Chapter 1

INTRODUCTION

Organic compounds lately have found tremendous importance as reagents in inorganic analysis as their application often leads to characteristic properties like colour, solubility etc., which have greater sensitivity and selectivity than those displayed by inorganic reagents in general. Moreover, organic reagents have found a greater diversity of uses in inorganic analysis. Yoe[1] has listed more than twenty different ways in which they could be used covering a variety of purposes. In many cases the same reagent may be used in different ways.

1.1. Definitions

Organic reagents used in chemical analysis may conveniently be defined as carbon-containing substances which interact with other substances (ions and molecules) in such a way that the reaction (i) leads to complete conversion of the latter substances so that it is possible to measure one of the reaction products or one of the reactants in a reasonable time in order to determine these substances quantitatively, or (ii) can be observed easily, indubitably and in the shortest possible period leading to the qualitative detection of the substances. Organic reagent can also be used as

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sequestering or masking agents so that by reaction with a particular ion they maintain the concentration of the latter below a level at which this ion interferes with the reaction designed to separate or otherwise characterise other molecules or ions.

The most desirable requirements in a chemical analysis are expressed by two characteristics, (i) Sensitivity, which determines the limit of detection of the smallest possible amount in the highest possible dilution and (ii) Selectivity, which determines the extent of interference in the detection or estimation by other substances present. In extremely favourable cases the second characteristic is expressed as specificity. Feigl[2] has defined and elaborated the significance of these terms in detail.

1.2. Organic Reagents : A Rational Approach

The use of organic reagents started generally in a 'hit or miss' way with a few empirical hypotheses, as these reactions between the organic compounds and inorganic ions are not generally selective. The recent developments in theoretical chemistry have afforded a wider picture of the nature of such interactions and the factors governing them, so that some predictions are now possible regarding the course of the reaction, the products and their stabilities and properties.

Most of the methods using organic compounds in the detection or determination of inorganic ions involve complex formation. As the inorganic species in solutions are generally ionic while the

complexes formed with organic substances are often nonionic, the
changes in the properties due to the formation of the latter are used
in developing analytical procedures. Even when the complexes formed
are ionic, they differ widely in properties like conductivity,
absorption spectra etc..

The metal ions, especially those with high charges, themselves
exist as complexes by orientation of water molecules surrounding them.
Thus in aqueous solutions, copper(II) and iron(III) produce species
like $\angle Cu(H_2O)_4 \angle^{2+}$ or $\angle Fe(H_2O)_6 \angle^{3+}$ and the complex formation with
the organic reagent is naturally a process of replacement involving
dynamic equilibrium, the position of which is determined rapidly and
directly by free energy considerations.
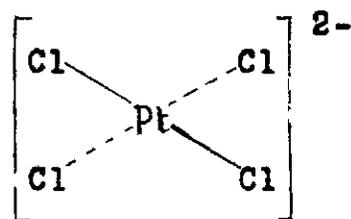
1.3. Coordination Compounds

Since the introduction of the concept of metal centered
octahedral structure and the recognition of the existence of the
entity, $\angle Co(NH_3)_6 \angle^{3+}$ in hexamine cobalt (III) salts by Werner[3], the
definition of these 'complex compounds' as "a species formed by the
association of two or more simpler species, each capable of
independent existance"[4] has not changed. These complexes, in which
the metal atoms occupy the centre, may carry positive (1-I),
zero (1 - II) or negative (1 - III) charges.
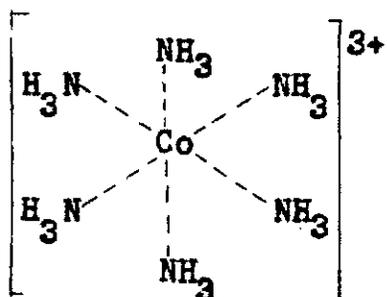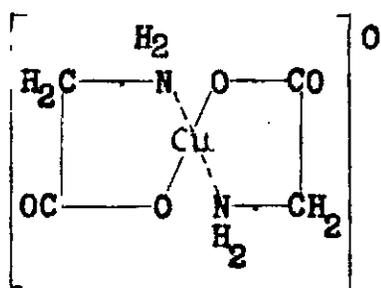
hexamine cobalt(III)   bis-(glycinato)-copper(II)   tetrachloro-
  (1 - I)   (1 - II)   platinum(IV)
                                                       (1 - III)

These examples illustrate Werner's[5] idea of the 'first
sphere of attraction' around the central atom or ion in which a
definite number of neutral molecules or oppositely charged ions is
grouped or 'coordinated'. The number of the latter, called the
'ligands', which are arranged around the central metal atom is the
'coordination number'. Several distinctly different theoretical
approaches[6,7], e.g., valence bond theory, molecular orbital theory,
crystal field theory or ligand field theory, have been made to
explain the nature of chemical bonding in coordination compounds, but
all of them are only approximate. The choice of any one of these
theoretical approaches is determined mainly by the nature of the
information sought.

1.3.1   Types of Metal- Ligand Bonds

Craig and Nyholm[8] have recognised two types of metal-ligand
bonds, viz., covalent and ionic, and subdivided the former into
σ -type, π -type and multicentre bonds. The ionic bonds may be
of ion-ion or ion-dipole type.

Generally, a σ -bond is formed by the overlapping of a
lone-pair orbital of the ligand with a 'dsp' hybrid orbital of the
metal in which the electron density is maximum along the internuclear
axis. The σ -bonds may further be catagorised as (a) Equivalent
covalent, (b) Mixed covalent, (c) Mixed ionic and covalent,
(d) Partially covalent and (e) Pure ionic. On the other hand, the

π -bonds in metal complexes may be formed in two different ways, either by donation of ligand as exemplified in the $p\pi$ - $p\pi$ bond in $(CH_3)_2$ B $\rightleftharpoons$ N $(CH_3)_2$ or by donation by the metal. The examples of the second type are $\angle I$ (pyridine)$_2\angle 7$ ClO_4 ($p\pi$ - $p\pi$), $Ni(CO)_4$ ($d\pi$ - $p\pi$) and $Ni(PF_3)_4$ ($d\pi$ - $d\pi$). This second type involves the donation of electrons by the metal atom to the ligand and require the use of an empty p- or d- orbital on the ligand or an anti-bonding π -type molecular orbital. In the first type, ligands having available π-lone pairs readily form double bond with metals having vacant orbitals. Both experimental evidences[9] and theoretical calculations[10] have supported the existence of such double bonds between metals and ligands.

1.3.2. Coordination Number (C.N.)

The factors which determine the coordination number (C.N.) in a complex compound are (a) the properties of the metal atom like its oxidation number, electronegativity etc., (b) the number of available bonding orbitals and (c) in some cases, the nature of the donor atom. Thus, the coordination number of cobalt (III) or chromium(III) has a fixed value of six, while it is changed from six to eight when molybdenum(III) is oxidised to the tetravalent state. The C.N. of iron (II) changes with ligands, e.g., with Cl^- it is four and with CN^- it is six.

1.3.3. Chelates and Chelating Ligands

Werner[3] explained the structure of bis-(ethylene-diamine) - platinum(IV) chloride (1 - IV) as a 5- membered heterocyclic ring in which one molecule of ethylenediamine occupied two of the four coordination positions. In its complex with nickel(II), salicylal- dehyde-ethylenediamine
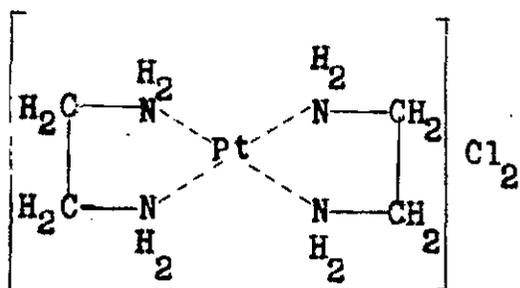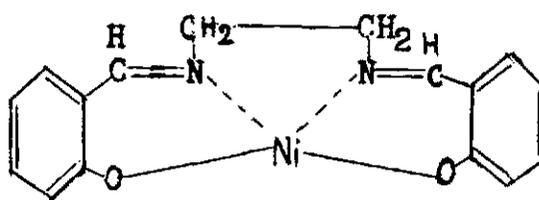
(1 - IV)   (1 - V)

fills up all the four coordination positions (1 - V). Morgan and Drew[11] introduced the term 'chelation' in which the central atom may be joined producing a ring stfucture and such compounds were named 'chelates'. In the more stable chelates, the ring size is usually five or six. On the higher side, formation of seven or eight membered rings in the case of some sexadentate ligands and on the other side, the existence of four-membered rings have been estab- lished.
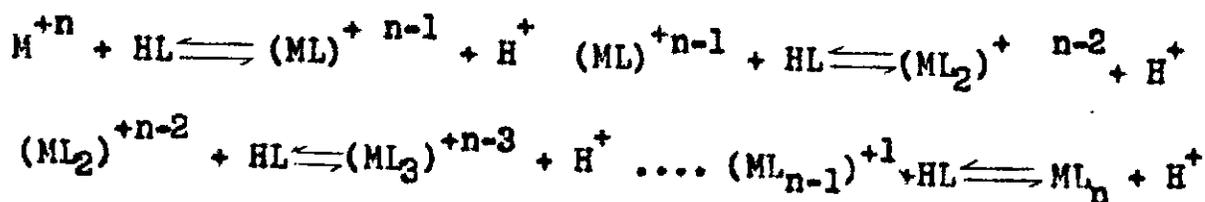
Diehl[12] classified chelating agents based on the number of reacting atoms combining with a metal, e.g., unidentate, bidentate etc. Again within each class subdivisions may be made by the distribution of groups between acidic or coordinating types. Among

these chelating agents, the bidentate ligands are not only most common and of varying types, but also are widely used as reagents in inorganic analysis.

There are two essential characteristics necessary for a ligand to act as a chelating agent, (a) the existence of at least two appropriate functional groups; the donor atoms of which are capable of combining with a metal atom by donating a pair of electrons and (b) the two groups must be situated in such a way that they permit the formation of a ring with the metal atom as the closing member. The most familiar chelating ligands used in inorganic analysis contain two distinct types of functional groups, (a) acidic groups like, imino (=NH), oxime (=N.OH), carboxyl (-COOH), sulphonic(-SO$_3$H), sulphinic (-SO$_2$H), hydroxyl (-OH), sulphohydryl (-SH), phosphinic $/$-P(O)(OH)$_2/$ etc., which combine with the metal atom by the replacement of hydrogen and (b) purely coordinating groups like amino (-NH$_2$), imino (=NH), oxime (=N.OH), carbonyl (=CO), thio-carbonyl (=CS) etc. However, in addition to the existence of these essential groups in the ligands other conditions like steric factors, dissociation of the ligand etc., may play important roles in determining the formation of chelates.

1.4. Stability Constants of Metal Complexes

Let us consider the general equilibria between a central metal ion, M^{+n} and n- number of ligands HL,
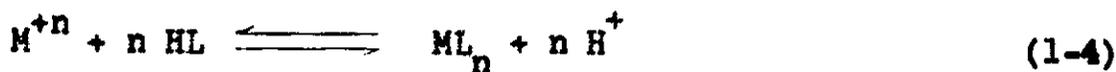
$$M^{+n} + HL \rightleftharpoons (ML)^{+n-1} + H^+ \quad (ML)^{+n-1} + HL \rightleftharpoons (ML_2)^{+n-2} + H^+$$

$$(ML_2)^{+n-2} + HL \rightleftharpoons (ML_3)^{+n-3} + H^+ \quad \cdots \quad (ML_{n-1})^{+1} + HL \rightleftharpoons ML_n + H^+$$

Then the successive formation or stability constants would be expressed by,

$$K_1 = [(ML)^{+n-1}][H^+] / [M^{+n}][HL] \qquad \cdots \quad (1\text{-}1)$$

$$K_2 = [(ML_2)^{+n-2}][H^+]/[(ML)^{+n-1}][HL] \qquad \cdots \quad (1\text{-}2)$$

and $\qquad K_n = [ML_n][H^+] / [(ML_{n-1})^{+1}][HL] \qquad \cdots \quad (1\text{-}3)$

and the overall constant , for the reaction,

$$M^{+n} + n\, HL \rightleftharpoons ML_n + n\, H^+ \qquad (1\text{-}4)$$

by,

$$\beta = k_1, k_2 \cdots \quad k_n = [ML_n][H^+]^n/[M^{+n}][HL]^n \qquad (1\text{-}5)$$

where the terms in the brackets express activities of species in solution.

The magnitude of the stability constants of the complexes formed in solution between particular metal ions with specific ligands are very important in analytical chemistry. The difference between these values and the corresponding stability constants for complexes of other metal ions with the same ligand determines the

level of interference caused by such species in the determination of the former metal using this ligand as the reagent.

1.5. Stability of Complexes and Acid Dissociation Constant of the Ligand.

The factors involved in the formation of σ-bond between a ligand and metal ions are similar to those concerned in the protonation of the ligand. The stability constants of complexes of a metal with a series of structurally similar ligands is generally correlated with the basic strengths of the ligands,

$$\log \beta \simeq a p K_a + b$$

.. (1-6)

where Ka is the acid dissociation constant of the ligand and the quantity b, gives an approximate measure of the π -bond character of the metal-ligand bond[13].

1.6. Stereochemistry

The stability and reactivity of metal complexes are determined by the number of groups around the central metal ion and the stereochemistry of the complex. For example, tris-iron(II) - 1,10- phenanthroline (low-spin) is more stable than the corresponding high-spin bis-complex. Perrin[14] has listed the possible stereo - chemical configurations of different 4- and 6- coordinated metal complexes according to the number of d-electrons in the cation. Co-ordination number, however, often vary with the ligand (Section 1.3.2) and the variation mainly depends on the polarisability of the ligand[15]. Provided steric factors (Section 1.7) do not intervene

and the ligands can be accomodated around the metal ion, as many of them will be coordinated as needed, to reduce the charge of the metal ion nearly to zero. If the ligand is not easily polarised, the donation of charge from the ligand to metal is relatively little and a higher coordination number is expected. Thus, iron is hexacoordinated in $\angle FeF_6\,\mathbf{J}^{3-}$, but tetracoordinated in $\angle FeCl_4\,\mathbf{J}^-$ with more polarisable chloride ion.

1.7. Steric Effect

The most stable complexes are likely to be formed when vacant orbitals of the metal ion are so directed that they overlap filled ligand orbitals (or vice versa) without serious distortion. But steric factors may render the attainment of this impossible. Often the steric hindrance to coordination can result from rather small changes in ligand structure. It is well known that 1,10-phenanthroline forms a coloured tris-iron (II)- complex having high stability. The corresponding 2,9 - dimethyl-1,10-phenanthroline complex is supposed to be more stable due to the rise in basicity of the substituted ligand (section 1.5), while in practice only a colourless high-spin bis-complex is formed. Steric hindrance prevents the formation of the tris-iron(II) complex, of the substituted reagent.

1.8. Thermodynamics of Complex Formation

The stability constant of a complex is quantitatively related to the free energy change ($\triangle G$) and corresponding changes in

entropy (ΔS) and enthalpy (ΔH) of the reaction for its formation
from its components as expressed by,

$$- \Delta G = 2.303 \ RT \ \log k \qquad \qquad .. \ (1\text{-}7)$$

and $\log k \quad = \dfrac{\Delta S - \Delta H/T}{2.303 \ R} \qquad \qquad .. \ (1\text{-}8)$

where R and T are the usual gas-constant and Kelvin temperature. It
is evident from equation 1-8 that the most favourable condition for
the formation of the complex will be when the entropy change is
positive, (i.e. the system is more disorganised or contains more
particles) and the enthalpy change is negative (i.e., heat is
evolved). During complex formation, when the ligand ions or molecules
are arranged around the central metal ion the number of free particles
seems to be reduced indicating a negative entropy change. However,
the metal ions are usually hydrated in aqueous solutions and the
effect of the solvent should also be considered while determining
the change in entropy. The entropy changes on complex formation are
mainly due to the varied degree of hydration in the complex in
comparison to its components and to the differences in the extent of
the disordered solvent region.

In the formation of a multidentate chelate there is a loss
of configurational entropy, but at the same time a greater dis -
placement of water from the hydration spheres of the reactants occurs.
The net entropy change is higher than that for the formation of a
nonchelate complex. Moreover, it is greater for a charged than for
a neutral ligand. Thus, the ΔS for the formation of copper-ethylene-
diamine tetraacetate is much higher than the corresponding acetyl -
acetonate.

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