Chapter 6
ANALYSIS OF RESULTS-GENERAL COMMENTS

This chapter gives general comments on the interaction of copper(I) and silver(I) salts with thio-ligands shown in Charts Ia and Ib (see chapter 5). The oxidation of copper(I) salts occurred in some cases when allowed to react with a thio-ligand and formed copper(II) compounds. The work is split into two parts: Copper complexes and Silver complexes.

6.1 Copper complexes

Heterocyclic thioamides are split into two types: (a) Five-membered heterocyclic thioamides and (b) Six-membered heterocyclic thioamides.

6.1.1 Chemistry of heterocyclic thioamides having five-membered rings

Imidazolidine-2-thione (imdzSH)

It was observed recently that reaction of copper(I) bromide with imdzSH in 1 : 2 molar ratio in acetonitrile under stirring condition at room temperature formed an insoluble product which became soluble on addition of chloroform. Slow evaporation of this solution yielded a polymer \{Cu₆(μ₃-S-imdzSH)₂(μ₂-S-imdzSH)₄Br₂(μ-Br)₄\}ₙ 3 (polymerization via bromide), and a symmetrical sulfur-bridged dimer, \[\text{[Cu}_2(\mu-S-imdzSH)\eta^1\text{-S-imdzSH})\eta^1\text{-Br}₂] \] [17]. This reaction when carried out in 1 : 1 molar ratio in acetonitrile under stirring again formed an insoluble product. So it was thought to carry out reactions under mild conditions by keeping the contents undisturbed at room temperature. For this, a solution of copper(I) bromide in acetonitrile was slowly mixed with the solution of imdzSH in acetonitrile in 1 : 1 molar ratio at room temperature (25- 30°C) and let the contents to react slowly. After a week, colorless crystals of polymer \{Cu₆(μ₃-S-imdzSH)₂(μ-S-imdzSH)₄Br₂(μ-Br)₄\}ₙ 3 were formed in 68% yield. There was no dimeric product formed by this procedure. This is unlike two products as discussed.

The reaction of copper(I) iodide with imdzSH in 1 : 2 molar ratio in acetonitrile-chloroform mixture under stirring yielded two isomers, \{Cu₆(μ₃-S-imdzSH)₂(μ₂-S-imdzSH)₄I₂(μ-I)₄\}ₙ
(polymerization via iodide) and \( \{\text{Cu}_6(\mu_3-\text{S-imdzSH})_4(\mu-\text{S-imdzSH})_2(\mu-\text{I})_2\text{I}_4\}_n \) (polymerization via sulfur) [14]. This reaction has been carried out in 1 : 1 molar ratio in acetonitrile under mild conditions by letting the contents undisturbed and this has yielded only one polymer \( \{\text{Cu}_6(\mu_3-\text{S-imdzSH})_2(\mu_2-\text{S-imdzSH})_4\text{I}_2(\mu-\text{I})_4\}_n \ 4 \) (polymerization via iodide) in 69% yield unlike two as noted above. The structure of 4 is similar to that of 3.

![Diagram](image.png)

Reaction of copper(I) chloride with imdzSH in 1 : 2 molar ratio in acetonitrile-chloroform mixture under stirring conditions was found to form an unsymmetrical dimer, \( [(\text{Cl})(\eta^1-\text{S-imdzSH})\text{Cu}(\mu-\text{S-imdzSH})\text{Cu}(\eta^1-\text{S-imdzSH})_2\text{Cl}] \) [17]. This intriguing behavior of copper(I) chloride has also been reinvestigated under new conditions of the type mentioned above. A solution of copper(I) chloride was mixed with the solution of imidazolidine-2-thione (imdzSH) in 1 : 1 molar ratio in acetonitrile and contents allowed to react undisturbed at room temperature. After 4-5 days, pale olive green crystals of polymer \( \{\text{Cu}_8(\mu_3-\text{S-imdzSH})_4(\mu-\text{S-imdzSH})_4(\eta^1-\text{Cl})_8\}_n \ 1 \) were isolated in 67% yield. However, the same reaction when carried out in 1 : 2 molar ratio in acetonitrile, gave crystals of polymer 1 in 33% yield and from the filtrate, colorless crystals of polymer \( \{\text{Cu}_6(\mu_3-\text{S-imdzSH})_2(\mu-\text{S-imdzSH})_4\text{Cl}_2(\mu-\text{Cl})_4\}_n \ 2 \) were obtained in 35% yield. The structure of 2 is similar to that of 3. It is concluded here that just mixing the reactants and keeping them undisturbed gave new coordination polymers. The complex 1 showed intense fluorescent band at \( \lambda_{em} = 324 \) nm corresponding to excitation wavelength of 290 nm.
A plausible explanation of formation of polymers 1 and 2 is delineated below. It appears that four copper(I) chloride and four imidazolidine-2-thione ligand moieties form a tetranuclear repeat unit A. Two such units combine through sulfur atoms (µ₃-S mode) and this process generated a linear polymer 1 (Scheme 1). Likewise, three copper(I) chloride and three imdzSH ligand moieties have formed a trinuclear unit B, and two such units combined in side-on fashion through sulfur (µ₃-S mode) and chlorine (µ-Cl mode) atoms, resulting in the formation of repeat unit C. These C repeat units combined with other similar units through chlorine (µ-Cl mode) atoms forming the polymer 2 (Scheme 2).
Due to poor solubility of polymer 1, its electronic absorption spectrum was recorded in dimethyl sulfoxide, but the color of solution immediately changed to light blue which when allowed to stay at room temperature slowly turned to dark blue. After a month blue crystals of composition \( C_6H_{12}CuN_4O_5S_2 \) were obtained. An X-ray crystallographic study revealed the molecular structure of blue crystals to be an unusual sulfate bridged Cu\( \text{II} \) helical polymer \([\text{Cu}^{\text{II}}\{\eta^2-N,N-(\text{imdz})_2S\}(\mu-O,O\text{SO}_2)(\eta^1-\text{OH}_2)]_n \quad \{(\text{imdz})_2S = 2,2'-\text{thio-di-2-imidazoline}\} \quad 5\) (Figures 4a and 4b). It is the first example of in situ generation of 2,2'-thio-di-2-imidazoline \{(imdz)\_2S\} from imidazolidine-2-thione (imidzSH) and its coordination to Cu\( \text{II} \). The magnetic susceptibility measurement showed magnetic moment value of 1.975 BM per copper and it revealed the presence of Cu\( \text{II} \) in the polymer 5. To recheck the formation of complex 5, direct reaction of copper(I) chloride with imdzSH in dimethyl sulfoxide was carried out. It also formed the same product.
A plausible mechanism for the formation of Cu\textsuperscript{II} polymer 5 is discussed here. The reaction involved oxidation Cu\textsuperscript{I} to Cu\textsuperscript{II} which is believed to oxidize imidazolidine-2-thione (imdzSH) to its disulfide, namely, 2,2'-di-thio-di-2-imidazoline. The formation of sulfate, as confirmed by x-ray crystallography, suggests that the disulfide is undergoing air oxidation resulting in the formation of 2,2'-thio-di-2-imidazoline \{(imdz)\textsubscript{2}S\}. This newly formed thioether \{(imdz)\textsubscript{2}S\} and sulfate coordinate to Cu\textsuperscript{II} and formed polymer 5 (Scheme 3).

Reaction of copper(I) bromide with imdzSH in dmsu also formed same polymer 5. These reactions in dimethyl formamide are relatively fast. In contrast, reaction of copper(I) iodide with imdzSH in dmsu did not involve C-S rupture as color of solution remained colorless and no crystalline compound could be obtained.

*Imidazoline-2-thione (imzSH)*
The reaction of copper(I) chloride with imzSH in 1 : 1 or 1 : 2 molar ratios in CH$_3$CN did not yield any crystalline product as a slurry was formed on mixing. Even using CH$_3$CN-CHCl$_3$ mixture, no crystalline product could be obtained. To stabilize the system, triphenyl phosphine was added. So from a reaction of copper(I) chloride with imzSH in the presence of Ph$_3$P in 1 : 1 : 2 molar ratio, a compound of composition, [Cu$_2$(imzSH)(PPh$_3$)$_4$Cl$_2$]·CH$_3$OH 6 was obtained, whose x-ray crystallography study showed that these crystals consist of four coordinated [CuCl(η$^1$-S-imzSH)(PPh$_3$)$_2$] 6a and three coordinated [Cu(PPh$_3$)$_2$Cl] 6b independent molecules in the same unit cell which were intact even in solution state as confirmed by $^{31}$P NMR (δ = -3.42 (6a), 30.74 ppm (6b). Reactions of copper(I) bromide / iodide with imzSH under similar reaction conditions formed complexes [CuBr(η$^1$-S-imzSH)(PPh$_3$)$_2$]·H$_2$O 7 and [CuI(η$^1$-S-imzSH)(PPh$_3$)$_2$] 8 respectively. A related ligand, benz-imidazoline-2-thione (bzimzSH) behaved similarly and formed a mononuclear complex, [CuBr(η$^1$-S-bzimzSH)(PPh$_3$)$_2$]·CH$_3$COCH$_3$ 9. It is mentioned here that the reactions of copper(I) halides with imzSH in dmso did not yield any crystalline compound.

![Chemical Structures]

1-Methyl-imidazoline-2-thione (mimzSH)

The reaction of copper(I) chloride with 1-methyl-imidazoline-2-thione (mimzSH) in 1 : 1 molar ratio in acetonitrile under undisturbed conditions at room temperature did not form a polynuclear complex similar to 1 or 2, rather color of solution turned dark green in 2-3 days and surprisingly dark green crystals of Cu$^{II}$ chloro-bridged dinuclear complex, [Cu$_2${η$^2$-N,N-(mimz)$_2$S)$_2$(μ-Cl)$_2$Cl$_2$] 10 {(mimz)$_2$S = 1,1‘-dimethyl-2,2‘-di-imidazolyl sulfide} were obtained along with blue crystals of CuSO$_4$·5H$_2$O 11. It is added here that reaction of mimzSH with copper(I) chloride in dimethyl sulfoxide or acetonitrile-chloroform mixture also formed same products.
The proposed mechanism indicates that under aerobic conditions Cu$^+$ oxidizes to Cu$^{2+}$, which is believed to oxidize 1-methyl-imidazoline-2-thione (mimzSH) to its disulfide, namely, 1,1'-dimethyl-2,2'-di-imidazolyl disulphide. The formation of CuSO$_4$·5H$_2$O 11 as confirmed by x-ray crystallography suggests that the disulfide is undergoing air oxidation resulting in the formation of 1,1'-dimethyl-2,2'-di-imidazolyl sulphide \{(mimz)$_2$S\}. This newly formed thioether \{(mimz)$_2$S\} coordinated to Cu$^{2+}$ and formed complex 10 (Scheme 4).

The reaction of copper(I) bromide with 1-methyl-imidazoline-2-thione (mimzSH) in 1 : 1 molar ratio in acetonitrile at room temperature formed colorless crystals of a trinuclear Cu$^+$ complex \{Cu$_3$(η$^1$-Br)$_3$(μ-S-mimzSH)$_3$\}·CH$_3$CN 12. The complex showed intense fluorescent band at $\lambda_{em} = 319$ nm corresponding to excitation wavelength of 258 nm, which may be due to short Cu···Cu contacts.
In the above reaction, changing the solvent from acetonitrile to acetonitrile-chloroform mixture turned the reaction solution brownish green and after a week black crystals of composition C_{16}H_{20}Br_{10}Cu_{4}N_{8}O were obtained along with blue crystalline product, CuSO_{4}·5H_{2}O. An X-ray crystallography revealed the structure of black crystals to be a Cu^{II} tetranuclear cluster, [Cu_{4}(η^{1}-N-(mimzBr))_{4}(μ_{4}-O)(μ-Br)_{6}] 13 (mimzBr = 2-bromo-1-methyl-imidazole). The magnetic susceptibility measurement showed the magnetic moment value of 1.972 BM per copper supporting the presence of Cu^{II}. The IR spectrum showed that the diagnostic peak due to ν(C=S) in the free ligand at 930 cm\(^{-1}\) disappears in the spectrum of complex 13, which indicates that there is extrusion of sulfur atom of the ligand. It is weakly fluorescent at \(\lambda_{em} = 329\) nm corresponding to excitation wavelength of 270 nm. The ESI-mass spectrum of complex 13 did not show molecular ion peak but it has shown peaks which support various components of this complex. The important peak at m/z value 163.4 corresponds to 2-bromo-1-methyl-imidazole (N\(_2\)C\(_4\)H\(_5\)Br\(^{81}\)). Another important peak at m/z value 268.3 corresponds to Cu\(^{63}\)O species. The peak at m/z value 385.2 corresponds to (Cu\(^{63}\)Br\(^{81}\)N\(_2\)C\(_4\)H\(_5\)Br\(^{79}\)). Other peaks at m/z values, 225.3 and 243.3 correspond to (Cu\(^{63}\)Br\(^{81}\)) and (Cu\(^{65}\)ON\(_2\)C\(_4\)H\(_5\)Br\(^{81}\)) respectively.

This reaction involves \textit{in situ} conversion of 1-methyl-imidazoline-2-thione (mimzSH) into 2-bromo-1-methyl-imidazole (mimzBr) via bromination of mimzSH ring at C2 carbon with extrusion of sulfur as sulfate (Sandmeyer type bromination). Scheme 5 shows plausible
mechanism of formation of 2-bromo-1-methyl-imidazole and its coordination to Cu$^{II}$ in the tetranuclear complex 13. Under the experimental conditions Cu$^I$ oxidizes to Cu$^{II}$, which in turn oxidizes the thio moiety (A, B) into its disulfide (C). This disulfide is converted to 2-bromo-1-methyl-imidazole (ring bromination) along with formation of sulfate. Copper(II) in presence of bromide ions coordinates to 2-bromo-1-methyl-imidazole forming tetranuclear complex [Cu$_4$(η$^1$-N-(mimzBr)$_4$(μ$_4$-O)(μ-Br)$_6$]. It is the first example of metal mediated in situ bromination of 1-methyl-imidazoline-2-thione (mimzSH) into 2-bromo-1-methyl-imidazole (mimzBr).

The mixing of a solution of copper(I) bromide with the solution of 1-methyl-imidazoline-2-thione (mimzSH) in dimethyl sulfoxide changed the color of solution to sky blue in a few minutes which slowly turned to dark blue. After 2 weeks, blue color crystals of sulfate chelated mononuclear Cu$^{II}$ complex, [Cu$^{II}$(η$^2$-N,N-(mimz)$_2$S)(η$^1$-O,OSO$_2$)(η$^1$-OH)$_2$] 14 were obtained. In addition, the reaction of CuSCN with mimzSH in acetonitrile – dimethyl sulfoxide mixture also formed complex 14.
Reaction of copper(I) iodide with 1-methyl-imidazoline-2-thione (mimzSH) in 1 : 1 molar ratio in acetonitrile did not involve any C-S rupture and solution remained colorless. Slow evaporation of solution formed colorless crystals of linear chain 1D polynuclear complex, \{Cu_2(\mu-I)_2(\mu-S-mimzSH)\}_n 15 with alternate iodo / sulfur bridged cores. The complex showed intense fluorescent band at \(\lambda_{em} = 322\) nm corresponding to excitation wavelength of 272 nm.

The above reaction when carried out in acetonitrile-chloroform mixture, three products were isolated. Polynuclear complex 15 was formed after about 24 hours in about 30% yield. The color of the filtrate changed to green in a week’s time and green crystals of Cu\textsuperscript{II} dimer, [Cu\(_2\){\(\eta^2\)-N,N-(mimz)\(_2\)S\}_2(\mu-Cl)\(_2\)Cl\(_2\)] 10, were obtained in about 18% yield along with CuSO\(_4\)·5H\(_2\)O. The formation of complex 10 is due to exchange of iodine with chlorine from solvent chloroform. The formation of polynuclear complex 15 is shown in Scheme 6.

As discussed above, reactions of copper(I) halides with mimzSH formed interesting novel polynuclear complexes, both with and without C-S bond rupture. For comparison, copper(I) salt, for example, [Cu(NCCH\(_3\))](BF\(_4\)) was taken to observe the effect of anion on the reaction product. A solution of [Cu(NCCH\(_3\))](BF\(_4\)) salt was mixed with a solution of 1-methyl-imidazoline-2-thione (mimzSH) in acetonitrile in 1 : 2 molar ratio under mild atmospheric
conditions. The reaction solution turned greenish-brown in 2-3 days and dark purple needles of 
Cu\textsuperscript{II} octahedral complex \([\text{Cu}\{\eta^2-N,N-(\text{mimz})_2\text{S}\}_2(\eta^1-\text{OH}_2)_2](\text{BF}_4)_2\cdot2\text{H}_2\text{O} \ 16\) were obtained along
with CuSO\textsubscript{4}·5H\textsubscript{2}O. This reaction also involved oxidation of Cu\textsuperscript{I} to Cu\textsuperscript{II}, C-S rupture, \textit{in situ}
generation of (mimz)\textsubscript{2}S, followed by its coordination to Cu\textsuperscript{II}.

The blue color solution of copper(II) nitrate in methanol was added to the solution of
mimzSH in acetonitrile in 1 : 2 molar ratio, the color of resulting solution changed to colorless
indicating the reduction of Cu\textsuperscript{II} to Cu\textsuperscript{I}. After 2-3 days, color of solution again changed
to brownish green and blue color crystals of Cu\textsuperscript{II} octahedral complex \([\text{Cu}\{\eta^2-N,N-(\text{mimz})_2\text{S}\}_2(\eta^1-
\text{OH}_2)_2](\text{NO}_3)_2 \ 17\) were isolated along with CuSO\textsubscript{4}·5H\textsubscript{2}O. Compound 17 has been reported in
literature using ethanol-nitromethane mixture [178].

![Diagram of Cu complex with mimzS and mimzSH](image)

\textit{Thiazolidine-2-thione (tzdSH)}

In literature, reaction of thiazolidine-2-thione (tzdSH) with copper(II) chloride in ethanol-
nitromethane mixture formed Cu\textsuperscript{II} polynuclear complex, \([\text{Cu}\{\eta^2-N,S-(tztzdS)\text{Cl}\}_n \ (tztzdS = 3-(2-thiazolin-2-yl)thiazolidine-2-thione)\]. The reaction of copper(II) bromide with tdzSH in
nitromethane yielded 3-coordinate Cu\textsuperscript{I} complex \([\text{CuBr}(\eta^2-N,S-tztzdS)]\) [180]. These reactions
have now been carried out in acetonitrile to observe the effect of solvent on reaction products. A
solution of copper(I) chloride was mixed with the solution of thiazolidine-2-thione (tzdSH) in
acetonitrile in 1 : 1 molar ratio at room temperature. The solution turned reddish green in 2-3
days and after a week reddish brown prismatic crystals of 3-coordinate complex \([\text{CuCl}(\eta^2-N,S-
tztzdS)_2] \ 18 \ \{tztzdS = 3-(2-thiazolin-2-yl)thiazolidine-2-thione\} were isolated along with
CuSO\textsubscript{4}·5H\textsubscript{2}O. This reactions involves \textit{in situ} generation of oxidized ligand 3-(2-thiazolin-2-
yl)thiazolidine-2-thione (tztzdS) via fusion of two thiazolidine-2-thione rings with extrusion of
sulfur as sulfate and with formation of new C-N bond. The \textit{in situ} generation of tztzdS from
tzdSH, like that of (mimz)$_2$S from mimzSH, also requires oxidative desulfurization of the parent thione.

Here there is occurring an oxidation of Cu$^+$ to Cu$^{II}$ under aerobic conditions, and Cu$^{II}$ oxidizes thiazolidine-2-thione (tzdSH) to its disulfide with concomitant reduction of the metal. It is followed by intramolecular nucleophilic attack of the imino nitrogen of one ring onto the trigonal (C(2)) carbon of the other ring forming 3-(2-thiazolin-2-yl)thiazolidine-2-thione (ttztzdS) along with elimination of sulfur as sulfate (Scheme 7). Reaction of copper(I) bromide with tzdSH in 1 : 1 molar ratio in acetonitrile yielded 3-coordinate complex [CuBr($\eta^2$-N,S-ttztdS)] (19) similar to that formed in literature [180].

A reaction of copper(I) iodide with thiazolidine-2-thione under similar reaction conditions did not involve C-S bond rupture and merely formed a four coordinate iodo-bridged dimer,
The use of $[\text{Cu}(\text{NCCH}_3)_4](\text{BF}_4)$ salt in place of copper(I) halides in the reactions of thiazolidine-2-thione (tzdSH) in 1 : 2 molar ratio in acetonitrile also involved C-S rupture along with ring fusion and formed Cu$^1$ mononuclear distorted tetrahedral complex $[\text{Cu}(\eta^2-\text{N},\text{S-tztzdS})_2](\text{BF}_4)$ 21 along with CuSO$_4 \cdot 5\text{H}_2\text{O}$.

**N-alkyl-imidazolidine-2-thiones.** A series of N-alkyl-imidazolidine-2-thiones have been prepared by reacting substituted ethylene diamines with carbon disulphide in EtOH / H$_2$O on refluxing for 8-10 h [299].

The products obtained from the reactions of copper(I) chloride / bromide with N-alkyl-imidazolidine-2-thiones could not be completely characterized. The reactions of copper(I) iodide with N-alkyl-imidazolidine-2-thiones involved C-S rupture and the products obtained were characterized by X-ray crystallography, which is explained below.

*I*-Methyl-imidazolidine-2-thione (imdzSH-Me)
A solution of copper(I) iodide was mixed with the solution of 1-methyl-imidazolidine-2-thione (imdzSH-Me) in 1:1 molar ratio in acetonitrile at room temperature. After 2-3 days, colorless crystals of Cu\(^{1}\) 1D polymer, \{Cu\(_{4}(\mu_{3}-I)_{2}(\mu-I)_{2}(\mu-S-imdzSH-Me)_{2}(\eta^{1}-S-imdzSH-Me)_{2}\}\}_n 22 were obtained in 32% yield. The formation of polymer 22 is shown in Scheme 8. Two copper(I) iodide and two 1-methyl-imidazolidine-2-thione ligand moieties appear to have formed a dinuclear unit A, and two such units combined in inverse fashion through iodide atoms (\(\mu_{3}-I\) mode), resulting in the formation of repeat unit B. These B repeat units combined with other similar units through iodide atoms (\(\mu-I\) mode) forming the infinite polymer 22.

The color of the filtrate of above reaction changed to greenish brown in about two days and black prismatic crystals of composition C\(_{16}\)H\(_{28}\)Cu\(_{3}\)I\(_{4}\)N\(_{8}\)S\(_{2}\) were formed (18% yield) along with CuSO\(_{4}\)·5H\(_{2}\)O. The X-ray crystallography revealed the black crystals to be a mixed-valent trinuclear cluster, [Cu\(_{2}^{I}\)Cu\(_{II}\)(\(\eta^{2}-N,S-imdzdzS-Me\))(\(\mu-S-imdzdzS-Me\))(\(\mu-I\))\(_{2}\)(\(\eta^{1}-I\))\(_{2}\)] 23 \{imdzdS-Me = 1-methyl-3-(1-methyl-2-imidazolin-2-yl)imidazolidine-2-thione\}.
The formation of complex 23 involves *in situ* generation of oxidized ligand, 1-methyl-3-(1-methyl-2-imidazolin-2-yl)imidazolidine-2-thione (imdSMe) via fusion of two 1-methylimidazolidine-2-thione (imdSHMe) rings with extrusion of sulfur as sulfate and formation of new C-N bond, behavior similar to shown by thiazolidine-2-thione (Scheme 7). The proposed mechanism indicates that 2 molecules of CuI combined with 2I⁻ forming dinuclear species Cu₂I₄⁻. In next step, Cu²⁺ coordinated to neutral imdSMe forming a four-coordinate species [Cu(η²-N,S-imdSMe)₂]²⁺. These two units further combined with each other forming trinuclear cluster [Cu₃Cu(η²-N,S-imdSMe)(μ-S-imdSMe)(μ-I)(μ-I)(η¹-I)₂] (23) (Scheme 8).

*n-Propyl-imidazolidine-2-thione (imdS-Pr*)

Reaction of copper(I) iodide with imdS-Pr* in 1 : 1 molar ratio in acetonitrile under undisturbed conditions formed 1D polymer [Cu(μ-I)₂(μ-S-imdS-Pr*)₂]ₙ 26 (31% yield) with alternate iodo / sulfur bridged cores, similar to polymer 15. The color of the filtrate of above reaction changed to greenish yellow in 2-3 days and black prismatic crystals of mixed-valent polynuclear complex [Cu₂Cu(μ-S-imdS-Pr*)₂(μ-I)(μ-I)(η¹-I)₂]ₙ {imdS-Pr* = n-propyl-3-(n-
propyl-2-imidazolin-2-yl)imidazolidine-2-thione} 27 were obtained (19% yield) along with CuSO$_4$·5H$_2$O.

In complex 27, there is *in situ* generation of n-propyl-3-(n-propyl-2-imidazolin-2-yl)imidazolidine-2-thione (imidSPr$^n$) from imdSH-Pr$^n$, similar to imdzSMe. The proposed mechanism indicates that oxidation of Cu$^I$ to Cu$^{II}$ occurs, which is followed by generation of I$_2$ molecule with concomitant reduction of Cu$^{2+}$. This I$_2$ molecule generates I$_3$ by combining with I. Further 2 molecules of Cul combined with 2I$_3$ forming dinuclear species Cu$_2$I$_8^{2-}$. These dinuclear units combined with four-coordinate species [Cu($\eta^2$-N$_2$S-imdzS-Pr$^n$)$_2$]$^{2+}$ forming polymer, [Cu$^I_2$Cu$^{II}$(μ-S-imdzS-Pr$^n$)$_2$μ-I$_2$($\eta^1$-I$_3$)$_2$]$_n$ (27) (Scheme 9).
1-Ethyl-imidazolidine-2-thione \((\text{imd}z\text{SH-Et})\)

Reaction of copper(I) iodide with 1-ethyl-imidazolidine-2-thione in 1 : 1 molar ratio in acetonitrile yielded colorless prismatic needles of polynuclear complex of composition, \([\text{CuI(imd}z\text{SH-Et})_n]\) \text{24} in 38% yield. The color of filtrate changed to brown and black crystals of composition \([\text{Cu}_3\text{I}_8(\text{imd}z\text{dzS-Et})_2]\cdot2\text{CH}_3\text{CN}\) \text{25} were obtained in 17% yield along with \(\text{CuSO}_4\cdot5\text{H}_2\text{O}\). The crystals of complexes \text{24} and \text{25} were not suitable for X-ray structure determination. From the analytical data of complexes \text{24} and \text{25}, it was expected to have structures similar to those of complexes \text{26} and \text{27} respectively.

\(n\)-Butyl-imidazolidine-2-thione \((\text{imd}z\text{SH-Bu})\)

Reaction of copper(I) iodide with imdzSH-Bu\(^n\) in 1 : 1 molar ratio in acetonitrile did not form any \(\text{Cu}^I\) complex, rather reaction solution turned brownish green next day and black crystals of \(\text{Cu}^II\) mononuclear complex \([\text{Cu}(\eta^2\text{-N,S-imd}z\text{dzS-S-Bu})_2]\cdot(\text{I}_3)_2\) \{imdzzdS-S-Bu\(^n\) = \text{n-butyl-3-}(\text{n-butyl-2-}i\text{m}d\text{a}z\text{ol}i\text{n}-2-\text{yl})i\text{m}d\text{a}z\text{oli}d\text{in}-2-\text{thione}\} \text{28} were obtained along with \(\text{CuSO}_4\cdot5\text{H}_2\text{O}\). This reaction also involves C-S bond rupture with \textit{in situ} generation of \(n\)-butyl-3-(\(n\)-butyl-2-imidazolin-2-yl)imidazolidine-2-thione \((\text{imd}z\text{dzS-S-Bu})\(^n\)) via fusion of two \(n\)-butyl-imidazolidine-2-thione \((\text{imd}z\text{SH-S-Bu})\(^n\)) rings, which further coordinate to \(\text{Cu}^II\) forming complex \text{28}. In this complex, triiodide ion is lying outside the coordination sphere.

![Complex 28](image)

The reaction of copper(I) chloride with 1-methyl-imidazolidine-2-thione \((\text{imd}z\text{SH-Me})\) in 1 : 1 molar ratio in acetonitrile / acetonitrile-chloroform mixture was carried out at room temperature. The solution turned bluish green and blue crystals of \(\text{CuSO}_4\cdot5\text{H}_2\text{O}\) were formed leaving behind uncharacterized sticky mass. Though this sticky product is soluble in acetonitrile
but no crystalline product could be obtained. Other N-substituted ligands, imdzSH-Et, imdzSH-Pr<sup>n</sup> and imdzSH-Bu<sup>n</sup> behaved similarly. These reactions in dmso turned green but no crystalline product could be obtained.

The reaction of copper(I) bromide with 1-methyl-imidazolidine-2-thione (imdzSH-Me) in 1:1 molar ratio in acetonitrile at room temperature formed light greenish crystalline complex of composition [CuBr(imdzSH-Me)]·0.25CHCl<sub>3</sub> in 38% yield. The color of filtrate changed to brownish green in 2-3 days and black crystals of mixed-valent polynuclear complex [Cu<sup>I</sup><sub>3</sub>Cu<sup>II</sup><sub>5</sub>Br<sub>5</sub>(μ-S-imdzdzS-Me)<sub>2</sub>]<sub>n</sub> 29 were obtained along with CuSO<sub>4</sub>·5H<sub>2</sub>O. The above reaction when carried out in 1:2 molar ratio in acetonitrile, no C-S rupture occurred and colorless crystals of 3-coordinate complex, [CuBr(η<sup>1</sup>-S-imdzSH-Me)<sub>2</sub>] 30 were obtained.

![Diagram](image)

The reaction of copper(I) bromide with other N-alkyl-imidazolidine-2-thiones (imdzSH-Et, imdzSH-Pr<sup>n</sup>, imdzSH-Bu<sup>n</sup>) in 1:1 molar ratio in acetonitrile turned the reaction solution brown and blue crystals of CuSO<sub>4</sub>·5H<sub>2</sub>O were formed, leaving behind the uncharacterized dark green sticky mass, a behavior similar to that of copper(I) chloride. These reactions in dmso turned green but no crystalline product could be established.

### 6.1.2 Six-membered heterocyclic ring thiones

The six-membered heterocyclic ring thiones, such as, 2,4-dithiouracil (dtucH<sub>2</sub>), 2-thiouracil (tucH<sub>2</sub>) and 2,4,6-trimercaptotriazine (H<sub>3</sub>tmt) did not exhibit C-S bond rupture as the six-membered ring is probably more stable.

#### 2,4-Dithiouracil (dtucH<sub>2</sub>)

Reaction of copper(I) chloride with 2,4-dithiouracil (1:1 molar ratio) in acetonitrile-methanol mixture formed an insoluble product and addition of 2 moles of triphenylphosphine (PPh<sub>3</sub>) clears the reaction. Slow evaporation of solution at room temperature yielded light yellow
crystals of $[\text{Cu}_2(\mu-\text{Cl})(\mu-\text{S,S-dtucH})(\text{PPh}_3)_4]$ 31 in 19% yield. The anionic dtucH ligand is bridging through sulfur atoms. From the filtrate of above reaction, light orange crystals of composition $[\text{Cu}_2\text{Cl}_2(\text{dtucH}_2)(\text{PPh}_3)_4]$ 32 were obtained in 18% yield along with dark orange crystals of polynuclear complex, $\{\text{Cu}(\mu-\text{S,S-dtucH})(\text{PPh}_3)\text{Cl}\}_n$ 33 in 23.5% yield (Scheme 10). Complex 32 was stable in mother liquor for a few days and slowly transformed to 33 after losing one PPh$_3$ per Cu atom. In complex 33, the dtucH$_2$ ligand in neutral form is bridging through sulfur atoms (structure of 32 could not be obtained, but the stoichiometry suggests the bonding by a neutral thio-ligand).

Reaction of copper(I) bromide and 2,4-dithiouracil in the presence of PPh$_3$ in 1 : 1 : 2 molar ratio in acetonitrile-methanol mixture yielded light yellow crystals of dinuclear complex, $[\text{Cu}_2(\mu-\text{Br})(\mu-\text{S,S-dtucH})(\text{PPh}_3)_4]$ 34 in 20% yield. From the filtrate, after 2-3 days light orange crystals of composition $[\text{Cu}_2\text{Br}_2(\text{dtucH}_2)(\text{PPh}_3)_4]$ 35 were formed in 19% yield, along with dark orange crystals of polynuclear complex $\{\text{Cu}(\mu-\text{S,S-dtucH})(\text{PPh}_3)\text{Br}\}_n$ 36 in 22% yield (same as in Scheme 10). Complex 35 was stable in mother liquor for a few days and slowly transformed to
complex 36 after losing one PPh₃ per Cu atom. In dinuclear complex 34, dtucH ligand in anionic form is bridging through sulfur atoms, while in complexes 35 and 36, dtucH₂ ligand in neutral form is bridging through sulfur atoms.

Reaction of copper(I) iodide with 2,4-dithiouracil in the presence of PPh₃ in 1 : 1 : 2 molar ratio in acetonitrile-methanol mixture yielded only light yellow crystals of a dinuclear complex [Cu₂(μ-I)(μ-S,S-dtucH)(PPh₃)₄] 37 in 68% yield. The above reaction in acetonitrile-methanol-chloroform mixture yielded dark orange crystals of polynuclear complex {Cu(μ-S,S-dtucH₂)(PPh₃)I}_n·nCHCl₃ 38. It is added here that redissolving complex 37 in acetonitrile-chloroform mixture also formed complex 38.

2-Thiouracil (tucH₂)

Reaction of copper(I) chloride with 2-thiouracil in 1 : 1 molar ratio in acetonitrile-methanol mixture formed an insoluble product and addition of 2 moles of PPh₃ clears the reaction. After 4-5 days, slow evaporation at room temperature yielded light yellow crystals of [CuCl(η¹-S-tucH₂)(PPh₃)₂] 39. The products with copper(I) bromide / iodide could not be established and all attempts gave support for preferential formation of known tetrahedral complexes, [CuX(PPh₃)₃] (X = Br, I).
2,4,6-Trimercaptotriazine (H₃tmt)

Reaction of copper(I) chloride with 2,4,6-trimercaptotriazine (H₃tmt) in 1 : 1 molar ratio in acetonitrile-methanol mixture formed an insoluble product and addition of 2 moles of PPh₃ clears the reaction. Slow evaporation of the solution at room temperature yielded yellow crystals of trinuclear complex [Cu₃Cl₂(η¹-S-H₃tmt)(PPh₃)₆] 40. The H₃tmt ligand in anionic form is coordinating through sulfur atoms. The above reaction with copper(I) bromide yielded similar trinuclear complex [Cu₃Br₂(η¹-S-H₃tmt)(PPh₃)₆] 41. However, similar reaction with copper(I) iodide formed preferentially a known complex [Cu₂(μ-I)₂(PPh₃)₃].

6.2 Silver (I) complexes

The chemistry of silver(I) with heterocyclic thioamides has been found to be different from that of copper(I). The major reason is due to the lack of solubility of silver(I) halides in acetonitrile or even in other common organic solvents. It thus became impossible to follow the procedures adopted in copper(I) reactions. Here one has to stir or reflux for reaction to take effect. Neither polymeric products nor C-S rupture phenomenon have been observed in this case. The results obtained are described below. Two methods have been used for preparing various silver(I) compounds.
Method I – According to this method, a silver(I) halide (X = Cl, Br) suspended in acetonitrile was made to react with one or two moles of PPh₃ (1:1 or 1:2 molar ratio) in the same solvent and contents were stirred for long period usually overnight to ensure that maximum or all the silver(I) halide has reacted. The resulting insoluble white precipitates analysed as [AgX(PPh₃)]₄ or [AgX(PPh₃)₂] respectively depending on ratio of reactants. The precipitates were then suspended in CHCl₃ and addition of one mole of thio-ligand (solid) resulted in a clear solution. This method formed both mono- and di-nuclear complexes (42 – 57). The crystals of complexes were grown from a mixture of CH₂Cl₂ with CH₃CN.

Method II - According to this method, a silver(I) salt (X = Cl, Br, NO₃⁻, CH₃COO⁻) suspended (silver(I) halides, silver(I) acetate) or dissolved (silver(I) nitrate) in CH₃CN was first slowly reacted with a thio-ligand under stirring (24 – 26 h for halides and 3 – 4 h for nitrate and acetate) at room temperature resulting in formation of precipitates. To these precipitates in same solvent was added one or two moles of PPh₃ resulting in a clear solution, which on slow evaporation yielded crystals of mono- and di-nuclear complexes (58 – 68).

Complexes of silver(I) formed H-bonded 1D and 2D supramolecular networks. The study of supramolecular networks have importance in the context of their possible applications such as carriers to transport drugs in biological systems, as mass and potentiometric sensors, and as probes to detect trace metals [310].

Earlier from this laboratory, sulfur-bridged dinuclear complexes of pyridine-2-thione, [Ag₂(μ-S-pySH)₂(PPh₃)₂X₂] (X = Cl, Br) have been synthesized using method 1 [279]. In case
of five-membered heterocyclic thioamides (Chart Ia), no complex of silver(I) halides with PPh₃ as coligand has been reported in literature. Without PPh₃, a mononuclear [Ag(η¹-S-imdzSH)₂Cl] [102], a dinuclear [Ag₂(η¹-S-imdzSH)₄(μ-Br)] [103] and a few polynuclear [Ag(η¹-S-imdzSH)(μ-S-imdzSH)Cl]ₙ [105], [Ag₂(μ-S-mimzSH)(μ₃-I)]ₙ [16] complexes have been reported with silver(I) halides. So a series of reactions of silver(I) halides with five-membered heterocyclic thioamides (Chart Ia) in the presence of PPh₃ have been carried out using method I.

The reaction of silver(I) chloride with one mole of PPh₃ in acetonitrile under stirring formed white precipitates of [AgCl(PPh₃)]₄. To these precipitates in chloroform resulted in a clear solution, which on slow evaporation resulted in a mass. This mass was dissolved in CH₂Cl₂–CH₃CN mixture and slow evaporation at room temperature formed colorless crystals of chloro-bridged dinuclear complex [Ag₂(μ-Cl)(η¹-S-imdzSH)₂(PPh₃)]²⁻ 42. The above reaction in 1 : 1 : 2 (M : L : PPh₃) molar ratio formed corresponding mononuclear complex [AgCl(η¹-S-imdzSH)(PPh₃)]·0.65H₂O 43. Reaction of silver(I) bromide with imdzSH in the presence of PPh₃ in 1 : 1 or 1 : 1 : 2 molar ratio formed only bromo-bridged dinuclear complex, [AgBr₂(imdzSH)₂(PPh₃)]₂ 44. Complexes 42 and 44 are halogen-bridged dimers in contrast to sulfur-bridged dimers formed by pySH, [Ag₂(μ-S-pySH)]₂(PPh₃)X₂] (X = Cl, Br) [279]. This may be due to better Lewis basicity of pySH as compared to imdzSH which has two electronegative N atoms in ring as compared to one in the former case. The latter ligand favors terminal coordination.
It is noted that reaction of silver(I) chloride with imdzSH in the presence of PPh₃ in 1 : 1 : 1 molar ratio formed a dinuclear complex 42 and in 1 : 1 : 2 molar ratio yielded a mononuclear complex 43, however, similar reaction of silver(I) bromide with imdzSH in the presence of PPh₃ in 1 : 1 : 1 or 1 : 1 : 2 molar ratio formed only dinuclear complex 44.

The above reactions with 1-methyl-imidazolidine-2-thione (imdzSH-Me) and 1-ethyl-imidazolidine-2-thione (imdzSH-Et) formed similar products. Reaction of silver(I) chloride with imdzSH-Me / imdzSH-Et in the presence of PPh₃ in 1 : 1 : 2 or 1 : 1 : 1 molar ratio formed anticipated mononuclear [AgCl(η₁-S-L)(PPh₃)₂] (L = imdzSH-Me 45, imdzSH-Et 47) and dinuclear [Ag₂(µ-Cl)(η₁-S-L)₂(PPh₃)₂] (L = imdzSH-Me 68, imdzSH-Et 48) complexes respectively. The above reaction with silver(I) bromide formed only dinuclear complexes [Ag₂(µ-Br)(η₁-S-L)₂(PPh₃)₂] (L = imdzSH-Me 46, imdzSH-Et 49). The dinuclear complexes 46, 48, 49 and 68 are halogen bridged, similar to complexes 42 and 44.

Reaction of silver(I) chloride with n-propyl-imidazolidine-2-thione (imdzSH-Prⁿ) in the presence of PPh₃ in 1 : 1 : 1 or 1 : 1 : 2 molar ratio formed only mononuclear tetrahedral complex [AgCl(η₁-S-imdzSH-Prⁿ)(PPh₃)₂] 50 contrary to the above reactions. The reaction of silver(I) bromide with imdzSH-Prⁿ in the presence of PPh₃ in 1 : 1 : 1 or 1 : 1 : 2 molar ratio formed bromo-bridged dinuclear complex [Ag₂(µ-Br)(η₁-S-imdzSH-Prⁿ)₂(PPh₃)₂] 51. The above reactions of silver(I) halides with n-butyl-imidazolidine-2-thione (imdzSH-Buⁿ) in the presence of PPh₃ in 1 : 1 : 1 or 1 : 1 : 2 molar ratio formed only mononuclear complexes [AgX(imdzSH-Buⁿ)(PPh₃)₂] (X = Cl 52, Br 53). It is noted that increasing the chain length of N-alkyl- group of imidazolidine-2-thiones has profound effect on the nuclearities of complexes formed.
Reaction of silver(I) chloride with 1-methyl-imidazoline-2-thione (mimzSH) in the presence of PPh₃ in 1 : 1 : 1 or 1 : 1 : 2 molar ratio formed mononuclear complex [AgCl(η¹-S-mimzSH)(PPh₃)₂] 54, while above reaction with silver(I) bromide formed bromo-bridged dinuclear complex [Ag₂(µ-Br)₂(η¹-S-mimzSH)₂(PPh₃)₂] 55, behavior similar to that of imdzSH-Pr⁺. Reaction of silver(I) halides with thiazolidine-2-thione (tzdSH) in the presence of PPh₃ in 1 : 1 : 1 or 1 : 1 : 2 molar ratio formed mononuclear complexes [AgX(η¹-S-tzdSH)(PPh₃)₂] (X = Cl 56, Br 57), similar to as imdzSH-Buⁿ does.

In literature, with silver(I) nitrate tetrahedral [Ag(pySH)₂(PPh₃)₂](NO₃) and trigonal planar [Ag(pymSH)(PPh₃)₂](NO₃) complexes have been reported with PPh₃ as co-ligand [311]. With five-membered heterocyclic thioamides (Chart Ia), there is no report of any complex of silver(I) nitrate with PPh₃ as co-ligand. Without PPh₃, a mononuclear [Ag(η¹-S-mimzSH)₃](NO₃) [101], and a few polynuclear [Agₙ(µ-N,S,S-tzdSₙ)(µ-S,S-tzdSH)ₙ] [107], [Ag(µ-S,S-tzdSH)(η¹-ONO₂)ₙ] and [Ag₂(µ-N,S,S-tzdS)(µ-S,S-tzdSH)₂] [18] complexes have been reported. So the reactions of silver(I) salts (halides, nitrate and acetate) with heterocyclic thioamides (Charts Ia and Ib) were carried out in the presence of PPh₃ using method II.

Reaction of 2,4-dithiouracil (dtucH₂) with silver(I) chloride in CH₃CN – MeOH mixture in 1 : 1 molar ratio under overnight stirring resulted in yellow precipitates. The addition of one mole of PPh₃ to the precipitates in same solvent did not form the clear solution, however, an
addition of another mole of PPh₃ dissolved the precipitates completely. Slow evaporation of the resulting solution yielded yellow crystals of hetero-bridged dinuclear complex [Ag₂(µ-Cl)(µ-S,S-dtucH)(PPh₃)₄] 58, similar to Cu¹ complex 31. The sulfur atoms of anionic dtucH ligand and chlorine atom are bridging silver centers forming an eight membered ring. There is loss of one chlorine atom in complex formation which is uncommon in case of silver(I) halides as silver is strongly bonded to halides. With silver(I) there is no complex reported earlier with 2,4-dithiouracil. The above reaction with silver(I) bromide yielded dinuclear complex [Ag₂(µ-Br)(µ-S,S-dtucH)(PPh₃)₄] 59, similar to Cu¹ complex 34. These compounds are the first structurally characterized complexes of 2,4-dithiouracil with silver(I) halides.

\[
\text{Ph}_3\text{P} - \text{Ag} - \text{S} - \text{PPh}_3 \\
\text{Ph}_3\text{P} \\

(X = \text{Cl 58, Br 59})
\]

Reaction of silver(I) nitrate with thiazolidine-2-thione (tzdSH) in 1 : 2 molar ratio in acetonitrile under stirring for 2h at room temperature formed colorless precipitates. The addition of one mole of PPh₃ to the precipitates in same solvent clears the reaction. Slow evaporation of solution formed light yellow prismatic crystals of dinuclear complex, [Ag₂(µ-S-tzdSH)₂(η¹-S-tzdSH)₂(PPh₃)₂](NO₃)₂ 60. The neutral tzdSH ligand is coordinating through sulfur atom, where two tzdSH ligands are bridging, while the other two are terminally coordinating.

Reaction of silver(I) nitrate with imidazolidine-2-thione (imdzSH) in 1 : 2 molar ratio in acetonitrile under stirring for 2h at room temperature formed precipitates. The addition of one mole of PPh₃ to the precipitates in same solvent did not dissolve the precipitates completely. An addition of methanol to the reaction mixture clears the reaction. Slow evaporation of solution formed colorless crystals (stable in mother liquor) of sulfur-bridged dinuclear complex, [Ag₂(µ-S-imdzSH)₂(η¹-S-imdzSH)₂(PPh₃)₂](NO₃)₂⋅2CH₃OH 61. The above reaction with imidazoline-2-thione (imzSH) formed similar dinuclear complex [Ag₂(µ-S-imzSH)₂(η¹-S-imzSH)₂(PPh₃)₂](NO₃)₂⋅2CH₃OH 62. When halide is not bonded to the silver(I), the behavior of thio-ligands changed from being terminal to involving µ-S bridging.
Reaction of silver(I) nitrate with 1-methyl-imidazoline-2-thione (mimzSH) in the presence of PPh₃ in 1 : 2 : 1 molar ratio in acetonitrile did not form a dinuclear complex similar to 60–62, rather a 3-coordinate mononuclear complex \([\text{Ag}(\eta^1-S-\text{mimzSH})_2(P\text{Ph}_3)](\text{NO}_3)\) 63 has been isolated. The above reaction with 1-methyl-imidazolidine-2-thione (imzdSH-Me) formed similar 3-coordinate complex \([\text{Ag}(\eta^1-S-\text{imzdSH-Me})_2(P\text{Ph}_3)](\text{NO}_3)\) 64.

Reaction of silver(I) nitrate with benz-imidazoline-2-thione (bzimzSH) in 1 : 2 molar ratio in acetonitrile formed an insoluble product. Addition of one mole of PPh₃ did not clear the solution, however, an addition of second mole of PPh₃ dissolved the precipitates completely. Slow evaporation of the resulting solution yielded crystals of 3-coordinate complex \([\text{Ag(bzimzSH)(PPh}_3)_2](\text{NO}_3)\) 65.
Reaction of silver(I) acetate with thiazolidine-2-thione (tzdSH) in 1 : 2 molar ratio in acetonitrile-acetone mixture under stirring for 2h at room temperature formed precipitates. The addition of one mole of PPh₃ to the precipitates in same solvent did not form the clear solution, however, an addition of another mole of PPh₃ dissolved the precipitates completely. Slow evaporation of the resulting solution yielded pale yellow crystals of mononuclear complex [Ag(η¹-S-tzdSH)(η¹-S-tzdS)(PPh₃)₂] 66. Here, one tzdSH ligand is neutral while the other is anionic and both are coordinating through sulfur atoms.

The above reaction with benz-imidazoline-2-thione (bzimzSH) formed mononuclear complex [Ag(η¹-S-bzimzSH)(PPh₃)₂](OAc)·H₂O 67. Here, bzimzSH ligand in neutral form is coordinating through sulfur and acetate ion is lying outside the coordination sphere.

Reaction of silver(I) acetate with 1-methyl-imidazoline-2-thione (mimzSH) in the presence of PPh₃ in 1 : 2 : 2 molar ratio in acetonitrile-acetone mixture was carried out but it did not form mononuclear complex similar to 66 or 67 rather it formed a complex of composition C₄₀H₃₆AgClN₂P₂S, whose x-ray crystallography revealed it to be a mononuclear complex [AgCl(η¹-S-mimzSH)(PPh₃)₂], same as complex 54. The formation of this complex involves picking up chlorine from laboratory atmosphere or from solvent. Similarly, the above reaction when carried out with 1-methyl-imidazolidine-2-thione (imdzSH-Me) / 1-ethyl-imidazolidine-2-
thione (imidzSH-Et), it formed chloro-bridged dinuclear complexes [Ag₂(μ-Cl)(η¹-S-L)₂(PPh₃)₂] (L = imdzSH-Me 68, imdzSH-Et 48) involving chlorine picking from atmosphere or solvent.