Chapter 7

SUMMARY AND CONCLUSION

The chemistry of coinage metal ions (Cu$^1$, Cu$^{II}$, Ag$^1$) with a series of heterocyclic thioamides (Charts Ia and Ib) under aerobic conditions at room temperature (Cu) by keeping the reaction contents undisturbed or by magnetic stirring (Ag) has been investigated. Using these mild conditions, 68 new complexes have been obtained. Complexes of different nuclearities, namely, mononuclear (Cu$^1$, Cu$^{II}$, Ag$^1$), dinuclear (Cu$^{II}$, Ag$^1$), trinuclear (Cu$^1$, Cu$^{I, II}$ mixed-valent), tetranuclear (Cu$^{II}$) and polynuclear (Cu$^1$, Cu$^{II}$, Cu$^{I, II}$ mixed-valent) have been isolated. Triphenylphosphine (PPh$_3$) has been used as a co-ligand in some cases. These complexes have been characterized with the help of physical properties (color, solubility, and melting point), analytical data (CHN analysis), IR spectroscopy, electronic absorption spectroscopy and NMR ($^1$H, $^{13}$C, $^{31}$P) spectroscopy. Out of 68 complexes synthesized, 56 complexes have been characterized by X-ray crystallography. Fluorescence studies for some complexes have also been carried out. The oxidation of copper(I) occurred during reaction time under certain conditions. A brief summary of work is presented below.

![Chart Ia](chart.png)
Copper(I) chloride with imidazolidine-2-thione (imdzSH) in 1 : 2 molar ratio in acetonitrile-chloroform mixture under stirring conditions formed an unsymmetrical dimer, [(Cl)(η^1-S-imdzSH)Cu(µ-S-imdzSH)Cu(η^1-S-imdzSH)Cl] [1]. Using the new procedure, copper(I) chloride with imdzSH has yielded two new polymers, {Cu₈(µ₃-S-imdzSH)(µ-S-imdzSH)(η^1-Cl)}ₙ (1) and {Cu₆(µ₃-S-imdzSH)(µ-S-imdzSH)Cl₂(µ-Cl)}ₙ (2). This reaction in dimethyl sulfoxide has formed an unusual sulfate bridged Cu^{II} helical polymer [Cu^{II}(η^2-N,N-(imidz)₂S)(µ-O,OSO₂)(η^1-SOH₂)]ₙ, (imidz)₂S = 2,2’-thio-di-2-imidazoline (5). Copper(I) bromide with 1-methyl-imidazoline-2-thione (mimzSH) in acetonitrile has formed a Cu¹ trinuclear complex {Cu₃(η^1-Br)(µ-S-mimzSH)}ₙ·CH₃CN (12). This reaction in acetonitrile-chloroform mixture has yielded a Cu^{II} tetranuclear cluster [Cu₄(η¹-N-(mimzBr)₄(µ₄-O)(µ-Br)₄] (mimzBr = 2-bromo-1-methyl-imidazole) (13) and in dimethyl sulfoxide, it formed sulfate chelated Cu^{II} mononuclear complex [Cu^{II}(η^2-N,N-(mimz)₂S)(η^2-O,OSO₂)(η^1-SOH₂)] (mimz)₂S = 1,1’-dimethyl-2,2’-di-imidazolyl sulfide (14). Copper(I) iodide has formed Cu¹ polynuclear complex {Cu₂(µ-I)₃(µ-S-mimzSH)}ₙ (15).

Copper(I) halides (chloride / bromide) with thiazolidine-2-thione (tzdSH) in acetonitrile have involved C-S rupture and ring fusion and formed 3-coordinate complexes [CuX(η^2-N,S-tztdS)] (tztdS = 3-(2-thiazolin-2-yl)thiazolidine-2-thione) (X = Cl 18, Br 19) along with CuSO₄·5H₂O. Copper(I) iodide has formed an iodo-bridged dimer, [Cu₂(η¹-S-tzdSH)₄(µ-I)] (20).

The reaction of 1-methyl-imidazolidine-2-thione (imidzSH-Me) with copper(I) iodide in acetonitrile has formed 1D Cu¹ polymer, {Cu₄(µ₃-I)₂(µ-I)₂(µ-S-imdzSH-Me)₂(η¹-S-imdzSH-Me)₂}ₙ (22) along with a mixed-valent trinuclear cluster, [Cu²Cu^{II}(η^2-N,S-imdzdzS-Me)(µ-S-imdzdzS-Me)(µ-I)₂(η^1-I)₂] (23) from the filtrate. This reaction with n-propyl-imidazolidine-2-
thione (imidzSH-Prn) has formed a CuI polynuclear complex, [Cu(µ-I)2(µ-S-imdzSH-Prn)2]n (26) and a mixed-valent polynuclear complex, [CuI2CuII(µ-S-imdzdzS-Prn)2(µ-I)2(η1-I3)2]n {imiddzS-Prn = n-propyl-3-(n-propyl-2-imidazolin-2-yl)imida-zolidine-2-thione} (27).

Reaction of copper(I) chloride with 2,4-dithiouracil in the presence of 2 moles of PPh3 has formed a hetero-bridged dinuclear complex [Cu2(µ-Cl)(µ-S,S-dtucH)(PPh3)4] (31). From the filtrate two products have been isolated, one is dimer, [Cu2Cl2(dtucH2)(PPh3)4] (32) and the other is 1D helical chain polymer, {Cu(µ-S,S-dtucH2)(PPh3)Cl}n (33). The above reaction with copper(I) bromide or iodide formed similar type of products (34-38).

Reaction of silver(I) halides (X = Cl, Br) with heterocyclic thioamides (Chart Ia) in the presence of PPh3 have formed mononuclear and halogen-bridged dinuclear complexes (42–57). 2,4-Dithiouracil (dtucH2) with silver(I) halides have formed dinuclear complexes [Ag2(µ-X)(µ-S,S-dtucH)(PPh3)4] (X =Cl 58, Br 59). Reaction of silver(I) nitrate with thio-ligands (Chart Ia) in presence of PPh3 have formed sulfur-bridged dinuclear (60-62) and mononuclear (63-65) complexes. Reaction of silver(I) acetate with thiazolidine-2-thione (tzdSH) and benz-imidazoline-2-thione (bzmzSH) in the presence of PPh3 has formed mononuclear complexes, [Ag(η1-S-tzdSH)(η1-S-tzdS)(PPh3)2] (66) and [Ag(η1-S-bzmzSH)2(PPh3)2](OAc)·H2O (67) respectively.

**Conclusion**

Some important conclusions are drawn from this study. The coinage metals (Cu, Ag) have yielded broadly two types of compounds.

1. The first category has neutral or anionic thio-ligands bonded to metal centers in trigonal planar (30, Cu; 63, 64, Ag), tetrahedral (6-9, 39, Cu; 43, 45, 47, 50, 52–54, 56, 57, 66, 67, Ag), dinuclear (hetero-bridged, 31, 34, 37, Cu; 58, 59 Ag; halogen-bridged, 42, 44, 46, 48, 49, 51, 55, Ag; sulfur-bridged 60–62, Ag), trinuclear (12, 41, Cu) and polynuclear (1–4, 15, 22, 26, Cu) complexes.

2. The second category consists of essentially copper compounds which involve C-S bond rupture, oxidation of CuI to CuII, formation of sulfate, C-N bond formation and bromination of ring (5, 10, 13, 14, 16–19, 21, 23, 25, 27, 28, 29).
(a) Copper(I) bromide with 1-methyl-imidazoline-2-thione (mimzSH) in acetonitrile formed Cu\(^{I}\) trinuclear complex, \{Cu\(_3(\eta^1\text{-Br})_3(\mu-S\text{-mimzSH})_3\}\}\cdot\text{CH}_3\text{CN (12)}. This reaction when carried out in the presence of chloroform, involved C-S bond rupture, oxidation of sulfur to sulfate and bromination of ring and formed tetranuclear cluster, \([\text{Cu}_4(\eta^1\text{-N}\text{-mimzBr})_4(\mu_4\text{-O})(\mu\text{-Br})_6]\) (mimzBr = 2-bromo-1-methyl-imidazole) (13). Here, 1-methyl-imidazoline-2-thione changed into 2-bromo-1-methyl-imidazole which coordinated to Cu\(^{II}\) in the cluster. Copper(I) chloride with mimzSH in acetonitrile also involved C-S rupture and formed chloro-bridged dinuclear complex \([\text{Cu}_2\{\eta^2\text{-N,N-(mimz)}_2\text{S}\}_2(\mu\text{-Cl})_2\text{Cl}_2\} \text{ (10). Here, 1-methyl-imidazoline-2-thione changed into 1,1'-dimethyl-2,2'-di-imidazolyl sulfide (thioether) which coordinated to Cu\(^{II}\) in dimeric complex. Thus chloride being more electronegative is facilitating oxidation of Cu\(^{I}\) to Cu\(^{II}\) and it is Cu\(^{II}\) which leads to oxidation of thio-ligand to thio-ether. Copper(I) bonded to bromide is less prone to oxidation in the acetonitrile alone and addition of the polar solvent appears to hydrogen bond to bromide which weakens Cu-Br bond leading to oxidation of Cu\(^{I}\) to Cu\(^{II}\). Significantly copper(I) bonded to more polarisable iodide ion (Cu-I) does not involve C-S rupture and formed Cu\(^{I}\) polynuclear complex, \{Cu\(_2(\mu\text{-I})_2(\mu-S\text{-mimzSH})_2\}_n (15).

(b) Both copper(I) chloride and copper(I) bromide with mimzSH in dmsO involved C-S rupture and oxidation of sulfur to sulfate and formed sulfate chelated Cu\(^{II}\) complex, \([\text{Cu}^{II}\{\eta^2\text{-N,N-(mimz)}_2\text{S}\}_2(\eta^2\text{-O,OSO}_2)(\eta^1\text{-OH})_2\}] (14). Here, thio-ligand (mimzSH) changed to thio-ether \{(mimz)\text{S}\}. Dimethyl sulfoxide being a coordinating solvent appears to replace halogen by coordinating through its O donor atoms probably forming species, \([\text{Cu(dmsO)}_n\text{X} (X = \text{Cl, Br; } n = 3-6) \text{ or } [\text{Cu(dmsO)}_m\text{X} (X = \text{Cl, Br; } m = 2-6). Copper(I) of the species in the fluid state readily undergoes oxidation of Cu\(^{II}\), which further oxidizes thio-ligand to thio-ether.

(c) Imidazolidine-2-thione (imdzSH) with copper(I) chloride / bromide in acetonitrile or acetonitrile-chloroform mixture did not involve C-S bond rupture but in presence of dimethyl sulfoxide, sulfate bridged polynuclear complex, \([\text{Cu}^{II}\{\eta^2\text{-N,N-(imdz)}_2\text{S}\}_2(\mu\text{-O,OSO}_2)(\eta^1\text{-OH})_2\}_n \text{ (5) has been obtained. The presumed species } [\text{Cu(dmsO)}_n\text{X} (X = \text{Cl, Br; } n = 3-6) \text{ or } [\text{Cu(dmsO)}_m\text{X} (X = \text{Cl, Br; } m = 2-6) \text{ has ability to oxidize thione of the saturated ring, namely, imidazolidine-2-thione into 2,2'-thio-di-2-imidazoline. Polymers 1–3 in dmsO also gave complex 5.}
(d) Copper(I) iodide not prone to invoke C-S rupture as discussed above, becomes susceptible to oxidation of Cu$^I$ to Cu$^{II}$ after coordination to N-alkyl-imidazolidine-2-thiones {1-methyl-imidazolidine-2-thione (imidzSH-Me), 1-ethyl-imidazolidine-2-thione (imidzSH-Et), n-propyl-imidazolidine-2-thione (imidzSH-Pr$^n$), n-butyl-imidazolidine-2-thione (imidzSH-Bu$^n$)}. Here, electron releasing alkyl groups at nitrogen enhance electron density at the metal center making it easily susceptible to oxidation to Cu$^{II}$. This Cu$^{II}$ involved C-S rupture, ring fusion and oxidation of sulfur to sulfate and formed square planar Cu$^{II}$ complex (28), mixed-valent (Cu$^{I, II}$) trinuclear and polynuclear complexes (23, 25, 27).

(e) Thiazolidine-2-thione with copper(I) salts (Cl, Br, BF$_4$) in acetonitrile involved C-S rupture, ring fusion and oxidation of sulfur to sulfate formed trigonal planar (18, 19) and square planar (21) complexes. Here, thiazolidine-2-thione changed to 3-(2-thiazolin-2-yl)thiazolidine-2-thione.

(f) Five-membered heterocyclic thioamides with copper(I) halides under stirring conditions formed insoluble precipitates. So these reactions were carried out by slowly mixing the reactants and let them react under atmospheric conditions.

(g) The addition of thio-ligand to copper(II) salts immediately reduce Cu$^{II}$ to Cu$^I$, which slowly oxidizes again to Cu$^{II}$. So the reactions were carried out starting from copper(I) salts.

3. 2,4-Dithiouracil showed unusual coordination behaviour with strong ability to even knock out halogen bonded to silver(I). It formed heteo-bridged dinuclear complexes (Cu, Ag) and polynuclear complexes (Cu).