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Chemistry of Heterocyclic 2-Thiones: In Situ Generation of 3-(2-Thiazolin-2-yl)thiazolidine-2-thione and 1,1'-Dimethyl-2,2'-diimidazolyl Sulfide and Their Coordination to Cu^I and Cu^{II}

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The chemical reactivity of copper(I) chloride/copper(I) bromide, $[Cu^{I}(NCCH_{3})_{4}](BF_{4})$, and copper(II) nitrate towards a series of heterocyclic-2-thiones under aerobic conditions is described. Thiazolidine-2-thione (NC₃H₅S₂) in CH₃CN in the presence of copper(I) chloride/bromide and [Cu^I(NCCH₃)₄]-(BF₄) was transformed into 3-(2-thiazolin-2-yl)thiazolidine-2thione (C₃H₄S₂N-C₃H₄SN) through C-S bond cleavage and the formation of a C-N bond between two heterocyclic rings. This new thio ligand $(C_3H_4S_2N-C_3H_4SN)$ chelates to Cu^I through N,S-donor atoms, and the third site is occupied by the halogen atoms (Cl, Br), which leads to the formation of C_3H_4SN [X = Cl (1), Br (2)], and a four-coordinate N₄S-chelated complex, $[Cu^{I}(\kappa^{2}-N_{1}S-C_{3}H_{4}S_{2}N-C_{3}H_{4}SN)_{2}](BF_{4})$ (3), is obtained in the presence of BF_4^- . In each case, the formation of CuSO₄·5H₂O was also observed. Upon reaction of 1-methyl-

Introduction

Sulfur-containing ligands such as heterocyclic thioamides or closely related ligands bearing the $-N(H)C(=S) \rightarrow N=C(-SH)- \text{ or } -N(H)C(=S)-N(H)-\leftrightarrow -N=C(-SH)-N(H)$ functional groups have shown interaction with a wide range of metals owing to the presence of both nitrogen (hard) and sulfur (soft) donor atoms, and thus, these thio ligands have

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imidazoline-2-thione $(N_2C_4H_6S)$ with $[Cu^I(NCCH_3)_4](BF_4)$ or copper(II) nitrate in CH₃CN or CH₃CN/MeOH, respectively, the thio ligand is converted into 1,1'-dimethyl-2,2'-diimidazolyl sulfide $(N_2C_4H_5)_2S$ (a thioether), which prefers to bind to Cu^{II} (in situ formed) to yield six-coordinate N₁N-chelated octahedral complexes, namely, $\{Cu^{II}[\kappa^2-N, N-(N_2C_4H_5)_2 S_{2}(\kappa^{1}-OH_{2})_{2}X_{2} [X = BF_{4} (6), NO_{3} (7)],$ with water in the axial positions. The transformation of the thio ligand into 1,1'-dimethyl-2,2'-diimidazolyl sulfide is also observed in its copper(I) chloride reaction in acetonitrile, which yields an N,Nchelated chloro-bridged dimer, $\{Cu^{II}_{2}[\kappa^{2}-N,N-(N_{2}C_{4}H_{5})_{2}S]_{2} (\mu$ -Cl)₂Cl₂ (5). Reaction of copper(I) iodide with thiazolidine-2-thione and 1-methylimidazolidine-2-thione $(N_2C_4H_8S)$ in acetonitrile yields an iodo-bridged dimer, $[Cu_2(\kappa^1-S NC_{3}H_{5}S_{2}_{4}(\mu-I)_{2}$ (4), and a novel polymer, $[Cu_{4}(\mu_{3}-I)_{2}(\mu-I$ $S-N_2C_4H_8S_2(\kappa^1-S-N_2C_4H_8S)]_n$ (8), respectively.

exhibited variable bonding modes in neutral and anionic forms, which has led to the formation of mono-, di-, tri-, and polynuclear complexes.^[1] In addition to the diversity of metal-ligand interactions, the above ligands have caught the attention of many workers as a result of their applications as biomimics in biological systems,^[2] as fungicides,^[2,3] as electric conductors,^[4] in the pharmaceuticals industry,^[5] as anticancer agents,^[6] and in catalysis.^[1]

During our studies of the chemistry of copper(I) halides in reactions with heterocyclic-2-thioamides (Scheme 1), it was found that variation of the reaction conditions, including solvent and ratio of reactants, produced different types of products.^[7-10] During the course of these reactions, C-S bond cleavage was observed upon treatment of copper(I) bromide with 1-methylimidazoline-2-thione ($N_2C_4H_6S$, II) and upon treatment of copper(I) chloride/bromide with imidazolidine-2-thione (N₂C₃H₆S, III)^[11] in DMSO. Additionally, the reaction of thio ligand II with copper(I) bromide in acetonitrile/chloroform also involved C-S bond cleavage with subsequent conversion of II into 2-bromo-1methylimidazole (N₂C₄H₅Br).^[12] In the literature, cleavage

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of C–S bonds by Cu^{II} salts under ambient conditions followed by in situ aerobic oxidation of sulfur to sulfate has been observed to a limited extent.^[13–18] Apart from copper, reactions of heterocyclic thioamides with metal carbonyls also involve cleavage of C–S bonds by splitting of sulfur, which subsequently acts as a tri- or tetradentate bridge to generate homo- or heteronuclear clusters.^[19a–19f] Activation, cleavage, and transformations of C–S bonds by using transition-metal compounds have found wide interest in synthetic chemistry and the petroleum industry^[20] and have relevance in biological reactions.^[21–23]



Scheme 1. Different heterocyclic bases.

In continuation of our studies on the chemistry of copper heterocyclic thioamides,^[7–12] in this paper, reactions of copper(I) halides and some other Cu^{I,II} salts such as [Cu(NCCH₃)₄](BF₄) and Cu(NO₃)₂ with thiazolidine-2thione (NC₃H₅S₂, **I**), 1-methylimidazoline-2-thione (N₂C₄H₆S, **II**), and 1-methylimidazolidine-2-thione (N₂C₄H₈S, **IV**) are described with the sole purpose to determine the effect of anions and other conditions on the nature of the products and on C–S bond cleavage.

Results and Discussion

Synthesis Comments

Reactions of copper(I) halides and some other copper salts with I, II, and IV in different solvents are described. Except with iodide as the anion, in all cases C–S bond cleavage and C–N bond formation are observed. The newly formed ligands then complex either Cu^I or Cu^{II} present in solution to yield different types of compounds.

Reactions Involving C–S bond Cleavage/C–N Bond Formation

Equimolar solutions of copper(I) chloride and I $(NC_3H_5S_2)$ in acetonitrile were mixed, and the mixture was left undisturbed to react under aerobic conditions at room temperature. The color of the solution changed from colorless to greenish brown slowly, and red-brown prismatic crystals of composition C₆H₈ClCuN₂S₃ were formed over a period of 1 week. X-ray analysis of the red-brown crystals revealed that I (NC₃H₅S₂) was transformed into 3-(2-thiazolin-2-yl)thiazolidine-2-thione $(C_3H_4S_2N-C_3H_4SN)$ through C-S bond cleavage, followed by C-N bond formation (fusion of two thiazolidine-2-thione rings) with extrusion of sulfur as sulfate. The C₃H₄S₂N-C₃H₄SN ligand subsequently chelated to Cu^I through N,S-donor atoms, and the third site was occupied by a chloride, which led to the formation of a three-coordinate Cu^{I} complex, $[CuCl(\kappa^{2}-$

N,*S*-C₃H₄S₂N-C₃H₄SN)] (1, Scheme 2). Copper(I) bromide showed similar activity and formed a three-coordinate complex, [Cu^IBr(κ^2 -*N*,*S*-C₃H₄S₂N-C₃H₄SN)] (2). Further, upon reaction of a solution of [Cu^I(NCCH₃)₄](BF₄) with a 2 M solution of I (acetonitrile), 3-(2-thiazolin-2-yl)thiazolidine-2-thione (C₃H₄S₂N-C₃H₄SN) was again formed. Owing to the lack of the coordinating ability of the BF₄⁻ anion, two molecules of this thio ligand chelate to Cu^I present in solution to yield a four-coordinate complex, [Cu(κ^2 -*N*,*S*-C₃H₄S₂N-C₃H₄SN)₂](BF₄) (3).





Scheme 2. Plausible mechanism for the formation of complexes 1-3.

With the help of mass spectrometry, a plausible explanation for the formation of 3-(2-thiazolin-2-yl)thiazolidine-2thione and its coordination to Cu^I in complexes 1-3 is shown in Scheme 2. Under the experimental conditions, Cu^I oxidizes to Cu^{II}, which in turn oxidizes A into disulfide B with concomitant reduction of the metal. This is followed by the oxidation of **B** to **C** (m/z = 268.9; calcd. for $C_6H_8N_2S_4O_2$, m/z = 268.4), which generates copper(II) sulfate (m/z = 179.0; calcd. for CuSO₄·H₂O + 2H, m/z = 179.6) and E (m/z = 173.0; calcd. for C₆H₈N₂S₂, m/z = 172.3) via **D**. The interaction of **D** with **A** appears to give a new thio ligand, namely, 3-(2-thiazolin-2-yl)thiazolidine-2-thione (C₃H₄S₂N-C₃H₄SN, F). The mass spectrometry data support the formation of $CuCl(C_3H_4S_2N-C_3H_4SN)$ (m/z = 304.9, calcd. m/z = 303.3 for complex 1), CuBr(C₃H₄S₂N- $C_{3}H_{4}SN$ (*m*/*z* = 346.9, calcd. *m*/*z* = 347.8 for complex 2), and symmetrical complex 3 (m/z = 470.9, calcd. m/z =471.0) from the reactions of CuCl and CuBr with I.

Similar to the reactions of I, equimolar solutions of II $(N_2C_4H_6S)$ and copper(I) chloride in acetonitrile (or acetonitrile/chloroform) were allowed to react under aerobic conditions at room temperature. Green crystals of composition



C₈H₁₀Cl₂CuN₄S were formed over a period of 2 weeks. Xray analysis showed that ligand \mathbf{II} was converted into 1,1'dimethyl-2,2'-diimidazolyl sulfide [(N2C4H5)2S] (a thioether), which bonded to Cu^{II} through its N,N-donor atoms to yield a dinuclear complex, $\{Cu^{II}_{2}[\kappa^{2}-N, N-(N_{2}C_{4}H_{5})_{2}S]_{2}$ $(\mu$ -Cl)₂Cl₂ (5). Further, upon reaction of a solution of $[Cu^{I}(NCCH_{3})_{4}](BF_{4})$ with a 2 m solution of II (N₂C₄H₆S) in acetonitrile, dark purple crystals of composition C₁₆H₂₈B₂CuF₈N₈O₄S₂ were formed over a period of 1 week, and X-ray analysis showed that II $(N_2C_4H_6S)$ was again converted into 1,1'-dimethyl-2,2'-diimidazolyl sulfide $[(N_2C_4H_5)_2S]$. Two molecules of this new thio ligand chelated to Cu^{II} in a *trans* position and two axial sites were occupied by water molecules, which led to the formation of an octahedral complex, $\{Cu[\kappa^2-N, N-(N_2C_4H_5)_2S]_2(\kappa^1 OH_2)_2$ (BF₄)₂·2H₂O (6). Interestingly, a blue solution of copper(II) nitrate in methanol turned colorless upon addition of a 2 M acetonitrile solution of II ($N_2C_4H_6S$) as a result of the reduction of Cu^{II} to Cu^I, which then showed chemical activity similar to that of $[Cu^{I}(NCCH_{3})_{4}](BF_{4})$ and formed an octahedral complex, $\{Cu^{II}[\kappa^2-N,N (N_2C_4H_5)_2S_2(\kappa^1-OH_2)_2$ (NO₃)₂ (7), which is similar to 6; a reaction in nitromethane/methanol also yielded the same product.^[13]

Scheme 3 shows a plausible explanation for the formation of 1,1'-dimethyl-2,2'-diimidazolyl sulfide $[(N_2C_4H_5)_2-S]$, which was arrived at with the help of mass spectrometry for the reaction of CuCl with **II** for the formation of **5**. As before, under the experimental conditions, Cu^I oxidizes to



Scheme 3. Plausible mechanism of formation of complexes 5-7.

 Cu^{II} , which in turn oxidizes **G** into disulfide **H** (*m*/*z* = 225.5; calcd. for $C_8H_{10}N_4S_2$, m/z = 226.0) with concomitant reduction of the metal. This is followed by the oxidation of **H** to I (m/z = 257.0; calcd. for C₈H₁₀N₄S₂O₂, m/z = 258.0). Species I is transformed into J $[(N_2C_4H_5)_2S]$ along with the formation of $CuSO_4$. Species J combines with Cu^{II} in the presence of halide ions to preferentially generate 5. The mass spectrometry data for $\{[(N,N-J)Cu(\mu-Cl^{35})_2Cu-$ (N, N-J)]·0.5H₂O}²⁺(m/z)= 297.0; calcd. for $C_{16}H_{20}N_8Cu_2S_2Cl_2^{35} \cdot 0.5H_2O, m/z = 296.5), \{[(N,N-J)Cu(\mu - 1)]$ $Cl^{37}_{2}Cu(N,N-J)] \cdot 0.5H_{2}O^{2+}$ (*m*/*z* = 299.0; calcd. for $C_{16}H_{20}N_8Cu_2S_2Cl_2^{37} \cdot 0.5H_2O, m/z = 298.5), \{[(N,N-J)Cu(\mu - 1)]$ $Cl^{35}_{2}Cu(N,N-J)]^{2+}(m/z)$ = 292; calcd. $C_{16}H_{20}N_8Cu_2S_2Cl_2^{35}$, m/z = 292), and {[(N,N-J)Cu(μ -Cl³⁷)₂-Cu(N,N-J)]²⁺ (*m*/*z* = 294; calcd. for $C_{16}H_{20}N_8Cu_2S_2Cl_2^{37}$, m/z = 294) support the formation of **5** from **J** (thioether) as an N,N donor. However, the molecular ion is not observed; rather, these degraded components clearly support various species depicted in Scheme 3. Finally, the mass spectrometry data for $[(N,N-J)Cu(O_2SO_2)\cdot H_2O]^+(m/z = 370.0; calcd.$ for $C_8H_{10}N_4SCu \cdot SO_4 \cdot H_2O$, m/z = 371), and [(N, N-J)Cu- $(\mu-Cl)_2Cu(O_2SO_2)]^+$ (m|z)= 486; calcd. for $C_8H_{10}N_4SCu_2Cl_2$ ·SO₄, m/z = 486) support the formation of sulfate, which is in a complexed state.

Reactions with No C-S Bond Cleavage

Equimolar solutions of copper(I) iodide and I in CH_3CN were mixed, and the solution was left undisturbed as done in the above reactions. Colorless crystals of a dinuclear complex, $[Cu_2(\kappa^1-SNC_3H_5S_2)_4(\mu-I)_2]$ (4), were obtained, and there was no C–S bond cleavage unlike that in the above reactions. Introduction of methyl group at the nitro-



Scheme 4. Rings at S are omitted.



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gen atom yielded IV (N₂C₄H₈S), and it was treated with copper(I) iodide in the same way as in the above reactions, but it did not involve C–S bond cleavage. It formed a polymeric product, $[Cu_4(\mu_3-I)_2(\mu-I)_2(\mu-SN_2C_4H_8S)_2(\kappa^1-SN_2C_4H_8S)]_n$ (8, Scheme 4). In this polymer, Cu^I and two molecules of IV appear to have formed a hetero-bridged core, Cu(μ -S)(μ -I)Cu, with one terminal iodide bonded to one Cu and the thio ligand bonded to the second Cu (species **K**). This acts as a building block, and two **K** units combine through the bridging iodide to form a tetranuclear core (species **L**). Two such **L** cores combined to form an octanuclear unit, and the process continues to form the polymer.

Magnetism, Spectroscopy, and Fluorescence

Magnetic susceptibility studies revealed that complexes 5–7 are paramagnetic with $\mu_{\rm eff}$ values of 1.966 (per Cu), 1.971, and 1.974 BM, respectively, and all of the other complexes are diamagnetic. The IR spectra of these complexes show the presence of characteristic bands for the v(C-H), $v(C-N) + \delta(C-H)$, v(C-S), and $\delta(N-CH_3)$ moieties. The v(N-H) bands were observed in the spectra of complexes 4 $[v(N-H) = 3206 \text{ cm}^{-1}; \text{ free ligand, } 3138 \text{ cm}^{-1}] \text{ and } 8 [v(N-H)]$ H) = 3196 cm^{-1} ; free ligand, 3272 cm^{-1}], which supports the fact that the thio ligands in these complexes remained unchanged; this is in contrast to the C-S bond cleavage that occurred in the other reactions. The bands resulting from the BF₄⁻ anions in complexes **3** [1030 (s, v_3), 710 (s, v_1), 510 $(m, v_4) \text{ cm}^{-1}$ and 6 [1022 (s, v₃), 717 (s, v₁), 502 (m, v₄) cm^{-1}] as well as those that are due to NO₃⁻ in 7 [1407 (m, v_3), 800 (m, v_2), 708 (m, v_4) cm⁻¹] support their ionic nature.^[24] The ¹H NMR spectrum of complex 4 shows one broad resonance resulting from the NH proton at δ = 10.0 ppm and two sets of signals that are due to C⁴H at δ = 3.54 ppm and C⁵H at δ = 4.02 ppm. The ¹H NMR spectra of Cu^{I} complexes 1–3 in [D₆]DMSO did not show any signals, and this indicates that these complexes are not stable in DMSO and oxidation to Cu^{II} occurred. Complex 8 was not soluble in DMSO.

The UV/Vis spectra of Cu^{II} complexes 5-7 in DMSO showed intense absorption with λ_{max} values in the range from 260 to 286 nm (10⁻⁴ M solution). To observe d-d transitions in the visible region, a 10^{-3} M solution was used. A very intense absorption occurred in the region of 260 nm for this concentrated solution; however, a weak band at $\lambda_{\text{max}} = 739 \text{ nm}$ attributed to the d-d transition pertaining to $\mathrm{Cu}^{\mathrm{II}}$ was also observed.^[31] The UV/Vis spectra of Cu^{I} complexes 1-3 in DMSO showed two absorption bands at 285 and 312 nm. The band at 312 nm can be attributed to a charge transfer (S \rightarrow Cu) transition and that at 285 nm is due to the $\pi \rightarrow \pi^*$ transition. Complex 3 showed more intense bands owing to the presence of two N,S-chelating thio ligands versus one in complex $2^{[25]}$ (Figure 1). Complexes **2** and **3** are weakly fluorescent at $\lambda_{em} = 344$ and 352 nm, respectively, which corresponds to an excitation wavelength of 285 nm (Figure 2); other complexes did not show emission.



Figure 1. UV/Vis spectra of complexes 2, 3, 6, and 7.



Figure 2. Fluorescence spectra of complexes 2 and 3.

Molecular Structures

The formation of 1-3 and 5-7 involved C-S bond cleavage and is discussed in this sequence. The in situ generated 3-(2-thiazolin-2-yl)thiazolidine-2-thione ligand chelates to Cu^I of complex 1 through its N,S-donor atoms [Cu-S 2.187(1) Å, Cu–N 1.989(1) Å] with a N–Cu–S bite angle of 98.52(6)°. The third position is occupied by a chloride ion [Cu-Cl 2.150(1)°], which gives rise to a three-coordinate complex. The N-Cu-Cl and S-Cu-Cl angles (125.14 and 136.30°, respectively) and the N-Cu-S bite angle suggest a distorted trigonal planar geometry (Figure 3). The bond lengths are comparable to literature trends.^[1] The bonding and geometry of bromide complex 2 are similar to those of 1, except that there are two independent molecules in the same unit cell with slightly different bonding parameters (Figure 4). The S···S contact between two independent units (4.181 Å) is longer than twice the sum of the van der Waals radii of the sulfur atoms (3.60 Å).^[32] In complex 3, two molecules of the 3-(2-thiazolin-2-yl)thiazolidine-2-thione ligand chelate to Cu^I and the BF₄⁻ anion lies outside the coordination sphere. There is a decrease in the N-Cu-S bite angle $[93.8(1)^\circ]$ in 3 relative to that in 1 or 2, and this is clearly the result of the increase in the coordination number of the complex. The Cu-N and Cu-S distances are some-



what longer than those of the three-coordinate complexes discussed above (Table S2, Supporting Information). Two N,S-chelating thio ligands lie in mutually perpendicular planes in a twisted fashion (Figure 5).



Figure 3. Molecular structure of $[CuCl(\kappa^2-N,S-C_3H_4S_2N-C_3H_4SN)]$ (1).



Figure 4. Molecular structure of $[CuBr(\kappa^2-N,S-C_3H_4S_2N-C_3H_4SN)]$ (2).



Figure 5. Molecular structure of $[Cu(\kappa^2-N,S-C_3H_4S_2N-C_3H_4SN)_2]-(BF_4)$ (3).

The 1,1'-dimethyl-2,2'-diimidazolyl sulfide $[(N_2C_4H_5)_2S]$ ligand is a thioether that is chelated to Cu^{II} in complexes 5–7. Complex 5 is a chloride-bridged dimer in which the Cu(μ -Cl)₂Cu core is a parallelogram with unequal Cu–Cl bond lengths [2.2931(1), 2.7159(1) Å; Figure 6]. The Cu···Cu separation of 3.665(3) Å is longer than the sum of the van der Waals radii of the Cu atoms (2.80 Å).^[26] As regards complexes 6 and 7 (Figure 7), both have identical octahedral cations, and in these complex cations, copper(II) is bonded to N,N-chelating 1,1'-dimethyl-2,2'-diimidazolyl sulfide ligands in the basal plane with a pair of water molecules occupying the axial positions. Considering the O–Cu– O bond angle of 180° as the *z* axis, other angles in the square plane formed by the CuN₄ core are nearly 90° and the *trans* N–Cu–N bond angles are again 180°.

Complexes **4** and **8** did not involve C–S bond cleavage. Dinuclear complex **4** is an iodide-bridged complex with four terminally bonded thiazolidine-2-thione (NC₃H₅S₂, **I**) ligands. The central Cu(μ -I)₂Cu core is a parallelogram with unequal Cu–I bond lengths [2.713(5), 2.757(5) Å], which are longer than those observed in iodo-bridged complexes reported in the literature.^[20,21] The bond angles around each Cu atom vary in the range from 98.59(2) to 123.29(4)°, which results in severe distortion from a tetrahedral geometry (Table S2, Supporting Information). In com-



Figure 6. Molecular structure of complex { $Cu^{II}_{2}[\kappa^{2}-N,N-(N_{2}C_{4}H_{5})_{2}S]_{2}(\mu-Cl)_{2}Cl_{2}$ } (5).





Figure 7. Structure of $\{Cu[\kappa^2-N,N-(N_2C_4H_5)_2S]_2(\kappa^1-OH_2)_2\}(BF_4)_2 + 2H_2O$ (6).

plex 8 (Figure 8), two Cu-I and two 1-methylimidazolidine-2-thione (IV) moieties appear to have formed a heterobridged $Cu(\mu-S)(\mu-I)Cu$ core in which one terminal iodide is bonded to one Cu atom and the thio ligand is bonded to the second Cu atom. This acts as a building block, and two such units combine through the bridging iodide to form a tetranuclear core. Two such tetranuclear cores combine to form an octanuclear unit, and the process continues to form an infinite polymeric zigzag chain. An interesting feature of this chain is the existence of alternate $Cu(\mu-S)(\mu-I)Cu$ and $Cu(\mu-I)_2Cu$ cores. Further, variation in the Cu cores follows the trend \cdots AABBAABB \cdots (A = CuS₂I₂, B = CuSI₃). The Cu···Cu distance in the Cu(μ -I)₂Cu core is 2.787(2) Å, which is less than the sum of the van der Waals radii of the Cu atoms (2.80 Å).^[26] Notably, the imidazolidine-2-thione forms six- or eight-membered repeating units, $Cu_3(\mu-S)_3$ or $Cu_4(\mu$ -S)₄, to construct polynuclear compounds, namely, $[Cu_6(\mu_3-SN_2C_3H_6)_2(\mu-SN_2C_3H_6)_4X_2(\mu-X)_4]_n (X = Cl, Br, I),$ $[Cu_6(\mu_3-SN_2C_3H_6)_4(\mu-SN_2C_3H_6)_2(\mu-I)_2I_4]_n$, and $[Cu_8(\mu_3-I)_2I_4]_n$ $SN_2C_3H_6)_4(\mu-SN_2C_3H_6)_4(\kappa^1-Cl)_8]_n^{[21,22]}$



 $\label{eq:Figure 8} \begin{array}{lll} Figure 8. & Structure & of & [Cu_4(\mu_3\text{-}I)_2(\mu\text{-}S\text{-}N_2C_4H_8S)_2(\kappa^1\text{-}S\text{-}N_2C_4H_8S)_2]_n \\ N_2C_4H_8S)_{2]_n} (\textbf{8}). \end{array}$

Effect of Anions on C–S Bond Cleavage and Preferential Binding to Cu^{I} or Cu^{II}

During these investigations, it was found that anions such as Cl^- , Br^- , BF_4^- , and NO_3^- support cleavage of C-S

bonds. The Cu^{II} ions in salts such as copper(II) nitrate initially undergo reduction to Cu^I upon the addition of a thio ligand. Thus, in all cases we preferred to use Cu^I salts, as the reactions appeared to proceed through Cu^I. The Cu^I ions in solution in the presence of a thio ligand slowly react under aerobic conditions through oxidation–reduction reactions, which yields a variety of products as described above. The higher polarity of the Cu–X bond (X = Cl⁻, Br⁻, BF₄⁻, NO₃⁻) results in easy bond cleavage and the formation of Cu^{II} ions, which are believed to oxidize the thio ligand through a variety of probable steps, as proposed in the mechanism cited in the above discussion. The more bulky iodide is reducing nature, which tends to stabilize the Cu^I state, and the redox reactions are slow or do not occur.



The new 3-(2-thiazolin-2-yl)thiazolidine-2-thione (VI) thio ligand has one N atom and one thione sulfur atom as donor atoms, and they prefer to bind to Cu^I. It is well known that thiones prefer to bind to Cu^I, and if thiones are treated with Cu^{II}, they reduce it to Cu^I. Thus, ligand VI binds to Cu^I ions. The ethereal sulfur does not show binding to either of the ions. In contrast, ligand VII has two ring nitrogen atoms that prefer to bind to Cu^{II}. This can also be understood in terms of hard–soft acid–base theory: soft–soft and hard–hard preferences.

Conclusions

Reactions of copper(I) halides and other copper salts with five-membered heterocyclic thiones under aerobic conditions were studied. Interesting chemical reactivity was observed, and some important points are summarized here. The use of a lower metal-to-ligand ratio prevented C-S bond cleavage and the Cu^I oxidation state seemed to be stabilized; thus, a 1:1 molar ratio was optimum to perform reactions at room temperature. Cleavage of the C-S bond occurred in the presence of Cl⁻, Br⁻, BF₄⁻, and NO₃⁻ anions. More polar solvents assisted Cu-X bond cleavage, which involves Cu-X--solvent interactions, and allowed the ready formation of Cu⁺ ions. Similarly, DMSO and DMF coordinated to the metal center in Cu-X, but the electronegative O donor atom of DMSO did not stabilize the Cu^I state. The more readily that CuI could be formed, the greater was the tendency to induce C-S bond cleavage. The use of copper(II) salts also involved initial reduction to Cu^I with similar products; thus, reactions were performed with copper(I) halides. The bulky iodide stabilized Cu^I, which prevented cleavage under the experimental conditions. Upon the addition of a metal salt to a stirred solution of the thione ligand, there was a general tendency to form a



precipitate, which prevented crystal formation. However, if a mixture of the metal salt and the thione ligand was left undisturbed, crystalline products were obtained.

Experimental Section

Materials: Copper(I) halides were prepared by the reduction of $CuSO_4 \cdot 5H_2O$ by using SO_2 in the presence of stoichiometric amounts of NaCl, NaBr, and NaI in water.^[27] [Cu(NCCH₃)₄](BF₄) was prepared by the slow addition of HBF₄ to a suspension of copper(I) oxide in acetonitrile until the solution was colorless. [Cu(NCCH₃)₄](BF₄) was extracted by using diethyl ether. Copper(II) nitrate, thiazolidine-2-thione (I), 1-methylimidazoline-2-thione (IV) were procured from Aldrich Sigma, Ltd., and used as such.

Methods: Elemental analyses for C, H, and N analysis were obtained with a Thermoelectron Flash EA1112 CHNS analyzer. UV/ Vis spectra were recorded by using a UV-1601PC Shimadzu spectrophotometer. Fluorescence spectra were recorded by using a RF-1501 Shimadzu spectrophotometer (10^{-4} M concentration at 20 °C). IR spectra were recorded by using KBr pellets in the 4000–400 cm⁻¹ range with a Varian 660-IR FTIR spectrophotometer. Melting points were determined with a Gallenkamp electrically heated apparatus. Magnetic moments were determined by using a magnetic susceptibility balance (Johnson Matthey, Catalytic Systems Division Equipment).

Synthesis of [CuCl(κ^2 -*N*,*S*-C₃H₄S₂N-C₃H₄SN)] (1): To a solution of copper(I) chloride (0.025 g, 0.25 mmol) in acetonitrile was added a solution of I (0.030 g, 0.25 mmol) in acetonitrile. The reaction mixture was left undisturbed. The color of the solution started to change to greenish brown after about 3–4 d, and after about 1 week, red-brown prismatic crystals of 1 along with light bluish crystals of CuSO₄·5H₂O were formed and then manually separated. Data for 1: yield 0.019 g, 63%, m.p. 172–175 °C. C₆H₈ClCuN₂S₃ (303.31): calcd. C 23.74, H 2.64, N 9.23, S 31.65; found C 23.53, H 2.55, N 9.57, S 30.21. IR: $\tilde{\nu} = 2922-2855$ (m, C–H); 1587 (s), 1480 (sh.) (C–N + δ C–H); 942 (s, C=S) cm⁻¹. Data for CuSO₄·5H₂O: yield 0.010 g, 16% (see the Supporting Information for analytical data).

Synthesis of [CuBr(κ^2 -*N*,*S*-C₃H₄S₂N-C₃H₄SN)] (2): To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in acetonitrile was added a solution of I (0.021 g, 0.25 mmol) in acetonitrile. The reaction mixture was left undisturbed. After 2–3 d, the color of the solution changed to yellow. Slow evaporation of the solution at room temperature led to red-violet plates of **2** along with light blue crystals of CuSO₄·5H₂O (0.008 g, 18%), which were manually separated. Data for **2**: yield 0.031 g, 68%, m.p. 187–190 °C. C₆H₈BrCuN₂S₃ (347.80): calcd. C 20.70, H 2.30, N 8.06, S 25.5; found C 20.55, H 2.40, N 8.19, S 25.3. UV/Vis (10⁻⁴ M in DMSO): λ_{max} (ϵ , L mol⁻¹ cm⁻¹) = 285 (1.153 × 10⁴), 312 nm (8160). Fluorescence (10⁻⁴ M in DMSO): λ_{ex} = 285 nm, λ_{em} = 344 nm. IR: \tilde{v} = 2995–2817 (m, C–H); 1584 (s), 1450 (sh.) (C–N + δ C–H); 940 (s, C=S) cm⁻¹.

Synthesis of $[Cu(\kappa^2-N,S-C_3H_4S_2N-C_3H_4SN)_2](BF_4)$ (3): To a solution of $[Cu(CH_3CN)_4](BF_4)$ (0.050 g, 0.16 mmol) in acetonitrile was added a solution of I (0.038 g, 0.32 mmol) in acetonitrile. The color of the solution changed to greenish brown in 3–4 d. After 1 week, dark purple needles of 3 were formed along with blue crystals of $CuSO_4$ ·5H₂O (0.006 g, 14%). Data for 3: yield 0.048 g, 52%, m.p. 210–213 °C. $C_{12}H_{16}BCuF_4N_4S_6$ (559.00): C 25.76, H 2.86, N 10.01, S 34.34; found C 25.84, H 3.00, N 10.16, S 33.20. UV/Vis

(10⁻⁴ M in DMSO): λ_{max} (ϵ , Lmol⁻¹cm⁻¹) = 286 (2.592 × 10⁴), 310 nm (1.946 × 10⁴). Fluorescence (10⁻⁴ M in DMSO): λ_{ex} = 285 nm, λ_{em} = 352 nm. IR: \tilde{v} = 3077–2920 (w, C–H); 1532 (s), 1497 (sh.) (C–N + δ C–H); 1030 (s), 710 (s), 510 (m) (BF₄); 930 (m, C=S) cm⁻¹.

Synthesis of [Cu₂(κ¹-S-NC₃H₅S₂)₄(μ-I)₂] (4): To a solution of copper(I) iodide (0.025 g, 0.13 mmol) in acetonitrile was added a solution of **I** (0.015 g, 0.13 mmol) in acetonitrile. The reaction mixture was left undisturbed. After 1 week, slow evaporation of the solution at room temperature resulted in colorless crystals of **4**, yield 0.072 g, 64%, m.p. 120–125 °C. C₁₂H₂₀Cu₂I₂N₄S₈ (857.68) calcd. C 16.79, H 2.33, N 6.53, S 29.84; found C 16.94, H 2.41, N 6.62, S 28.90. UV/Vis (CHCl₃, partially soluble): $\lambda_{max} = 280$, 330 nm. IR: $\tilde{\nu} = 3206$ (br., N–H); 3018–2943 (w, C–H); 1522 (s), 1456 (m) (C–N + δ C–H); 994 (s, C=S) cm⁻¹. ¹H NMR (CDCl₃): $\delta = 10.0$ (br., 1 H, NH), 3.54 (t, 2 H, C⁴H), 4.02 (t, 2 H, C⁵H) ppm.

Synthesis of {Cu^{II}₂[κ^2 -*N*,*N*-(N₂C₄H₅)₂S]₂(μ -Cl)₂Cl₂} (5): To a solution of copper(I) chloride (0.025 g, 0.25 mmol) in acetonitrile was added a solution of **II** (0.029 g, 0.25 mmol) in acetonitrile, and the solution was left undisturbed. The color of the solution changed to greenish brown in 4–5 d. After about 2 weeks, green prismatic crystals of **5** as well as light blue crystals of CuSO₄·5H₂O (0.008 g, 13%) were formed. The products were separated manually. Data for **5**: yield 0.044 g, 58%, m.p. 233–237 °C. C₁₆H₂₀N₈S₂Cu₂Cl₄ (657.44) calcd. C 29.20, H 3.04, N 17.04, S 9.73; found C 29.00, H 3.26, N 16.90, S 9.55. UV/Vis (10⁻⁴ m in DMSO): λ_{max} (ϵ , Lmol⁻¹cm⁻¹) = 261 nm (2.889 × 10³). UV/Vis (10⁻³ m in DMSO): λ_{max} (ϵ , Lmol⁻¹cm⁻¹) = 261 (very intense), 739 nm (117). IR: \tilde{v} = 3026–2948 (w, C–H); 1525 (s), 1481 (s) (C–N + δ C–H); 870 (s, C=S); 763 (s, δ N–CH₃) cm⁻¹. Magnetic moment: 1.97 BM per copper.

Synthesis of {Cu[κ²-*N***,***N***-(N₂C₄H₅)₂S]₂(κ¹-OH₂)₂}(BF₄)₂·2H₂O (6): To a solution of [Cu(NCCH₃)₄](BF₄) (0.050 g, 0.16 mmol) in acetonitrile was added a solution of II** (0.036 g, 0.32 mmol) in acetontrile. The reaction mixture was left undisturbed. The color of the solution changed to brownish green in 3–4 d and dark blue prismatic crystals of **6** were formed in about 1 week along with light blue crystals of **CuSO**₄·5H₂O (0.006 g, 14%). Data for **6**: yield 0.049 g, 49%, m.p. 220–223 °C. C₁₆H₂₈B₂CuF₈N₈O₄S₂ (697.74) calcd. C 27.51, H 4.01, N 16.05, S 9.17; found C 27.64, H 4.10, N 16.10, S 8.30. UV/Vis (10⁻⁴ m in DMSO): λ_{max} (*ε*, Lmol⁻¹cm⁻¹) = 286 nm (1.152 × 10⁴). IR: \tilde{v} = 3444 (br., OH); 3101–2947 (m, C– H); 1547 (s), 1458 (sh.) (C–N + δ C–H); 1022 (s), 717 (s), 502 (m) (BF₄); 883 (m, C–S); 782 (s, δ N–CH₃) cm⁻¹. Magnetic moment: 1.971 BM.

Synthesis of $\{Cu[\kappa^2-N, N-(N_2C_4H_5)_2S]_2(\kappa^1-OH_2)_2\}(NO_3)_2$ (7): To a solution of copper(II) nitrate (0.025 g, 0.10 mmol) in methanol was added a solution of II (0.024 g, 0.20 mmol) in acetonitrile. The blue color of the copper(II) nitrate solution changed to colorless upon the addition of the thio ligand, as a result of the reduction of CuII into CuI by the thio ligand. The reaction mixture was left undisturbed. The color of the solution again changed to greenish blue in about 5-6 d. Blue prismatic crystals of 7 were obtained after 2 weeks along with blue crystalline $CuSO_4 \cdot 5H_2O$ (0.006 g, 18%). Data for 7: yield 0.032 g, 52%, m.p. 173-175 °C. C₁₆H₂₄CuN₁₀O₈S₂ (612.11): calcd. C 31.37, H 3.92, N 22.87, S 10.45; found C 31.50, H 4.03, N 23.00, S 9.83. UV/Vis (10⁻⁴ M in DMSO): λ_{max} (ε , $L mol^{-1} cm^{-1}$) = 264 nm (1.477 × 10⁴). IR: \tilde{v} = 3432 (br., OH); 3107–2935 (m, C–H); 1570 (s), 1483 (sh.) (C–N + δ C–H); 1407 (m), 800 (m), 708 (w) (NO₃); 887 (m, C–S); 770 (s, δ N–CH₃) cm⁻¹. Magnetic moment (BM): 1.974.

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Synthesis of [Cu₄(μ₃-I)₂(μ-I)₂(μ-S-N₂C₄H₈S)₂(κ¹-S-N₂C₄H₈S)₂]_n (8): To a solution of copper(I) iodide (0.025 g, 0.13 mmol) in acetonitrile was added a solution of IV (0.015 g, 0.13 mmol) in acetonitrile. After 2–3 d, colorless prismatic crystals of **8** were obtained, yield 0.005 g, 32%, m.p. 157–160 °C. C₄H₈CuIN₂S (306.62): calcd. C 15.65, H 2.61, N 9.13, S 10.44; found C 15.76, H 2.70, N 9.17, S 9.84. IR: $\tilde{v} = 3272$ (m, N–H); 2930–2878 (w, C–H); 1536 (s), 1503 (m) (C–N + δ C–H); 1190 (m, C=S); 958 (m, δ N–CH₃) cm⁻¹.

Crystal Structure Determinations: Single crystals of 1–8 were mounted on glass fibers and data were collected by using Xcalibur R (for 1, 3, 6, 7), Bruker X8 Kappa APEXII (for 4), Siemens P4 (for 5), and Bruker SMART APEXII CCD area detector (for 2, 8) diffractometers, each equipped with a graphite monochromator and Mo- K_{α} radiation ($\lambda = 0.71073$ Å). The unit cell dimensions and intensity data were measured at 296 (for 2, 5), 123(2) (for 1, 7), 110(2) (for 3, 6), and 100(2) (for 4, 8). The data were processed

(data collection, refinement, and reduction) with XSCANS^[28] and SHELXTL-PC (for 7), CrysAlisPro (for 1, 3, 5, 6, 7), SMART and SAINT (for 2), and APEX2 (for 4, 8)^[29,30] and corrected for absorption by using SADABS.^[31] The structures of 1–8 were solved by direct methods by using SIR-92 (for 5) and SHELXS-97 (for 1– 4, 6–8)^[32] and refined by full-matrix least-squares techniques based on F^2 by using SHELXL-97^[32] All non-hydrogen atoms were refined anisotropically. The crystallographic data are given in Tables 1 and 2. For complex 2, if higher symmetry ($P\overline{1}$) was introduced, refinement was not performed finely. So we employed lower symmetry (P1) without centrosymmetry in an exact sense. However, the chemical formula was defined, as elemental analysis was calculated regardless of discrepancy between actually bridged structures and crystallographically asymmetric unit.

CCDC-852658 (for 1), -852659 (for 2), -852660 (for 3), -880493 (for 4), -769469 (for 5), -852657 (for 6), -852661 (for 7), and -880492

Table 1. Crystallographic data for complexes 1-4.

	1	2	3	4
Empirical formula	C ₆ H ₈ ClCuN ₂ S ₃	C ₆ H ₈ BrCuN ₂ S ₃	C ₁₂ H ₁₆ BCuF ₄ N ₄ S ₆	$C_{12}H_{20}Cu_2I_2N_4S_8$
Formula weight	303.31	347.80	559.00	857.68
<i>T</i> [K]	123(2)	296	110(2)	100(2)
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	$P\overline{1}$	<i>P</i> 1	$C2_1$	$P\overline{1}$
a [Å]	7.3104(4)	7.4773(7)	18.67(4)	7.5969(2)
b [Å]	8.5765(6)	8.5574(8)	4.93(1)	9.2259(3)
c Å	9.4759(8)	9.5302(9)	12.35(3)	9.6091(3)
a [°]	67.830(7)	70.051(1)	90	96.511(2)
β ^[°]	68.854(6)	67.410(1)	120.17(3)	109.542(1)
γ [°]	82.517(5)	84.450(1)	90	90.080(2)
	513.14(6)	528.82(9)	983.3(4)	630.04(3)
Z	2	2	2	1
$D_{\rm calcd}$ [g cm ⁻³]	1.963	2.184	1.888	2.261
$\mu [\mathrm{mm}^{-1}]$	2.949	6.388	1.792	4.810
All reflections collected	7565	3034	3469	14476
Unique reflections, R_{int}	7569, 0.000	2611, 0.0100	2652, 0.0319	2486, 0.0368
Observed reflections	3763	2284	2094	2244
Final R indices		2		
R_1	0.0426	0.024	0.0652	0.0271
wR_2 (all)	0.1135	0.0809	0.1833	0.0598

Table 2.	Crystallographic	data for	complexes	5-8
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	5	6	7	8
Empirical formula	$C_{16}H_{20}Cl_4Cu_2N_8S_2$	$C_{16}H_{28}B_2CuF_8N_8O_4S_2$	C ₁₆ H ₂₄ CuN ₁₀ O ₈ S ₂	C ₄ H ₈ CuIN ₂ S
Formula weight	657.44	697.74	612.11	306.62
<i>T</i> [K]	296(2)	110(2)	123(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_{1/n}$	$P2_1/n$	$P2_1/n$	$P\overline{1}$
<i>a</i> [Å]	9.053(1)	7.6059(2)	8.6442(3)	9.386(2)
b [Å]	8.402(1)	13.7908(4)	13.6041(4)	9.584(2)
c [Å]	15.754(3)	13.1488(4)	10.3827(3)	10.00(2)
	90	90	90	111.38(3)
β[°]	94.28(1)	96.807(3)	100.382(3)	96.05(3)
γ [°]	90	90	90	105.42(3)
V[Å ³]	1195.0(3)	1369.47(7)	1200.98(7)	786.7(3)
Z	2	2	2	4
$D_{\rm calcd.}$ [g cm ⁻³]	1.827	1.692	1.693	2.589
$\mu [\mathrm{mm}^{-1}]$	2.425	1.045	1.149	36.533
All reflections collected	2365	9021	9180	14651
Unique reflections, R_{int}	2219, 0.0193	4506, 0.0258	3975, 0.0249	2817, 0.0296
Observed reflections	1859	3421	2929	2791
Final R indices				
R_1	0.0344	0.0377	0.0296	0.0350
wR_2 (all)	0.0929	0.1017	0.0703	0.1207



(for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Copper(II) sulfate data; ligand data; molecular structure of **7**; molecular structure of **4**; packing network of the complexes; tables of hydrogen bonds, bond lengths, and bond angles.

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