



Chapter II

Theory

2.1 Coordination Compounds and the Lewis Acid - Base Concept

The complexation reaction can also be described by acid - base reaction since acid and base collective terms defined by chemist in such a way as to include all compounds having similar properties. Lewis' propose has broadened the chemists' definition of bases to include any species that can donate a pair of electrons. Such species are now commonly called Lewis bases, donors or ligands ; organic chemists commonly call them nucleophiles. Correspondingly, Lewis' propose has broadened the definition of acids to include not only hydrogen-ion-producing materials, but species as metal ions since they are also species that can accept a pair of electrons. Thus species are now often called Lewis acids or acceptors ; organic chemists commonly call these electrophiles. In the product (usually a solid) the two are held together by the sharing of the pair of electrons. The resulting bond is called a coordinate covalent bond and is distinguished from an ordinary covalent bond by the fact that both electrons in the bond came from the same atom in the Lewis base, the donor atom of the base. The species in which the Lewis acid and base are joined together in chemical matrimony is known by various names. It may be call an acid - base adduct, a coordination complex or coordination compound, or (if it is charged) a complex ion (113).

Generally, the stability of a complex will obviously be related to (114) :

1. Complexing ability of metals The relative complexing ability of metals is conveniently described in terms of the Schwarzenbach Classification which is broadly based upon the division of metal into class A and class B Lewis acids, i.e., electron acceptors. Class A metals are distinguished by an order of affinity (in aqueous solution) towards the halogens $F^- \gg Cl^- > Br^- > I^-$ and form their most stable complexes with the first member of each group of donor atoms in the Periodic Table (i.e., nitrogen, oxygen and fluorine). Class B metals coordinate much more readily with I^- than with F^- in aqueous solution, and form their most stable complexes with the second (or heavier) donor atom from each group (i.e., P, S, Cl). The Schwarzenbach Classification defines three categories of metal ion acceptors :

1.1 Cations with noble gas configurations: The alkali metals, alkaline earths and aluminium belong to this group which exhibit Class A acceptor properties. Electrostatic forces predominate in complex formation so interactions between small ions of high charge are particularly strong and lead to stable complexes. Thus fluoro - complexes are particularly stable, water is more strongly bound than ammonia which has a smaller dipole moment and cyanide ions have little tendency to form complexes since they only exist in alkaline solutions where they cannot compete successfully with hydroxyl ions.

1.2 Cations with completely filled d-subshells: Typical of this group are copper (I), silver (I) and gold (I) which exhibit Class B acceptor properties. These ions have high polarizing power and the bonds formed in their complexes have appreciable covalent character. The more noble the metal and the less electronegative the donor atom of the ligand the more stable the complexes ; thus cadmium (II) and mercury (II) form strong complexes with I^- and CN^- ions but weak complexes with F^- .

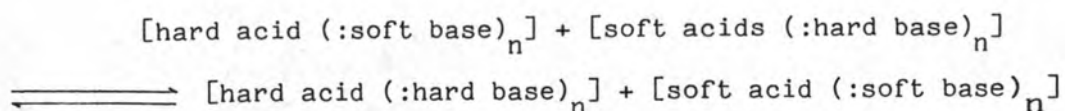
1.3 Transition metal ions with incomplete d-subshells. The elements with Class B characteristics form a roughly triangular group within the periodic table with the apex at copper and the base extending from rhenium to bismuth. To the left of this group, elements in their higher oxidation states tend to exhibit Class A properties while to the right of the group, the higher oxidation states of a given element have a greater Class B character.

The concept of Hard and Soft Acids and Bases (115) is useful in characterising the behavior of Class A and Class B acceptors. A soft base may be defined as one in which the donor atom is of the largest of the nonmetal atoms with ionic radii in excess of 170 pm, high polarizability and of low electronegativity (2.1 to 2.9), is easily oxidized, or is associated with vacant low-lying orbitals. These terms describe, in different ways, a base in which the donor atom electrons are not tightly held but are easily distorted or removed. Hard bases have the opposite properties, i.e., the donor atom is of the smallest of the nonmetal atoms which ionic radii of about 120 pm, low polarizability and high electronegativity (3.44

and 3.98), is difficult to reduce and is associated with vacant orbitals of high energy which are inaccessible.

On this basis, it is seen that Class A acceptors prefer to bind hard bases, e.g., with nitrogen, oxygen and fluorine donor atoms, whilst Class B acceptors prefer to bind to the softer bases, e.g., P, As, S, Se, Cl, Br, I donor atoms. Examination of the Class A acceptors shows them to have the following distinguishing features ; small size (ionic radii less than 90 pm) high positive oxidation state, low electronegativity (0.7 to 1.6), and the absence of outer electrons which are easily excited to higher states. These are all factors which lead to low polarizability and such acceptors are called **hard acids**. Class B acceptors, however, have one or more of the following properties: low positive or zero oxidation state, high electronegativity (1.9 to 2.54), large size (ionic radii in excess of 90 pm) and several easily excited outer electrons (for metals these are the d electrons). These are all factors which lead to high polarizability and Class B acids may be called **soft acids**.

Hard and soft acid - base (HSAB) principle may now be stated which permits correlation of the complexing ability of metals: **"Hard acids prefer to associate with hard bases and soft acids with soft bases"**. Put in equation form, the equilibrium will tend to favor the products on the right side of equation.



This statement must not, however, be regarded as exclusive, i.e., under appropriate conditions soft acids may complex with hard bases or hard acids with soft bases.

2. Characteristics of the ligand Among the characteristics of the ligand which are generally recognized as influencing the stability of complexes in which it is involved are

2.1 the basic strength of the ligand

2.2 its chelating properties (if any)

and 2.3 steric effect

From the point of view of the analytical applications of complexes, the chelating effect is of paramount importance and therefore merits particular attention.

The term "chelate effect" refers to the fact that a chelated complex, one formed by a bidentate or a multidentate ligand, is more stable than the corresponding complex with monodentate ligands. The greater the number of points of attachment of ligand to the metal ion, the greater the stability of the complex. It is appropriate to emphasise here the significance of the chelate effect and to that the features of the ligand which affect chelate formation:

1. The basic strength of the chelating group The stability of the chelate complexes formed by a given metal ion generally increases with increasing basic strength of the chelating agent, as measured by the pK_a values.

2. The nature of the donor atoms in the chelating agent

This factor involves hard and soft acid - base (HSAB) principle which is described above.

3. Ring size Five- or six - membered conjugated chelate rings are most stable since these have minimum strain. The functional groups of the ligand must be so situated that they permit the formation of a stable ring.

4. Resonance and steric effects The stability of chelate structures is enhanced by contributions of resonance structures of the chelate ring. The most common steric effect is that of inhibition of complex formation owing to the presence of a large group either attached to or in close proximity to the donor atom.

A further factor which must also be taken into consideration from the point of view of the analytical applications of complexes and of complex - formation reaction is the rate of reaction : to be analytically useful it is usually required that the reaction be rapid. An important classification of complexes is based upon the rate at which they undergo substitution reactions and leads to the two groups of labile and inert complexes. The term labile complex is applied to those cases where nucleophilic substitution is complete within the time required for mixing the reagent. Kinetic inertness or lability is influenced by many factors but the following general observations form a convenient guide to the behaviour of the complexes of various elements :

- (i) main group elements usually form labile complexes

(ii) with the exception of Cr(III) and Co(III), most first - row transition elements form labile complexes

(iii) second- and third - row transition elements tend to form inert complex

2.2 Liquid - Liquid Extraction

Complexing in solution can be detected in many different ways and solvent extraction (116) is one of the methods for assaying the complexing tendency of metal - macrocycle salt systems. An aqueous metal solution is brought into contact with an organic macrocycle solution in order to bring about a transfer of one or more solutes into the organic solvent. The separations can be considered simple, clean, rapid and convenient. In this work, atomic absorption spectrometric method was used to quantitatively determine the concentration of the metal in aqueous phase after extraction. The decrease in the concentration of the metal in aqueous phase indicates that the complexes exist, more or less.

The various terms used for expressing the effectiveness of a separation must be considered. For a solute which dissolves in one phase in equilibrium with another immiscible phase will distribute itself between two phases so that a ratio of the concentrations in two phases is constant. The system may be defined by Nernst distribution law (117-118) as the following equation :

$$\frac{[S]_{1,1}}{[S]_{1,2}} = K_d \quad [1]$$

where $[S]_{1,1}$ is the concentration of solute 1 in the phase 1
 $[S]_{1,2}$ is the concentration of solute 1 in the phase 2
 and K_d is the distribution coefficient.

The distribution coefficient, K_d , is valid only when the solute is the same species in both phases. If the solute has a different form in one of the phases, a better description would be the distribution ratio, D (119) :

$$D = \frac{\text{total concentration of solute (all form) in phase 1}}{\text{total concentration of solute (all form) in phase 2}} \quad [2]$$

The total concentration of solute is the analytical concentration, C . The analytical concentration of a substance is equal to the sum of the equilibrium concentrations, thus :

$$C_{1,1} = \sum_{i=1} [S_i]_{1,1} \quad [3]$$

$$C_{1,2} = \sum_{i=1} [S_i]_{1,2} \quad [4]$$

$$D = \frac{C_{1,1}}{C_{1,2}} \quad [5]$$

The extraction efficiency is considered as the percent of solute extracted, %E (117-118). The total amount of solute in water - solvent system is the sum of the amount of solute in each phase of the system, as expressed by the equation :

$$C_s = [S]_o V_o + [S]_w V_w \quad [6]$$

where C_s is the analytical concentration of solute.

V_o is the volume of organic solvent.

$[S]_o$ is the concentration of solute in organic solvent.

V_w is the volume of water.

$[S]_w$ is the concentration of solute in water.

Since

$$[S]_o = K_d[S]_w \quad [7]$$

substitute equation [7] into equation [6] yields

$$C_s = K_d[S]_wV_o + [S]_wV_w \quad [8]$$

If the distribution coefficient is known, the percent of the solute extracted into the organic solvent can be calculated :

$$\%E = \frac{100K_d[S]_wV_o}{K_d[S]_wV_o + [S]_wV_w} \quad [9]$$

which can be simplified to

$$\%E = \frac{100K_d}{K_d + (V_w/V_o)} \quad [10]$$

The extractabilities of metals depend on various factors. One of the important factors is the extracting solvent. The choice of solvent for extraction is governed by the following considerations (118-119) :

1. The solute should be very soluble in the solvent so as to have a high value of K_d or D , and this requires only one or two extractions.

2. The solvent should be as immiscible with water as possible. One way of arriving at an excellent idea about the degree of immiscibility is through the comparison of the dipole moment of the liquid with that of water ($\mu=1.84$ debyes). Solvent such as benzene, hexane, and carbontetrachloride with a dipole moment of zero have very low water solubilities, whereas solvent such as diethylether ($\mu = 1.7$ debyes) has relatively high aqueous solubility.

3. The solvent should have as great a density difference from water as possible. This permits a clean - cut phase boundary between the two phases and facilitates the physical separation of the two liquids after extraction.

4. The viscosity of the solvent should be low to permit good contact between the two phases while shaking and rapid setting out of the two liquids after shaking.

5. The solvent should have a sufficiently high boiling point so that evaporation of the solvent is not a problem.

6. The solute should be able to be recovered readily from the solvent for subsequent operations.

7. The solvent should not form stable emulsion with water

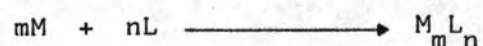
8. The solvent should be readily available in sufficient state of purity for convenient use.

9. The solvent should not be hazardous to health.

10. The solvent should be inexpensive.

The other factors, such as the fit of the metal ion in the macrocyclic cavity, the anion selected to form the ion - pair, pH, the extraction time and temperature depend primarily on the macrocycle - metal complex system being studied.

The complex formation can be investigated in many different ways such as conductometrically, optically and UV - visible spectrometrically. The formation of many complexes can be represented by the equation :



The molar ratio of metal ion and ligand forming the complex is important. In this work, Molar - Ratio Method (120) is used to investigate the empirical formulas of the complexes in solution. The concentration of the metal is fixed at a certain amount while that of the ligand varies to give a series of concentration ratios ($[L]/[M]$). The conductance of the solution is then measured and plotted against the molar ratio. The conductance decreases linearly upto the molar ratio of the complex (Fig 2.1). The curve may not show a sharp break at the molar ratio of the complex due to incomplete complex formation or dissociation of the complex.

