CHAPTER - I

INTRODUCTION
Sulphur and selenium being members of the same group of periodic table resemble in most of the properties and form structurally similar compounds. Both elements are donors in a variety of ligands which form complexes with metal ions. The complexing ability of donor and acceptor elements depends upon the nature of the respective elements.

Ligands in which sulphur or selenium act as donors have been classified as class 'b' donors by Arhland, Chatt and Davies (1) and soft bases by Pearson (2). Such ligands in which sulphur or selenium atom is a donor form more stable complexes with metal ions which have low or zero positive charge, large size and several easily excitable outer electrons and such metal ions have been classified as class 'b' acceptors (1) or soft acids (2).

Metal ions with d^{10} configuration, viz. Copper(I), Silver(I), Zinc(II), Cadmium(II) and mercury(II) and d^3 metal ions namely nickel(II), Palladium(II) and platinum(II) show very high formation constants particularly with sulphur ligands. Being class 'b' metal
ions they tend to form strong sigma bonds with these ligands due to polarization of sulphur atom (3) or due to greater covalent interaction (4). A $d_{e} - d_{e}$ bond by back donation of electrons to vacant 3d orbitals of sulphur atom is one of the reasons for the greater stability of such complexes.

The sulphur and selenium ligands can be broadly classified into two groups; inorganic and organic compounds.

Amongst the important inorganic ligands are:

(i) Sulphides and selenides.
(ii) Trithiocarbonates and triselenocarbonates.
(iii) Thiocynates and selenocynates.
(iv) Thiosulphates and selenosulphates.
(v) Sulphites and selenites.

The organic sulphur and selenium compounds are of more varied type - the simple ones are:

(i) Thiols and selenols - one co-ordinating site.
(ii) Thioethers and alkylselenides - one coordinating site.
(iii) Mercaptoacids and selenol - acids, - two bonding sites.
(iv) Thioketones and selenoketones, -thioacetylacetone and selenoacetylacetone each have two bonding sites.

The other class of compounds is represented by thioureas and selenoureas, thiocarbamates and selenocarbamates; these ligands have each two bonding sites nitrogen, sulphur or selenium act as donating atoms in these ligands.

The formation of sulphur or selenium ligand complexes of typical class 'b' metal ions like mercury(II) and zinc(II) with high stabilities is quite obvious.

The organic multidentate ligands like 2- mercaptopropanoic acid and 3- mercaptopropanoic acid which are isomers contain oxygen as well as sulphur based functional groups act as excellent chelating agents for all 'a', 'b' and borderline metal ions.

Similarly thioureas and selenoureas having sulphur, nitrogen and selenium, nitrogen respectively as donors form a variety of complexes with class 'b' and borderline metal ions.
The important aspects of the studies on the complexation are: (i) physico-chemical investigation leading to understanding of nature of complex species and their equilibria, (ii) synthesis and determination of structure of metal complexes (iii) the analytical applications. A review of literature reveals an intense interest in all the three directions.

1. **EQUILIBRIUM STUDIES ON MERCAPTOCARBOXYLATE METAL COMPLEXES.**

Fernando and Freiser (5) studied the chelating properties of 3-mercaptopropanoic acid and determined stepwise formation constants of Nickel(II) and Zinc(II) with the ligand and observed that Nickel(II) complex is less stable than Zinc(II) complex. With mercaptoacetic acid as chelating agent they have determined the relative stability of five and six membered ring chelates using the relation $\Delta \log K_i / \Delta p K_{av}$, $\Delta \log K_i$ is decrease in value of first formation constant of the chelates in going from five to six membered rings and $\Delta p K_{av}$ is increase in arithmetic mean of negative logarithm of acid dissociation constants of ligand.
molecules, they found five membered rings are more stable than six membered rings in each complex.

Leussing (6) reported the stability constants of manganese(II), iron(II), nickel(II), and zinc(II) with thioglycollic acid; only the formation of 1:1 and 1:2 (metal:ligand) complexes were reported and zinc complex was found to be more stable than nickel complex. The formation of polynuclear complexes between nickel(II) and thioglycollic acid ions have been described by Leussing and co-workers(7), they have reported the formation of 2:2, 3:4, 4:6 (metal:ligand) complexes with the metal ion.

Bear et al (8) have investigated potentiometrically the formation constants of lanthanide metal complexes with 2-, and 3- mercaptopropanoic acids, they have reported that both the acid anions function as monodentate ligands. Nigam et al (9) have potentiometrically studied metal complex of uranyl(VI) with 3-mercapto-propanoic acid. The workers (10) have reported stability constants of 1:1 complexes of copper(II), cobalt(II), mercury(II) and 1:2 complexes of nickel(II), zinc(II),
palladium(II), iron(III), uranyl(VI), zirconium(IV) and thorium(IV) with thiolacetic acid using potentiometric technique. In case of palladium, nickel, zinc, the values of stability constants follow the order Pd Ni Zn. In case of copper(II) the value is low. Saxena and Gupta (11) reported the composition and stability constants of 3-mercaptopropanoic acid with zinc(II); 1:1 and 1:2 (metal:ligand) complexes, overall stability constant of 12.65 at 30°C has been observed. The workers (12) have investigated potentiometrically the stability and composition of thallium(I) with 3-mercaptopropanoic acid acid, 1:1 (metal:ligand) complex with logk value of 2.85 at 30°C is reported. Similar studies were conducted with nickel(II) and 1:1 and 1:2 (metal:ligand) complexes with the same ligand with overall stability constant value of 10.74 at 30°C were reported (13). Polarographic studies of the same ligand with cadmium(II) revealed formation of four complexes of 1:1, 1:2, 1:3 and 1:4 (metal:ligand) stoichiometry with overall stability value of 17.19 at 30°C (14).

Bhattacharya and Reddy (15) have investigated the nickel (II) and thallium(I) complex formation with
lactic acid and thiolactic acid by pH metric technique and have reported that nickel(II)-thiolactate complexes are more stable than the lactate complexes and reverse was the case with thallium(I). They have supported the observations on the assumption that 3d Pi orbitals in sulphur atom render metal to ligand Pi interactions possible in case of nickel-thiolactate complex, and such interactions were not existing in other complexes. Bhattacharya and co-workers (16) have also reported the stepwise formation constants of complexes of thioglycollic acid and thiolactic acid with Be(II), Zn(II) and Cd(II), they have observed the stability order: Cd > Zn > Be and thiolactic acid forms stronger complexes than thioglycollic acid with these metal ions. The stability of chelates is discussed in terms of metal-ligand Pi interactions. Nitriloacetic acid as primary ligand and thioglycollic acid or thiolactic acid and thiomalic acid as secondary ligands with zinc(II) have also been studied by Bhattacharya et al (17). They (18) also studied the mixed ligand systems of copper(II) and nickel(II) with nitriloacetic acid as primary ligand and a mercaptocid or an amino acid as secondary ligand. Similarly phenanthroline as primary
ligand and mercapto acids as secondary ligands have also been studied by Bhattacharya and co-workers (19). The objective of these studies was to find out the effect of Pi bonding, they concluded that the metal sulphur covalent bond is strengthened and effect of Pi interaction is not significant.

Tanaka and co-workers (20) have studied potentiometrically the complex formation between phenyl and methyl mercury and pencillamine and amino acids like cysteine and reported a 1:2 (metal: ligand) complex with the ligands. They have found that stability order of the bonds decreased in the order:

$$\text{MeHg - S} > \text{PhHg - N} > \text{PhHg - S} > \text{MeHg - N}$$

$$\gg \text{PhHg - O}.$$ 

They have also evaluated stability constants of complexes of thiolactic acid and pencillamine with Cr(III) which forms 1:1, 1:2 and 1:3 monomeric complexes with thiolactic acid and 1:3 complexes are of regular octahedral geometry. The complexes of pencillamine are more stable than complexes of thiolactic acid (21).
Van Pouke et al. (22) have conducted potentiometric and colorimetric studies of Ni(II) and Zn(II) with thiolactic acid and reported the formation of mononuclear and polynuclear species of the composition 1:2, 2:2, 3:4 (metal:ligand) with stability constants 14.33, 17.29 and 34.92 respectively. The non-existence of 4:6 complex is explained due to presence of steric hinderance by α-methyl group in thiolactic acid as the similar complexes are existing in case of Ni(II) and Zn(II) thioglycollic acid. A similar study has been extended to the systems of Ni(II) and Zn(II) and 3-mercaptopropanoic acid (23), with Zn(II) a number of species with 1:2, 3:4, 4:6 (metal:ligand) stoichiometries have been observed and in case of Ni(II) complexes of 5:10, 6:9 and 6:12 (metal:ligand) stoichiometric ratios have been reported. The absence of steric hinderance in 3-mercaptopropanoic acid being responsible for the formation of complexes with such high ligand ratios.

Sarin and Munshi (24) have investigated potentiometrically the complex formation of In(III) with several mercaptoacids and have reported that stability of complexes with various ligands decrease in order:
Thiolactic acid > Thioglycollic acid > Lactic acid > Glycollic acid > Alanine and Glycine.

They have correlated these values with stepwise formation constants of In(III)-3-mercaptopropanoic acid complexes and have found these to be less stable than those of thiolactic acid and thioglycollic acid and values of formation constants decrease with increase in temperature. Stepwise formation constants of Ga(III) complexes with thiolactic acid, thiomalic acid, thioglycollic acid, lactic acid, malic acid and glycollic acid increase with increase in temperature, and Ga(III) forms 1:1, 1:2, 1:3 (metal:ligand) complexes with thiolactic acid. Ga(III)-thioglycollic acid complexes are more stable than those of thiolactic acid (25).

Cassasas and co-workers (26) have investigated the Cd(II)-thiolactic system potentiometrically and reported the existence of polynuclear species of the composition, 1:2, 2:3 and 3:4 (metal:ligand) with overall formation constants values of 15.04, 28.45 and 40.80 respectively. The acid sulph-hydryl group tends to bridge metal ions in these complexes.
2. SOLID COMPLEXES OF MERCAPTO CARBOXYLIC ACIDS.

Fernando and Frieser (5) have reported complexes of 3-mercaptopropanoic acid of Pb(II), Cu(II) and Ag(I), the composition of these complexes reported is:

\[ \text{Pb}(\text{SCH}_2\text{CH}_2\text{COO})_2, \quad \text{Ag}(\text{SCH}_2\text{CH}_2\text{COO}) \cdot \text{H}_2\text{O}, \]
\[ \text{Cu}(\text{SCH}_2\text{CH}_2\text{COO}) \quad \text{and} \quad \text{Cu}(\text{HSCH}_2\text{CH}_2\text{COO}), \]

Copper formed two types of complexes.

Shindo and Brown (27) have reported complexes of L-cysteine, S-methyl-L-cysteine and 3-mercapto-propanoic acid with Zn(II), Cd(II), Hg(II) and Pb(II), they have observed that Hg(II) forms a number of complexes with stoichiometries -

\[ \text{Hg}_2\left[\text{SCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\right]_2, \]
\[ \text{Hg}_2\left[\text{SCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\right]_2 \cdot \text{HCl}, \]
\[ \text{Hg}_3\left[\text{SCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\right]_2 \cdot \text{Cl}_2, \]
\[ \text{Hg}\left[\text{SCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\right]_2 \quad \text{and} \]
\[ \text{Hg}_3\left[\text{SCH}_2\text{CH}(\text{NH}_2)_3\text{CO}_2\text{H}\right] \cdot 2\text{H}_2\text{O} \]
Zinc and cadmium form:

\[
\left[ M \underbrace{\text{L}^4}_2 \right]^{2+} \ M \ x_4^{2-} \ , \ M = \text{Zn or Cd}
\]

\[ L = \text{S-CH}_2\text{CH(}NH_2\text{)}\text{CO}_2^- \ , \ x = \text{Cl}^- \]

The metal is bound to sulphur and carboxylate oxygen, and sulphur atoms bridge the three metal atoms, the other types of complexes reported are:

\[
\left[ \text{ML}_2 \right]^{2-} \ ; \ M = \text{Zn or Cd} \ , \ L = -\text{SCH}_2\text{CH(NH}_2\text{)}\text{CO}_2^- 
\]

The metal atom is bound to sulphur atom of sulphhydryl group and nitrogen atom of amino group.

Mishra and Nigam (9) have isolated and characterized a uranyl complex of 3-mercaptopropanoic acid, its composition is reported to be:

\[
\left[ \text{UO}_2\text{L}_2 \right] \ 2\text{H}_2\text{O} ; \ L = -\text{SCH}_2\text{CH}_2\text{CO}_2\text{H}
\]

A cobalt complex of the composition

\[
\text{CoL}_2(\text{H}_2\text{O})_2 \ (L = -\text{SCH}_2\text{CH}_2\text{CO}_2^-) \ 	ext{with octahedral geometry has been reported (28); sulphur atom of -SH group and oxygen atom of -COOH group is involved in bonding with Co(II) ion. Nigam and co-workers (29) have}
\]


isolated complexes of Ag(I), Cd(II), Hg(II) and UO₂(VI) of 3-mercaptopropanoic acid, the reported composition of the complexes is:

\[ \text{Ag(C_3H_5O_2S).2H_2O, Cd(C_3H_4O_2S).2H_2O,} \]
\[ \text{Hg(C_3H_5O_2S)_2 and UO}_2(\text{C_3H_5O_2S).2H_2O.} \]

With Ag(I), Hg(II) and Uranyl ions the ligand acts as mono-negative bidentate ligand, co-ordinating through oxygen atom of -COOH and sulphur atom of -SH group. In case of cadmium the ligand acts in a binegative bidentate fashion. Srivastava and Nigam (30) have also isolated the complexes of thiolactic acid with Ag(I), Cd(II), Hg(II) and Pb(II) with compositions:

\[ \text{H [Ag(II)L].H}_2\text{O, Cd [HL].2H}_2\text{O} \]
\[ \text{Na}_2[\text{CdL}_2].2\text{H}_2\text{O, H}_2[\text{HgL}_2] \text{ and PbL.2H}_2\text{O (L = C_3H_4O_2S)} \]

They have found that thiolactic acid acts as bidentate ligand co-ordinating through sulphur of -SH and oxygen of -COOH groups. Complexes of Cr(III), Mn(II), Co(II), and Ni(II) with thiolactic acid have been reported (31), their compositions found are:
\[ H_3 \left[ \text{Cr} \left( C_2H_4O_2S \right)_3 \right], \quad \text{Mn} \left[ \left( C_2H_4O_2S \right) \left( H_2O \right)_2 \right] 2H_2O \]

\[ \text{Na}_2 \left[ \text{Co} \left( C_2H_4O_2S \right)_2 \left( H_2O \right)_2 \right], \]

\[ \left[ \text{Ni} \left( C_2H_4O_2S \right) \left( H_2O \right)_4 \right] \text{and} \]

\[ \text{Na}_2 \left[ \text{Ni} \left( C_2H_4O_2S \right)_2 \right] \]

In these complexes the ligand acts as bidentate chelating agent co-ordinating through sulphur of \(-SH\) and oxygen of \(-COOH\) groups. They have suggested Mn(II) complex a square planar geometry with magnetic moment of 4.51 B.M.

A trinuclear complex of thiolactic acid with Cu(II) having composition-

\[ \text{Cu}_3 \left( C_2H_4O_2S \right)_3 4.5H_2O \text{ has also been reported} \ (32). \]

Mehrotra and co-workers (33) have reported various complexes of Ti(IV) and Zn(IV) isopropoxides with 2-mercaptoethanol, thiolactic acid and 3-mercaptopropanoic acid.

Panchal and Bhattacharya (16) have prepared complexes of Zn(II), Cd(II), Hg(II) and Ag(I) with thiolactic acid and thio glycollic acid and compositions
of the complexes is represented as:

\[ \text{Zn(} \text{ZnL}_2\text{)}_2 \text{H}_2\text{O}, \text{Cd(CdL}_2\text{)}, \text{Hg(HgL}_2\text{)} \text{ and} \]

\[ \text{Ag}_3(\text{AgL}_2)^{\text{\textcircled{2}}} \]

\[ \text{L} = \text{C}_3\text{H}_4\text{O}_2\text{S and } \text{SC}_2\text{H}_2\text{O}_2 \]

Horii (34) has reported the preparation of mixed ligand complexes of 2-, and 3-mercaptopropanoic acids and ethylenediamine with Co(III). The reported composition of the complexes is:

\[ [\text{Co(SCH}_2\text{CH}_2\text{COO)} \text{en}_2]^x \]

\[ [\text{Co(CH}_3\text{S.CHCOO)} \text{en}_2]^x \]

(en = ethylenediamine, \(x = \text{Cl}^- \text{ or I}^-\))

complexes are mononuclear and the mercaptocarboxylic acids function as bidentate ligands.

Coleman et al (35) have prepared the dialkyl-tin complexes of mercaptocarboxylic acids, the reported composition of these complexes is:

\[ (\text{CH}_3)^2 \text{SnL}_2\text{H}_2\text{O} \]

\[ \text{L} = \text{SCH}_2\text{COOH}, \text{SOH}_2\text{CH}_2\text{CO}_2\text{H} \text{ and } \text{SC}_2\text{CHCO}_2\text{H} \]
From IR and NMR data they have suggested that tin binds two groups of two ligand molecules, two alkyl groups and a water molecule resulting in a penta-coordinate tin atom.

3. SOLID COMPLEXES OF SELENO-, AND THIOUREAS.

Podder et al (36) reported complexes of mercury(II) with guianyl-thiourea, in which they have shown co-ordination of the ligands through nitrogen and sulphur.

N,N'-disubstituted selenoureas have been shown to function as unidentate, Se-bonded ligands in Pd(II) and Pt(II) complexes which are similar to corresponding thiourea complexes but show an increased tendency to form five co-ordinate complexes (37, 38).

The selenourea complex of cadmium (II) has analogous structure to its thiourea complex (39) and its composition has been found to be :-

\[ \text{Cd(Su)}_2 \text{Cl}_2 \quad (\text{Su} = \text{Selenourea}) \]
Goddard et al \((40,41)\) have determined the stability constants of metal complexes of selenourea and selenosemicarbazides as well as of thiourea and thiosemicarbazides with class 'b' metal ions and have reported the order of stability with \(\text{Hg(II)}\):

\[
\text{Se} > \text{S} > \text{O}
\]

Domiano et al \((42)\) have inferred from X-ray powder data that bis (selenourea) metal(II) thiocyanates \(\text{M}(\text{Su})_2(\text{NCS})_2\) (where \(\text{M} = \text{Co, Ni, Cd}\)) are isostructural with corresponding thiourea complexes, having polymeric structure consisting of chains of octahedra joined by two selenourea molecules which form bridges between two metal atoms. Selenourea complexes of Mo(V) have been studied by e.s.r. Spectra \((43)\).

Adducts of thiourea \((\text{L})\) and selenourea \((\text{L}')\) to 1,6-dichlorobis (ethylenediamine) cobalt(III) halides have been characterized \((44)\). The adducts bear following compositions:

\[
1,6-\left[\text{CoX}_2\text{en}_2\right]x.n.L'; \quad 1,6-\left[\text{CoX}_2\text{en}_2\right]x.1.5.L 1.5.L'
\]

\[(x = \text{Cl, Br}, n = 1,3, \text{en} = \text{ethylenediamine})\]
In these complexes sulphur or selenium are not bonded to cobalt atom.

Tarantelli and Chiari (45, 46) have synthesized polymethylene bis(phenylthiourea) and polymethylene bis(phenylselenourea). On the basis of electronic spectra and magnetic moments these complexes have been characterized and bear the composition:

\[ \text{NiL}_2 X_2 ; \quad L = \text{polymethylene bis(phenylthiourea)}, \quad X = \text{Cl, Br} \]
\[ \text{NiL}' \text{Cl}_2 ; \quad L' = \text{trimethylene bis(phenylselenourea)} \]
\[ \text{NiL}_2 \text{Br}_2 ; \quad L' = \text{octamethylene bis(phenylselenourea)} \]
\[ \text{NiL}_3 (\text{ClO}_4)_4 ; \quad L' = \text{tetramethylene bis(phenylselenourea)} \]

In case of thiourea the \( \text{NiS}_4 \) is square planar and in case of selenourea both square planar and octahedral complexes have been found.

Various selenourea complexes of class 'b' metals have been prepared (47), the reported composition of the complexes is:

\[ (\text{CoL}_4) (\text{ClO}_4)_2 , \quad \text{CoL}_3 (\text{SO}_4) \]

and \( \text{HgL}_2 X_2 ; \quad L = \text{Selenourea}, \quad X = \text{Cl, Br} \).
Singh and Gupta (48) have reported synthesis and characterization of mixed ligand complexes of \(N,N'-\text{dimethylselenourea}\) and pyridine with potassium hexaisothiocyanatostannate (IV) and potassium hexaisothiocyanatotitanate (IV), these complexes have composition:

\[
[M'L_4][\text{Sn(NCS)}_6]
\]

\(M' = \text{Co, Mn, Hg} ; L = N,N', \text{dimethyl-selenourea or pyridene.}
\)

In selenourea complexes selenium is bonded to metal \(M'\).

Rivero (49) has reported complexes of Co(II) with \(N,N'-\text{dibenzylthiourea}\) and \(N,N'-\text{dibenzylselenourea}\) — the composition of the complexes is —

\[
\text{CoL}_2\text{Cl}_2, \text{ CoL}_2\text{Br}_2 \text{ and CoL}_2(\text{ClO}_4)_2
\]

\((L = N,N', \text{dibenzylthiourea or N,N' dibenzylselenourea})\)

Electronic spectra of these complexes has also been reported.

Kubicki et al (50) have reported crystal and molecular structure of tetrakis (selenourea) Pt(II) chloride — \(\text{Pt(Su)}_4\text{Cl}_2\). Compound is monochinic,
selenourea is bonded to platinum through selenium; PtSe\(_4\) is planar with Pt-Se distance 2.439 Å.

Proskina (44) have reported mixed co-ordination compounds of copper with heterocyclic amines acid selenourea. The composition of complexes reported is:

\[
[CuL_2Q](ClO_4)_2, \quad L=2,2'-dipyridyl, Q = \text{Selenourea}
\]

\[
[CuL'Q(ClO_4)], \quad L' = 1,10-\text{phenanthroline}
\]

Co-ordination number is five in first complex with trigonal bipyramidal geometry and later has co-ordination number of four. Analogous thiourea derivatives have also been reported.

4. ANALYTICAL APPLICATIONS OF MERCAPTOCARBOXYLIC ACIDS.

Formation of metal complexes have been utilized in qualitative and quantitative analysis of various metal ions. Buscarons and Casassas (51) have used thiolactic acid for detection of Pd and Mn. Solubilization of hydroxides and sulphides of heavy cations with
thiolactic acid (52) as masking agent in the precipitation reactions of metallic hydroxides and sulphides was used for separation of the cations - As, Sb, Sn, Mo, Se, Te, Au, Pt, Mn, Ni and Co, which are so stable that their sulphides do not precipitate. They have used mercaptoethanol; 2,3-dimercaptopropanol and mercaptosuccinic acid for such separations.

Busev and Nacu (53) have suggested a photometric method of determination of Palladium with 1-naphthylamide, 2-naphthylamide; 0,p - phenetidide derivatives of 1-mercapto propanoic acid; Pd reacts with the reagent in the ratio of 1:2 in presence of large amount of (1000 fold) Pt(IV), Rh(III), Ir(IV) and Os(IV) which do not interfere with the estimation of Pd. The workers (54) have also determined Mo(V) and Mo(VI) with 1-mercapto propanoic acid and its amide derivatives like 0,p - phenetidide, 0,p - anisidide and 0,p - toluidide. Mo(V) and Mo(VI) react with the reagents in 1:2 ratio over a wide pH range. Mo-1-mercapto propionato-phenetidide is extracted with 1:1-isoamylalcohol; CHCl₃ in presence of diphenylguanidinium or benzylthiouronium in aqueous phase. Extraction photometric method was
developed to determine Mo in presence of W, Cr(III), Ti, Co, Ni, Zn, Al, Fe(III) and V. Absorbance is measured at 350-65 nm, in presence of tungsten at 430 nm.

Shigco Hara (55) determined cobalt colorimetrically with 3-mercaptopropanoic acid at pH 9.0 and at 370 nm. Beer's law is obeyed, a 1:3 (metal:ligand) complex is formed, interference of copper is decreased by adding potassium cyanide, iron and nickel interfere.

Pribil and Vesely (56) have determined zinc and cadmium in presence of copper with 3-mercaptopropanoic acid as masking agent followed by direct titration of zinc with triethylene-tetramine hexa-acetic acid. After addition of diaminocyclohexane tetra-acetic acid cadmium is determined in directly by back titration with Zn(NO$_3$)$_2$ solution, all the titrations are carried in presence of xylene orange as indicator in acidic medium. Nacu and coworkers (57) have used thiolactic acid for gravimetric estimation of zirconium. Thiolaetic acid is added to zirconium salt at pH 4.5. ZrO$_2$ is precipitated and dried. Sn(II), Hg(II), Zn(II), Cd(II), Ti(IV), Th(IV), Cu(II), Pb(II), Ni(II) and Ca(II) interfere in the estimation. Fritz and Beumun (58) suggested a rapid selective Spectrophotometric determination
of molybdenum(IV) which is based on the formation of a yellow molybdenum-thiolactic acid complex at pH 1.0-1.6 and measuring absorbance at 365 nm.

In view of the literature cited it seems that mercury(II) complexes of 2-, and 3-mercaptopropanoic acids need further investigation. Besides this, it is worthwhile to study the complexes of group IIB metals with ligands having sulphur or selenium donors like selenoureas and thioureas.

Therefore, the following studies have been undertaken in the present work:

(i) The physico-chemical investigation of mercury(II)-mercaptopropanoic acid systems leading to calculation of stability constants and other related parameters.

(ii) Preparation and elucidation of structures of anionic complexes of mercury(II) with a mercaptopropanoic acids.

(iii) Determination of degree of dissociation of soluble complexes and solubilities of less soluble complex species.
(iv) Use of mercaptoalcoholic acids as masking agents for group IIB metal ions.

(v) Preparation and elucidation of structures of complexes of \(N,N'-\)disubstituted seleno-, and thioureas with mercury(II) and zinc(II).

The sulphur and selenium containing ligands whose complexation with various metal ions is being reported here, are:

(i) 2-Mercaptopropanoic acid or thiolactic acid (abbreviated as \(H_2\text{TLA}\))

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH} \quad \text{COOH} \\
\text{SH}
\end{align*}
\]

(ii) 3-Mercaptopropanoic acid: thiohydracrylic acid (abbreviated as \(H_2\text{MPA}\))

\[
\begin{align*}
\text{HSCH}_2\text{CH}_2\text{COOH}.
\end{align*}
\]

(iii) \(N,N'\)-Diphenyl selenourea: (abbreviated as \(\text{DPSU}\))

\[
\begin{align*}
\text{C}_6\text{H}_5\text{NH.C.NHC}_6\text{H}_5 \\
\text{Se}
\end{align*}
\]

(iv) \(N,N'\)-Dibenzyl Selenourea: (abbreviated as \(\text{DPSU}\))

\[
\begin{align*}
\text{C}_6\text{H}_2\text{CH}_2\text{NH.C.NH.CH}_2\text{C}_6\text{H}_5 \\
\text{Se}
\end{align*}
\]
(v) \( \text{N,N'}-\text{Dibenzyl thiourea} \) (abbreviated as DBTU) \( \text{C}_6\text{H}_5\text{CH}_2\text{NH} \cdot \text{C} \cdot \text{NH} \cdot \text{CH}_2\text{C}_6\text{H}_5 \)

5. STABILITY CONSTANTS

Stability of a complex refers to the extent of dissociation of a complex species in solution form or it is a measure of the extent to which a complex species will form, or will be transformed into another species under certain conditions when the system has reached to equilibrium. A complex molecule is considered to be formed from the free ligand (L) and a metal ion (M):

\[ M + L = ML; \quad ML + L = ML_2 \quad \text{and} \]
\[ ML + L_n = ML_{n+1} \]

when the concentration of metal ions and free ligand is considered and the logarithmic ratios of products to reactants give the stepwise stability constants.

\[ \log K_1 = \log \frac{[ML]}{[M][L]} \quad \ldots (1.1) \]
\[ \log K_2 = \log \frac{[ML_2]}{[ML][L]} \quad \ldots (1.2) \]
\[ \log K_n = \log \frac{[ML_n]}{[ML_{n-1}][L]} \]  \hspace{1cm} \ldots (1.3)

Summation of \( \log K_1, \log K_2, \ldots, \log K_n \) values give the overall stability constant \( \log \beta_n \) of a complex species which can be evaluated directly also -

\[ \log \beta_n = \frac{[ML_n]}{[M][L]^n} \]  \hspace{1cm} \ldots (1.4)

\( M \) is a metal ion and \( L \) may be either a charged ion or a neutral molecule, \( n = 1, 2, 3, \ldots \) \( \beta_n \) overall stability constant.

The logarithmic values of overall stability constants at various ionic strengths extrapolated to zero ionic strength give thermodynamic stability constants, which are related to free energy change, enthalpy change and entropy change by the equation:-

\[ \Delta G^0 = -RT \ln \beta_n = \Delta H^0 - T \Delta S^0 \]  \ldots (1.5)

where \( T \) = absolute temperature.

\( R = \text{gas constant} \ (1.987 \text{ cal.deg}^{-1} \text{ mole}^{-1}) \)

\( \beta^0 = \text{stability constant at zero ionic strength.} \)

\( \Delta G^0 = \text{standard free energy change.} \)
\[ \Delta H^0 = \text{standard enthalpy change} \]
\[ \Delta S^0 = \text{standard entropy change}. \]

The determination of enthalpy change and other thermodynamic parameters from the stability constants are helpful for thorough understanding of the factors influencing the complex formation (59). A number of methods can be used for determination of stability constants viz.,

(i) Potentiometry (pH metric method)
(ii) Measurement of E.M.F.
(iii) Spectrophotometry.
(iv) Polarography.

In the present work potentiometric technique of measuring E.M.F. of mercury (II) ions in presence of large excess of ligand has been used for determining stability constants. A potentiometer with mercury and saturated calomel electrodes is used to measure E.M.F. of the concentration cell which contained mercuric(II) ions and large excess of ligand. The E.M.F. in a concentration cell arises due to the cell reaction:

\[ \text{Hg} / \text{Hg}^{2+} \ || \ \text{Hg}_2\text{Cl}_2(s) / \text{Hg} \quad \ldots \ (I.6) \]
The E.M.F. of the concentration cell is related to free Hg(II) ion concentration by the relation:

\[ E_{\text{M.F.}} = E^{0}_{\text{Hg/Hg}^{2+}} + \frac{2.303 \text{RT}}{nF} \log \text{Hg}^{2+} - E_{S.C.E.} \]

...(1.7)

where \( E^{0}_{\text{Hg/Hg}^{2+}} \) = Standard electrode potential of mercury at 25°C (0.854 volts).

\( E^{0}_{\text{S.C.E.}} \) = Standard electrode potential of saturated calomel electrode at 25°C (0.242 volts).

\( \text{Hg}^{2+} \) = Free mercuric(II) ion concentration or activity of mercuric(II) ions.

\( R \) = Gas constant (8.314 J K^{-1} mol^{-1})

\( F \) = Faraday constant (96,500 coulombs)

\( n \) = Valency (2 in case of mercury(II))

At temperatures other than 25°C, the relation (1.7) is modified (60) as:

\[ E_{\text{M.F.}} = E^{0}_{\text{Hg/Hg}^{2+}} + \frac{2.303 \text{RT}}{nF} \log \text{Hg}^{2+} - E^{0}_{\text{S.C.E.}} + 0.00076 \\
(t-25) \]

 ...(1.8)

\( t = \) temperature °C.
In presence of large excess of ligand mercury(II) ions are supposed to exist as the highest co-ordinated species \( \text{HgLn} \). The pH of the reaction mixture is adjusted above the pK\(_n\) (dissociation constant) of the ligand so that all the ligand exist in completely dissociated form ( \( \text{HnL} \rightarrow n\text{H}^+ + \text{Ln}^{n-} \)).

The overall stability constant was evaluated with the help of experimentally determined concentration of free \( \text{Hg}^{2+} \) ions using the relation:

\[
\log \beta_n = \log \frac{[\text{HgLn}]}{[\text{Hg}^{2+}][\text{L}]^n} \quad \ldots \ (I.9)
\]

The free ligand concentration \( \text{L}^n \) under the experimental conditions is approximately equal to total ligand concentration.

6. SOLID MERCAPTOCARBOXYLATE COMPLEXES OF Hg(II).

(1) Preparation and composition:

Sodium bis(3-mercaptopropionato)-mercurate and potassium bisthiolacetatomercurate were crystallized
with ethanol from a solution of mercuric oxide and respective mercaptoacid. Their other metal derivatives were prepared from the solutions of sodium bis(3-mercaptopropionato)-mercurate(II) and potassium bis-thiolactato mercurate(II) and respective salt solutions of various metals.

The complexes were analysed for the metal, sulphur and mercury content and thus composition was established.

(ii) **Structures:** The infrared spectra of metal-bis(mercapto-carboxylato)mercurates were recorded between 4000 cm$^{-1}$ - 600 cm$^{-1}$ using potassium bromide on Pye unicam IR Spectrophotometer. Magnetic moments of some complexes were measured at room temperature using Gouy balance. Proton magnetic resonance spectrum of sodium-bis(3-mercaptopropionato)-mercurate(II) complex was recorded on EM-390, 90 MHz Varian NMR Spectrometer. IR, magnetic moments and NMR data were used to assign structures to metal complexes.

(iii) **Solubility:** Complexometric and conductometric technique was used to determine solubility of less soluble complexes in their saturated solutions at different temperatures.
(iv) **Other investigations:** The apparent molecular weight and degree of dissociation of potassium bisthiolactatomercurate(II) and sodium bis(3-mercaptopropionato)-mercurate(II) was determined by cryoscopic method (62). The ionic mobilities of the anions \([\text{Hg(TLA)}_2]^2-\) and \([\text{Hg(MPA)}_2]^2-\) were determined by conductometric method.

(v) **Analytical Applications:** Use of thiolactic acid and 3-mercaptopropanoic acid as masking agent for group II B metal ions in the estimation of magnesium(II) has been studied.

7. **STUDIES ON N,N'-DISUBSTITUTED SELENO-, AND THIOUREA COMPLEXES OF ZINC(II) AND MERCURY(II).**

(i) **Preparation and composition:** Complexes of \(N,N'\)-diphenylselenourea, \(N,N'\)-dibenzylselenourea and \(N,N'\)-dibenzylthiourea have been prepared and their composition established on the basis of elemental analysis.

(ii) **Structure elucidation:** The infrared spectra of the complexes have been used in assigning the structures for the complexes.
The work presented in this thesis comprises of seven chapters.

First chapter deals with the review of literature and introduce the topics of the thesis.

Second chapter incorporates the studies of Hg(II)-TLA and Hg(II)-MPA systems leading to determination of stabilities of Hg(II) complexes and evaluation of related thermodynamic parameters.

Third chapter includes the preparation of metal-bis(mercapto-carboxylato)-mercurates and chloro-complexes of Hg(II) with 2-, and 3- mercaptopropanoic acids, determination of composition and structure of these complexes.

Fourth chapter includes determination of degree of dissociation and ionic mobilities and protonation constants of alkali metal-bisthiolactato-mercurate and bis(3-mercapto-propionato)-mercurate and solubilities of other less soluble metal derivatives.

Fifth chapter deals with analytical applications of 2-, and 3- mercaptopropanoic acids.

Sixth chapter incorporates preparation of Hg(II) and Zn(II) complexes of DPSU, DBSU and DBTU, determination of their composition and structure.

Seventh chapter gives a summary of entire work.
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