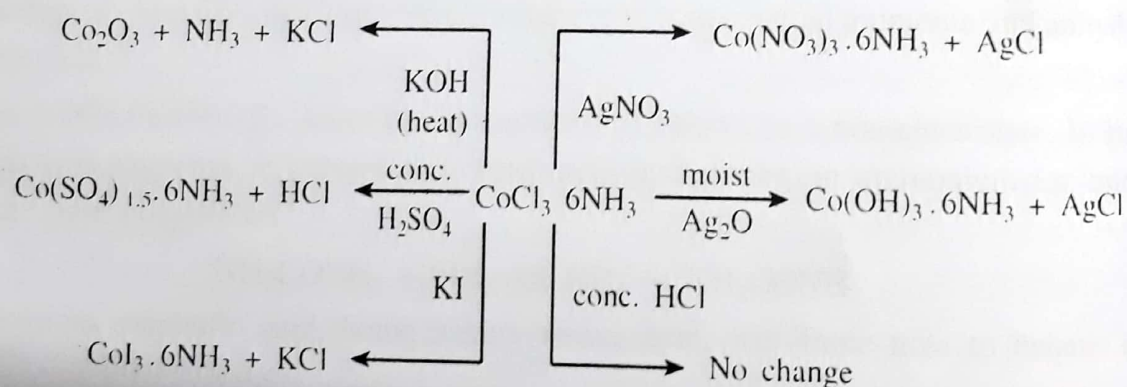
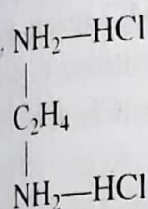


Chart 10-I. Werner's metathetic reactions on $\text{CoCl}_3 \cdot 6\text{NH}_3$.

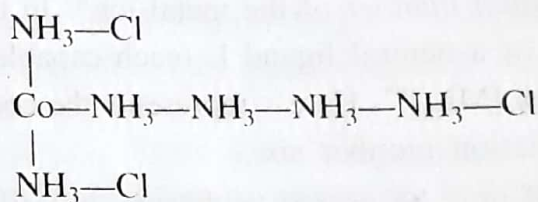
Werner's ideas were supported by experimental finding on many compounds. It was shown by a large number of simple metathetic reactions on $\text{CoCl}_3 \cdot 6\text{NH}_3$ in aqueous solution that changes were forced only on the chloride part leaving cobalt and the six NH_3 groups intact (chart 10-I).

Werner realised that $\text{CoCl}_3 \cdot 6\text{NH}_3$ should better be represented as a strongly bound unit $[\text{Co}(\text{NH}_3)_6]^{3+}$, leaving the three chloride units as anions outside the square bracket. The unit within the square bracket was recognised as a complex entity, formed as a result of coordination of the neutral NH_3 molecules to the Co^{3+} cation, both these being capable of independent existence. That such a formulation was indeed correct was amply verified by conductance measurements ($1024 - 432 \text{ ohms}^{-1} \text{ cm}^2 \text{ mole}^{-1}$). Werner named the zone within the square bracket as the first sphere of attraction, the anions being held in a second sphere of attraction.

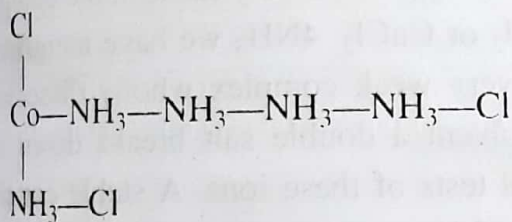
According to Werner the geometrical arrangement around cobalt(III) was octahedral and hence there should be six groups around cobalt(III). The primary valence of +3 of cobalt(III) in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is satisfied by the three chloride ions while the secondary valence is satisfied by the six NH_3 groups. Werner formulated $\text{CoCl}_3 \cdot 5\text{NH}_3$ as $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$ indicating once again that the primary valence of cobalt(III) is satisfied by one Cl^- inside the coordination zone and two Cl^- outside the coordination zone. In accordance with this formulation the compound is a bi-univalent electrolyte. The compound $\text{CoCl}_3 \cdot 3\text{NH}_3$ was given a non-electrolyte structure $[\text{CoCl}_3(\text{NH}_3)_3]$.



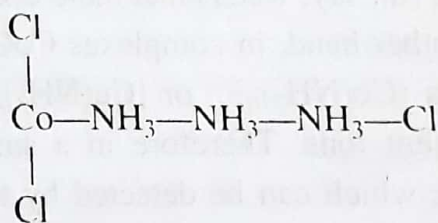
(a)



(b)



(c)



(d)

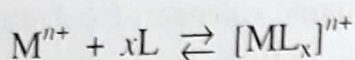
It is now quite amusing to note the way Jorgensen tried to explain the structure of the cobalt(III) amines. Following the structure of ethylenediamine chloride (a), Jorgensen represented the cobalt(III) amines with chains of different lengths. He thought that the valences of cobalt in these compounds were different and therefore stabilised chains of different lengths. Since in $\text{CoCl}_3 \cdot 6\text{NH}_3$ (b) all the three chlorines were some distance away from cobalt these were, according to Jorgensen, readily precipitated by silver nitrate while in $\text{CoCl}_3 \cdot 5\text{NH}_3$ (c) two chlorine were expected to be readily precipitated. Such reasoning would predict that for the then-unsynthesised $\text{CoCl}_3 \cdot 3\text{NH}_3$ (d) only one chlorine would be readily precipitated. This compound could not be prepared by Jorgensen but its iridium (III) analogue $\text{IrCl}_3 \cdot 3\text{NH}_3$ was prepared and it failed to give any precipitate with AgNO_3 . This showed that all the three chlorines were strongly bound and that Jorgensen could not be right.

Jorgensen's problem was that he refused to think of these complicated molecules in any other way outside the chain theory. But characteristic of a genius Alfred Werner brought in a bundle of fresh thoughts in this area and that made all the difference.

Alfred Werner played such a monolithic pivotal role in the development of coordination chemistry that the subject is now synonymous with his name. His researches on the coordination chemistry of metal amines are now classics. Metal amines and related complexes are often lovingly called Werner complexes.

10.2. DEFINITIONS : COMPLEX, LIGAND AND COORDINATION NUMBER

A metal ion (whether it is positively charged, neutral or even negatively charged) may combine with neutral molecules or anions to give a new reasonably identifiable entity called a *complex*. The groups that are bound to the metal ion in a complex are called *ligands*.



The ligands are arranged around the metal ion inside the first sphere of attraction in preferred geometries. The number of the ligands bound around a metal ion by σ bonds is called the *coordination number* of the metal ion*. In the above reaction a metal ion M^{n+} reacts with x moles of a neutral ligand L (each capable of taking one coordination position) to form a complex $[ML_x]^{n+}$. Here x represents the coordination number. In $[Co(NH_3)_6]Cl_3$, Co^{3+} has a coordination number six.

It will now be proper to discuss any difference between a double salt and a complex salt. A double salt such $AlK(SO_4)_2 \cdot 12H_2O$ or $3CsCl \cdot CoCl_2$ is so very dissociated into its component ions (in, say, water) that there does not exist any reasonably identifiable complex entity. On the other hand, in complexes $CoCl_3 \cdot 6NH_3$ or $CuCl_2 \cdot 4NH_3$ we have identifiable complex entities $[Co(NH_3)_6]^{3+}$ or $[Cu(NH_3)_4]^{2+}$. A very weak complex wholly dissociates into its component ions. Therefore in a suitable solvent a double salt breaks down into component ions, which can be detected by the usual tests of these ions. A stable complex ion, obviously, will not respond to the usual tests of its component units.

10.3 COMPLEXATION—A DONOR-ACCEPTOR INTERACTION

Structure determinations have shown that most polar ligand molecules are so oriented in a complex that one unshared pair of electrons points directly to the metal ion. The ligand usually is a donor of electrons (Lewis base) and the metal ion an acceptor (Lewis acid). However this statement will be profoundly modified when the metal ion is in a low oxidation state and when the ligand possesses acceptor orbitals in addition to donor orbitals. (Chapter 24, Part II).

*Ligands may be bound to the central atom both by sigma and pi-bonds but the pi-bonds are not considered to determine the coordination number.

10.4. CLASSIFICATION OF LIGANDS

Based on donor and acceptor properties ligands may be of the following types :

Ligands

(1) With one (or more) lone pair (s) of electrons

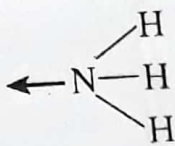
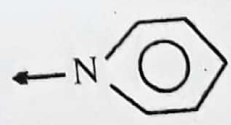
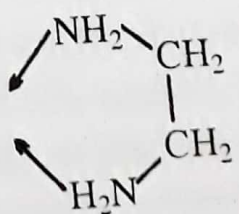
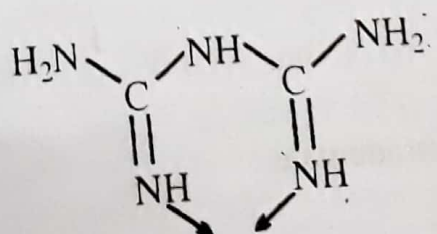
(2) Without a lone pair of electrons but with π -bonding electrons e.g. : ethylene, benzene, cyclopentadienyl ion.

(a) No vacant orbitals to receive back donated electrons from metal e.g. : H_2O , NH_3 , F^-

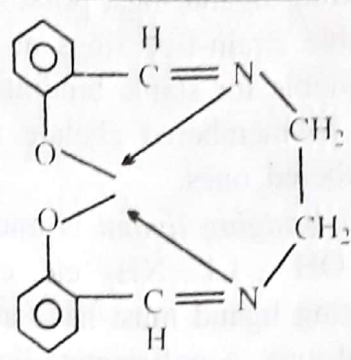
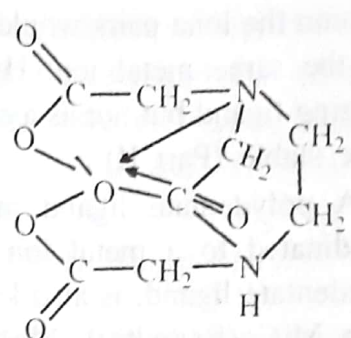
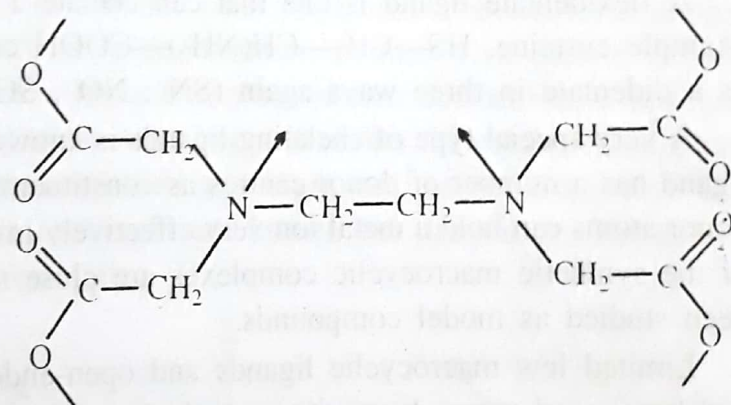
(b) Vacant orbitals that can be used to receive back donated π electrons from the low oxidation state metal e.g. : PR_3 , CN^- , CO

Ligands may also be classified according as the number of coordination positions they occupy around the metal ion (Table 10.1). A ligand having only one lone pair of electrons can only be bonded to a metal ion at just one stereochemical point, that is, it occupies one coordination position only. This is called a unidentate or a monodentate ligand. When the ligand can occupy two positions around the metal ion it is di(bi)dentate ; with three, four, five or six such links the ligands are called tri (ter) dentate, tetra (quadri) dentate, pentadentate or hexa (sexa) dentate respectively. Some authors prefer to classify ligands according to the number of donor atoms they can offer to metal ions. Thus, when a ligand has two atoms which can simultaneously serve as donors it is called didentate and so on. It follows that a didentate ligand has to have two lone pairs, a tridentate three lone pairs and so on. The

Table 10.1. : Some Monodentate and Polydentate Ligands

Ligand type	Name	Formula
Monodentate	Ammonia	
	Pyridine	
Didentate	Ethyl ediamine (en)	
	Biguanide (Hbig)	

Ligand type	Name	Formula
Didentate	Glycinate ion (gly)	
	Bipyridine (bpy)	
	o-Phenanthroline (o-phen) (phen)	
Tridentate	Oxalate ion (ox)	
	Diethylenetriamine (dien)	
	Iminodiacetate ion (ida)	
Tetradentate	Triethylenetetramine (trien)	

Ligand type	Name	Formula
	Ethylenebis(salicylaldehyde) anion (salen)	
Pentadentate	ethylenediamine triacetic acid anion	
Hexadentate (Sexadentate)	ethylenediaminetetraacetic acid anion (edta)	

polydentate ligands may be further subdivided according to the nature of their donor centres. Thus ethylenediamine is a didentate ligand with two neutral donors (N) whereas oxalate ion is didentate with two acidic (anionic) donors (O^-). Glycinate ion is again a didentate with one neutral donor (N) and an acidic donor (O^-). Such discussions may be extended to other polydentates as well.

A *chelating ligand* is one that contains two or more donor centres so disposed that they can simultaneously occupy more than one position around the same metal ion in the first sphere of coordination*. The resulting complexes are called metal chelates. Thus all

* A chelating ligand offers more than one sigma-electron pair donor groups to the same metal ion

polydentate ligands, when bonded to the same metal ion, are also chelating ligands. A chelating ligand must possess two or more lone pairs such distance apart that it may form suitable strain-free rings at the metal on. Too small-sized and too large-sized rings are unsuitable for stable binding. Usual strain-free rings are 5— or 6— membered ones. 4— and 7—membered chelate rings are also known but are less stable than 5— or 6— membered ones.

A *bridging ligand* is one that can simultaneously bond itself to more than one metal ion. OH^- , Cl^- , NH_2^- etc. can function as monodentate and also as bridging ligands. A bridging ligand must have at least two lone pairs so that it can get linked to at least two metal ions. A polydentate ligand may function both as a chelating ligand and as a bridging ligand. Note that OH^- , Cl^- or NH_2^- cannot serve as chelating ligands because the angle between the lone pairs would not allow them to span adjacent coordination positions of one and the same metal ion. Hydrazine, $\text{NH}_2\text{—NH}_2$, can serve as a monodentate and as a bridging ligand but not as a chelating ligand because a 3-membered ring will be too strained to be stable (Part II).

A polydentate ligand may not bring into play all its donor centres while getting coordinated to a metal ion. Thus ethylenediaminetetraacetic acid, usually a formidable hexadentate ligand, is also known to function as a pentadentate ligand in $\text{M}[\text{Cr}(\text{OH})(\text{edta})]$ or in $\text{M}[\text{Co}(\text{Br})(\text{edta})]$ (M =bipositive cation) or as a tetradentate ligand in $[\text{Pd}(\text{H}_2\text{edta})]$. Iminodiacetate anion, usually a tridentate ligand, functions as a didentate one in the mixed chelate $[\text{Co}(\text{ida})(\text{Hbig})_2]^+$. These behaviours are manifestations of *flexidentate* character of polydentate ligands (Appendix, Part II).

A *flexidentate ligand* is one that can chelate a metal ion in more than one way. For example cysteine, $\text{HS—CH}_2\text{—CH}(\text{NH}_2)\text{—COOH}$ can function as a tridentate (SNO) and as a didentate in three ways again (SN ; NO ; SO).

A very special type of chelating ligands is known as macrocyclic ligand. A *macrocyclic ligand* has a number of donor centres as constituents of a closed ring system such that the donor atoms can hold a metal ion very effectively inside the cavity of the macrocycle. Some of the synthetic macrocyclic complexes are close to living systems and hence they have been studied as model compounds.

Limited few macrocyclic ligands and open-ended polydentate ligands are big enough and have good many donor atoms such that they can accommodate two metal atoms side by side. Such ligands are called *compartmental ligands*. (cf. NONNON (10-LI) and (10-I.VIII) macrocycles).

Compared to monodentate ligands, chelating ligands form complexes of greater stability. Greater stability indicates smaller dissociation of the complex into its components in a particular solvent. Again closed ring macrocyclic ligands form complexes of much greater stability than those formed by similar open-ended polydentate ligands having an equal number of equivalent donor atoms.

When all the ligands around a metal ion are the same the complex is called *homoleptic*. When the ligands are different the complex is termed *heteroleptic*. Thus $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{NiCl}_4]^{2-}$, $[\text{Ni}(\text{CO})_4]$ are examples of homoleptic complex whereas $[\text{CoCl}(\text{NH}_3)_5]^{2+}$, $[\text{PtCl}_2(\text{PPh}_3)_2]$, $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$, $[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]^-$ are heteroleptic.

Currently it has been brought to light that very simple molecules like N_2 and O_2 can act as coordinating ligands (Chapter 24, Part II). N_2 has a triple bond and a lone pair on each of the two nitrogens. Hence it can function both as a monodentate as well as a bridging ligand eg : $[Ru(NH_3)_5(N_2)]^{2+}$, $[NH_3)_5 Ru \leftarrow (N_2) \rightarrow Ru(NH_3)_5]^{4+}$. Dioxygen (O_2) takes part in complex reactions as a didentate (obviously highly strained form) ligand eg $[Cr(CO)(O_2)(PPh_3)_2]$. Considerable lengthening of the O—O distance (1.3 to 1.63 Å) (cf. $O_2 \sim 1.32 \text{ Å}$).

COORDINATION NUMBER AND STEREOCHEMISTRY

Since a complex is the result of an interaction between a metal ion and a certain number of ligands, it follows that the qualities of the two reactants ultimately dictate the coordination number of the metal ion and the geometry, that is, the stereochemistry of the complex.

While it is necessary to point out that the coordination number and the resulting stereochemistry are not always predictable certain broad features, however, may be outlined. Since an attraction between a metal ion and dipolar molecules or anions is involved, the coordination number will tend to be as large as possible.

The arrangement of the coordinated ligands must be such that it minimises the electrostatic repulsion between ligands.

An ML_2 type complex therefore should be linear for such a geometry maximises the L—M—L distance and hence minimises the repulsion between the two L groups. Similarly an ML_3 complex should have the three L ligands at the vertices of an equilateral triangle. For a coordination number four (ML_4 complex) the four L groups may be placed at the corners of a regular tetrahedron or at the corners of a square plane, both stereochemistries assuming minimisation of repulsive forces. Likewise a coordination number five admits of two stereochemistries, a square pyramid and a trigonal bipyramid. An octahedron, a hexagonal trigonal prism satisfies a coordination number six but in reality the octahedron appears to be the preferred one. These stereochemistries are illustrated below (Fig. 10.1 and Fig. 10.2). Coordination numbers seven and eight are known but are scarce. Table 10.2 describes some stereochemistries with examples.

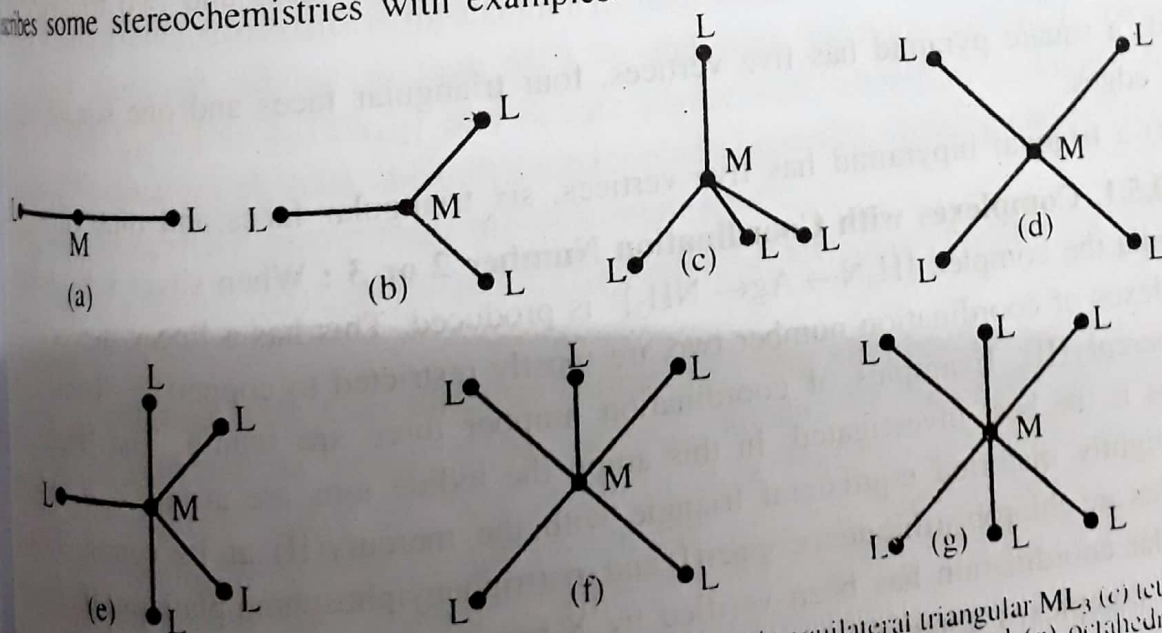


Fig. 10.1 Coordination numbers and stereochemistries (a) linear ML_2 , (b) equilateral triangular ML_3 , (c) tetrahedral ML_4 , (d) square planar ML_4 , (e) trigonal bipyramidal ML_5 , (f) square pyramidal ML_5 and (g) octahedral ML_6 .