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Stable Cu(I) Complexes with Thioamidoguanidine Possessing Halide-Bridge Structure

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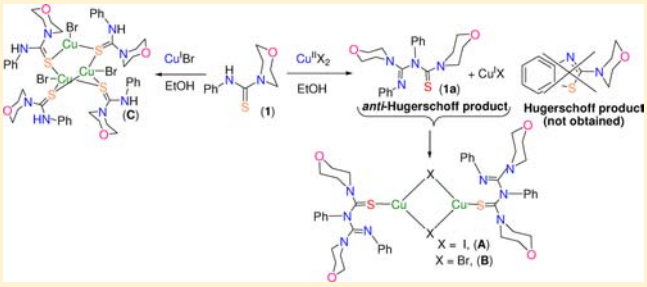
Supporting Information

ABSTRACT: Treatment of an aryl-*sec*-alkyl unsymmetrical thiourea (Tu) with $Cu^{II}X_2$ (X = I, Br) transform the thiourea (Tu) into a thioamidoguanidino (Tag) moiety with concomitant reduction of Cu^{II} to Cu^{I}, which forms a $[Cu_2^{I}(\mu_2\text{-}X)_2Tag_2]$ (X = I (for **A**) and X = Br (for **B**)) complex. Meanwhile, the treatment of same unsymmetrical thiourea (Tu) with $Cu^{I}X$ (X = Br) forms a stable cluster with a $[Cu^{I}_3(\mu_2\text{-}S)_4Tu_4X_3]$ core (**C**). Single crystal X-ray diffraction revealed that compounds **A** and **B** exhibit 1D chain with a $Cu_2(\mu_2\text{-}X)_2$ core, whereas compound **C** is a $Cu^{I}_3S_4Br_3$ cluster. Compound **A** is centrosymmetric due to the trans orientation of two Tag units whereas compound **B** is ascentric due to the cis orientation of two Tag units. In compound **A**, the Cu_2I_2 core is perfectly rhomboidal where the iodine atoms are trans oriented. However in compound **B**, the Cu_2Br_2 core is not perfectly rhomboidal (bowl shaped) and the bromine atoms are cis oriented. It is interesting to note that although the Tag moiety in compounds **A** and **B** contain two morpholine-O atoms; only one of the morpholine-O atoms (O2) is involved in the generation of three-dimensional network. The $Cu^{I}_3S_4Br_3$ cluster in compound **C** contains one tri- and two tetra-coordinated Cu^{I} centers. The Cu^{I} cluster in **C** contains a $Cu_2(\mu_2\text{-}S)_2$ rhomboidal plane exhibiting a chair and a boat form containing the $Cu^{I}_3S_3$ unit. In compounds **A** and **B**, the two Cu^{I} centers are μ_2-X bridged and have a μ_1-S linkage, whereas in compound **C** the linkages are opposite having four μ_2-S bridges and three μ_1-Br linkages.



INTRODUCTION

The classical Hugerschoff reaction known since 1901 involves the reaction of molecular bromine (Br_2) with 1,3-diarylthiourea in chloroform to produce 2-amino benzothiazole.[1] However, the products obtained by the reaction of aryl-*sec*-alkyl unsymmetrical thioureas **1** with bromine or its equivalents are different ones. While Jordan et al. and Le et al.[2] have reported the formation of 2-amino benzothiazole (Hugerschoff) as the exclusive product for certain substrates, we have reported the formation of thioamidoguanidine (Tag) (*anti*-Hugerschoff product) **1a** as the exclusive or major product.[3a] The use of molecular iodine instead of bromine also gave an identical result, thus further supporting our proposition.[3b] The formation of thioamidoguanidine (Tag) **1a** essentially involved an oxidative dimerization (S−S bond formation) of an unsymmetrical thiourea followed by an intramolecular imine-disulfide rearrangement.[3a] During the formation of the Hugerschoff product the thiophilic bromine activates the sulfur of a thiourea toward an intramolecular aromatic electrophilic substitution reaction while it acts as a mere oxidizing (S−S bond forming) agent during the formation of a thioamidoguanidine (Tag) moiety. Taking clues from the above observations we thought of using another mild thiophilic environmentally benign redox-active metal which would only promote oxidative dimerization of thiourea leading to the exclusive formation of the thioamidoguanidine (Tag)/anti-Hugerschoff product **1a**. If this strategy works, a competitive formation of Hugerschoff product could be avoided as was the case using bromine[3a] and iodine[3b] and only anti-Hugerschoff product could be achieved. Ideally salts of Cu^{II} suit the above envisaged strategy. Treatment of thiourea (Tu) with Cu^{II} salt gave our anticipated thioamidoguanidine (Tag) product along with the formation of an unprecedented Cu^{I} complex with Tag **1a**. The reduction of Cu^{II} to Cu^{I} is at the expense of thiourea getting oxidized to corresponding disulfide. Herein, we report the synthesis of a $[Cu_2^{I}(\mu\text{-}X)_2Tag_2]$ (**A** and **B**) complex and an air stable cluster $[Cu^{I}_3(\mu_2\text{-}S)_4Tu_4X_3]$ (**C**) from thiourea (Tu) using $Cu^{II}X_2$ and $Cu^{I}Br$ salts, respectively.

EXPERIMENTAL PROCEDURES

General Procedures. All reagents and solvents were purchased from commercial sources which were of reagent grade. Phenyl isothiocyanate was synthesized following the literature procedure.[4] UV−visible spectra were recorded on a Perkin-Elmer lambda 25 UV−visible spectrophotometer. FT-IR spectra were taken on a Perkin-Elmer spectrophotometer with sample prepared as KBr pellets. ^{1}H, ^{13}C NMR spectra were recorded with a 400 MHz Varian FT-spectrometer. Chemical shifts (ppm) were referenced either with an internal standard (Me_4Si) for organic compounds and complexes or to the residual solvent peaks in $CDCl_3$. The X-band electron para-

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Table 1. Crystallographic Data and Refinement Parameters for Compounds A, B, and C

	A	B	C
formula	$C_{22}H_{26}CuIN_4O_2S$	$C_{22}H_{26}BrCuN_4O_2S$	$C_{44}H_{56}Br_3Cu_3N_8O_4S_4$
CCDC number	8757778	876074	877794
formula weight	600.99	553.99	1319.60
T (K)	296(2)	296(2)	296(2)
wavelength (Å)	0.71073	0.71073	0.71073
crystal system	monoclinic	orthorhombic	triclinic
space group	$C2/c$	$Pccn$	$\bar{P}1$
a (Å)	22.3537(12)	15.4710(8)	12.8009(5)
b (Å)	15.7364(10)	20.2116(10)	14.6565(6)
c (Å)	14.7465(10)	14.6730(8)	14.8317(6)
α (deg)	90.00	90.00	81.033(2)
β (deg)	114.048(3)	90.00	75.174(2)
γ (deg)	90.00	90.00	77.727(2)
V (Å^3)	4737.1(5)	4588.2(4)	2613.34(18)
Z	8	8	2
θ_{min}, θ_{max}	1.63, 28.42 2	1.66, 25.25	1.91, 28.36
D_{calcd} (g·m^{-3})	1.685	1.604	1.677
μ (mm^{-1})	2.340	2.811	3.711
F(0 0 0)	2400.0	2256.0	1328.0
reflection collected	5953	4164	13060
unique reflections	3286	3316	7046
goodness of fit (GOF) on F^2	1.095	1.071	1.020
R1, wR_2 ($I \geq 2\sigma(I)$)	0.0799, 0.2332	0.0453, 0.1315	0.0366, 0.0756
R1, wR_2 (all data)	0.1177, 0.2485	0.0557, 0.1354	0.0896, 0.0898

magnetic resonance (EPR) spectra of the complexes were recorded on a JES-FA200 ESR spectrometer. Elemental analyses were obtained from a Perkin-Elmer Series II Analyzer. Mass spectra of the compounds in CH_3CN were recorded in a Waters Q-Tof Premier and Aquity instrument.

General Procedures for X-ray Structure Determinations. The crystals were mounted on a glass fiber and the intensity data were collected using a Bruker SMART APEX II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo Kα radiation (λ = 0.71073 Å) at 298(2) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s per frame. The SMART software was used for data acquisition. Data integration and reduction were under taken with SAINT and XPREP[5] software. Multiscan empirical absorption corrections were applied to the data using the program SADABS.[6] Structures were solved by direct methods using SHELXS-97[7a] and were refined by full-matrix least-squares on F^2 using the SHELXL-97[7b] program package. In all the three, non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to all carbon atoms are geometrically fixed. Structural illustrations have been generated using ORTEP-3[8a] and MERCURY1.3[8b] for Windows. The molecular structures of compounds **A**, **B**, and **C** were determined, and the crystallographic and refinement parameters are listed in Table 1. The selected bond distances and angles found in compounds **A** and **B** are listed in Table 2, and those in compound **C** are listed in Table 3.

*Experimental Procedure for the Synthesis of Thiourea (**1**).* To a stirred solution of phenyl isothiocyanate (405 mg, 3 mmol) in ethanol (10 mL) was added dropwise morpholine (261 mg, 3 mmol). Formation of thiourea **1** was observed within 15 min as judged from TLC. The crude thiourea **1** was used as such for the next step. For structural confirmation, ethanol was evaporated under a reduced pressure and dried in a vacuum drier, a white solid compound was obtained in nearly quantitative yield. Mp 124−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.65 (t, 4H, J = 4.8 Hz), 3.73 (t, 4H, J = 4.4 Hz), 7.13 (m, 3H), 7.30 (t, 2H, J = 8.0 Hz), 7.66 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.4, 66.1, 123.7, 125.4, 129.0, 139.9, 183.2. IR (KBr): 3436, 3170, 3027, 2917, 2851, 1651, 1594, 1532, 1495, 1409, 1321, 1264, 1205, 1111, 1026, 935, 853 cm^{-1}. Anal. calcd for $C_{11}H_{14}N_2OS$: C, 59.43; H, 6.35; N, 12.60; S, 14.42. Found: C, 59.48; H, 6.42; N, 12.53; S, 14.48; MS (ESI): 223.2543 (MH^+).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) in Compounds A and B

	complex **A** (X = I)	complex **B** (X = Br)
Cu(1)−X(1)	2.592(1)	2.457(1)
Cu(1)−X(1A)	2.560(1)	2.407(1)
Cu(1)−O(2)	2.635(1)	2.724(4)
Cu(1)−S(1)	2.259(2)	2.224(2)
Cu(1)−Cu(1A)	2.799(1)	2.945(1)
S(1)−Cu(1)−O(2)	79.2(1)	79.8(1)
S(1)−Cu(1)−X(1)	124.12(6)	128.45(5)
S(1)−Cu(1)−X(1A)	120.54(6)	126.69(5)
O(2)−Cu(1)−X(1)	93.6(1)	89.3(1)
O(2)−Cu(1)−X(1A)	109.2(1)	117.4(1)
X(1)−Cu(1)−X(1)	114.18(4)	103.14(4)

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) in Compound C

complex **C**			
Cu1−S1	2.3637(8)	Cu3−S2	2.4213(9)
Cu1−Br1	2.3603(7)	Cu3−Br3	2.4588(6)
Cu1−S3	2.392(1)	Cu3−S3	2.322(1)
Cu1−S4	2.487(1)	Cu3−S4	2.350(1)
Cu2−S1	2.245(1)	Cu1−Cu2	3.2197(7)
Cu2−Br2	2.3968(6)	Cu3−Cu1	2.7105(8)
Cu2−S2	2.261(1)	Cu3−Cu2	3.1196(6)
S1−Cu1−S3	97.96(3)	S2−Cu3−S3	104.61(3)
S1−Cu1−S4	102.52(3)	S2−Cu3−S4	103.15(3)
S1−Cu1−Br1	118.83(3)	S2−Cu3−Br3	113.40(3)
S3−Cu1−S4	106.61(3)	S3−Cu3−S4	113.72(4)
S3−Cu1−Br1	117.61(3)	S3−Cu3−Br3	111.18(3)
S4−Cu1−Br1	111.38(3)	S4−Cu3−Br4	110.47(3)

*Experimental Procedure for the Synthesis of Thioaminoguanidine (Tag) [anti-Hugerschoff Product] (**1a**).* To a solution of thiourea

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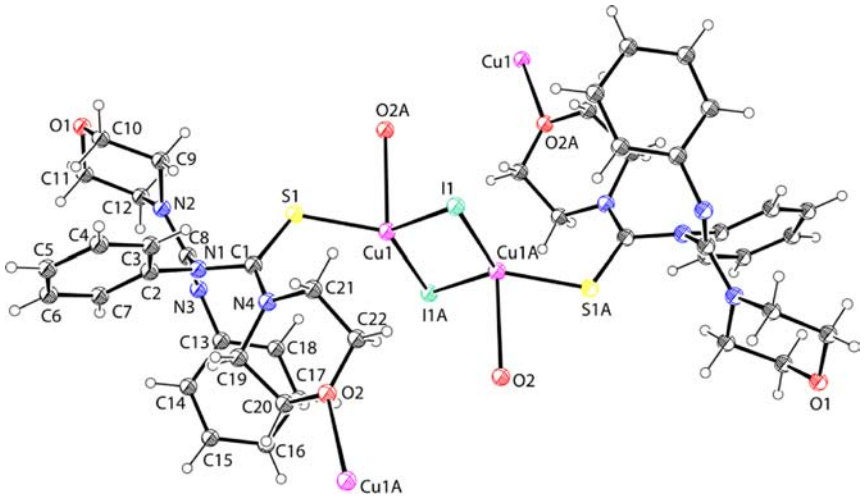

Figure 1. ORTEP view (30% probability ellipsoids) of compound **A**.

1 (3 mmol, 666 mg) dissolved in ethanol (30 mL) was added a solution of $CuBr_2$ (3 mmol, 672 mg) dissolved in ethanol (5 mL), and the resultant reaction mixture was stirred at room temperature for 20 min. During this period, a pale yellow solution along with yellow precipitate was obtained. After completion of the reaction, ethanol was evaporated completely and ethyl acetate (30 mL) was admixed to the reaction mixture. Aqueous ammonia (20%, 10 mL) was added to the above ethyl acetate suspended reaction mixture and the heterogeneous mixture was stirred at room temperature. During this time (10 min) the suspended insoluble yellow solid got dissolved into the ethyl acetate layer leaving the aqueous ammoniacal layer blue in color. The ethyl acetate layer was separated and dried over anhydrous Na_2SO_4 and concentrated under a reduced pressure. The product so isolated is sufficiently pure to be used for the next step. However, if desired it can be further purified by recrystallization using ethyl acetate and hexane (9:1) (550 mg, 88%). White solid. Mp 163−165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.90−3.52 (m, 16H), 6.95 (d, 2H, J = 8.0 Hz), 6.98 (d, 2H, J = 7.6 Hz), 7.09 (t, 2H, J = 7.6 Hz), 7.17 (t, 2H, J = 8.0 Hz), 7.30 (d, 2H, J = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.8, 50.6, 65.4, 66.2, 121.2, 122.1, 122.8, 122.9, 124.7, 128.8, 129.7, 142.8, 149.3, 185.2. IR (KBr): 2963, 2920, 2856, 1637, 1587, 1485, 1421, 1302, 1277, 1239, 1109, 1062, 994, 765, 753, 691 cm^{-1}. Anal. calcd for $C_{22}H_{26}N_4O_2S$: C, 64.36; H, 6.38; N, 13.65; S, 7.81. Found: C, 64.43; H, 6.41; N, 13.60; S, 7.89. MS (ESI): 411.2011 (MH^+).

General Procedure for Preparation of Complexes. *Method 1: [$Cu_2^I(\mu$-I)$_2$Tag$_2$] (**A**).* To a solution of thiourea **1** (1 mmol, 222 mg) dissolved in ethanol (15 mL) was added an ethanolic solution of CuI_2 (1 mmol, 317.5 mg), and the resultant reaction mixture was stirred for 20 min. During this period a yellow solution along with yellow precipitate was formed. The precipitate was dissolved by warming the reaction mixture. The resultant solution was filtered under hot condition and kept for crystallization. A pale yellow crystalline solid were obtained upon standing. Yield of first crops 204 mg (68%). Mp 212−213 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.45 (m, 16H), 6.97 (m, 4H), 7.11 (t, 2H, J = 7.2 Hz), 7.18 (t, 4H, J = 7.6 Hz). IR (KBr): 2964, 2920, 2853, 1640, 1587, 1486, 1422, 1356, 1299, 1276, 1239, 1108, 1063, 993, 850, 765, 753 cm^{-1}. Anal. calcd for $C_{44}H_{52}Cu_2I_2N_8O_4S_2$: C, 43.97; H, 4.36; N, 9.32; S, 5.34. Found: C, 44.01; H, 4.41; N, 9.27; S, 5.29.

*Method 2: [$Cu_2^I(\mu$-I)$_2$Tag$_2$] (**A**).* To a solution of thioamidoguanidino ligand **1a** (1 mmol, 410 mg) in acetonitrile (15 mL) was added CuI (1 mmol, 190 mg) dissolved in acetonitrile (15 mL), and the resultant reaction mixture was stirred for 20 min. A yellow solution was formed along with a yellow precipitate. The entire precipitate was dissolved by warming the reaction mixture in a water bath. The clear solution was kept for crystallization, which deposited a pale yellow crystalline solid. Yield of first crops 535 mg (89%). The compound so prepared was found to be identical in all respect to that prepared following method 1.

*Preparation of [$Cu_2^I(\mu$-Br)$_2$Tag$_2$] (**B**).* **B** was prepared following method 1, and $CuBr_2$ was used instead of CuI_2. Yield 440 mg (80%). Pale yellow solid. Mp 206−207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.46 (m, 16H), 6.97 (d, 4H, J = 8.0 Hz), 7.11 (t, 2H, J = 7.2 Hz), 7.18 (t, 4H, J = 8.0 Hz). IR (KBr): 2961, 2921, 2855, 1637, 1586, 1485, 1421, 1302, 1239, 1157, 1109, 1062, 994, 935, 765, 753, 691 cm^{-1}. Anal. calcd for $C_{44}H_{52}Cu_2Br_2N_8O_4S_2$: C, 47.70; H, 4.73; N, 10.11; S, 5.79. Found: C, 47.76; H, 4.78; N, 10.05; S, 5.72.

*Preparation of [$Cu^I_3(\mu_2$-S)$_4$Tu$_4$X$_3$] (**C**).* To a solution of thiourea **1** (1 mmol, 222 mg) dissolved in ethanol (15 mL) was added a solution of CuBr (1 mmol, 143.5 mg) dissolved in ethanol (5 mL), and the resultant reaction mixture was stirred for 20 min. A yellow solution was formed which was filtered and kept for crystallization, which deposited a pale yellow crystalline solid after few days. Yield of first crops 250 mg (76%). Pale yellow solid. Mp 138−139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.53 (s, 8H), 7.00 (t, 1H, J = 7.2 Hz), 7.19 (m, 4H), 10.22 (brs, 1H). IR (KBr): 3164, 3129, 2959, 2846, 1591, 1536, 1515, 1446, 1360, 1322, 1267, 1228, 1196, 1115, 1024, 951, 764, 689 cm^{-1}. Anal. calcd for $C_{44}H_{56}Cu_3Br_3N_8O_4S_4$: C, 40.05; H, 4.28; N, 8.49; S, 9.72. Found: C, 40.12; H, 4.34; N, 8.43; S, 9.67.

RESULTS AND DISCUSSION

The in situ generated unsymmetrical thiourea (Tu) **1** obtained by reacting phenyl isothiocyanate and morpholine in EtOH was treated with CuI_2. The greenish color of CuI_2 disappeared giving a pale yellow precipitate and leaving behind a pale yellow solution. A portion of this precipitate was dissolved in ethanol and was left aside for crystallization which gave a rod shaped pale yellow crystal **A**. The molecular structure of **A** was determined by X-ray crystallographic analysis (Figure 1). As revealed from the structure, the ligand bound to the Cu centers is nothing but the thioamidoguanidine (Tag) product **1a**. In keeping with our earlier observations,[3] it can be speculated that Cu^{II} being oxidizing in nature oxidizes thiourea in to a disulfide intermediately which then undergoes an imine disulfide rearrangement to give the Tag moiety; during the process, Cu^{II} gets reduced to Cu^{I}. The ligand (Tag) **1a** was isolated from the complex **A** by removing the Cu either using a disodium salt of ethylenediaminetetraacetic acid (EDTA) or an aqueous ammoniacal solution, and the product was characterized by spectroscopic analysis. No Hugerschoff product (2-amino benzothiazole) was isolated from the reaction mixture (Scheme 1). The ligand **1a** having a soft sulfur atom reacts with

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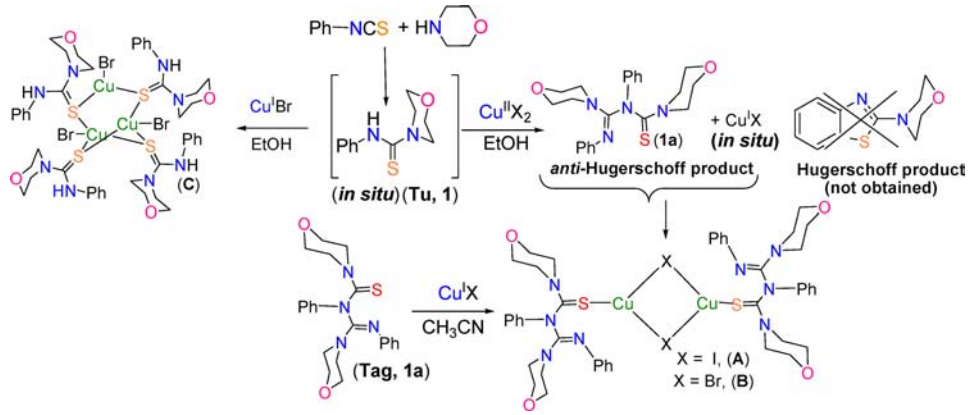
Scheme 1. Formation of Tag, $[Cu_2^I(\mu\text{-}X)_2Tag_2]$, Complexes A and B and $Cu^I_3S_4Br_3$ Cluster (C)



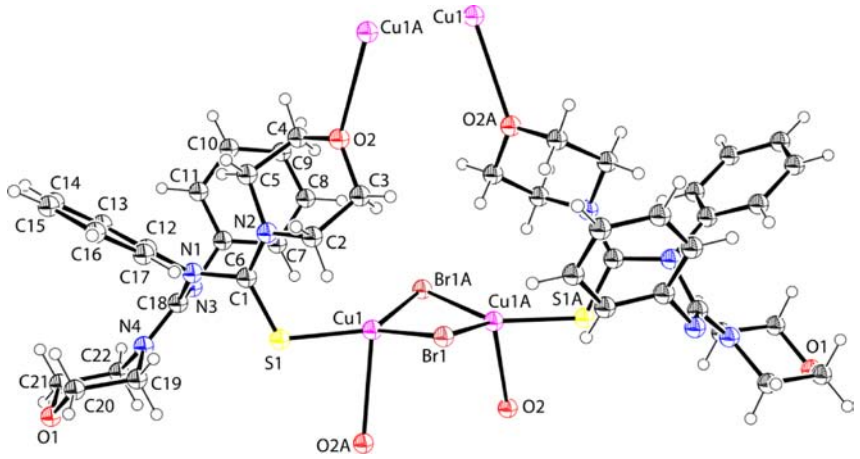


Figure 2. ORTEP view (30% probability ellipsoids) of compound **B**.

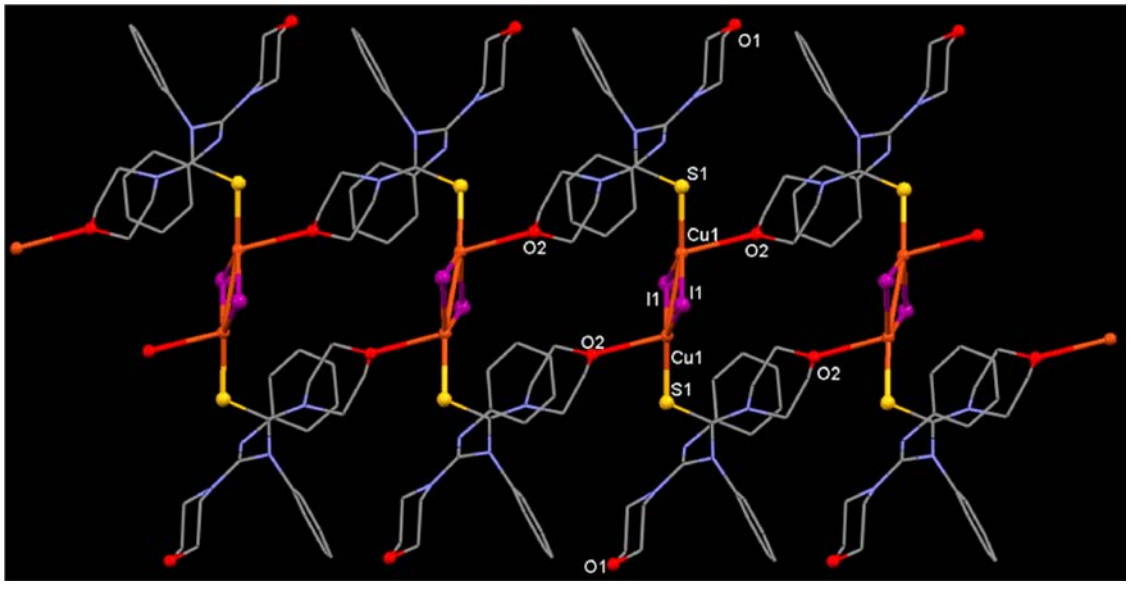


Figure 3. 1D coordination polymer of compound **A**.

the soft Cu^I center to form complex **A** (Scheme 1). The two Cu^I centers in the bimetallic complex **A** are held by two iodide ions. The EPR silence (see the Supporting Information, Figure S2), diamagnetic nature (μ_{eff} = 0), and the absence of d–d transition in the UV–vis spectrum (see the Supporting Information, Figure S1), support the existence of the +1 oxidation state for copper in complex **A**.[9]

Further, the reduction of Cu^{II} to Cu^I by the thiourea (Tu) has been independently confirmed by UV–vis titration. The d–d transition exhibited by green colored CuI_2 at λ_{max} = 804 nm in EtOH:H_2O (9:1) disappeared upon addition of an

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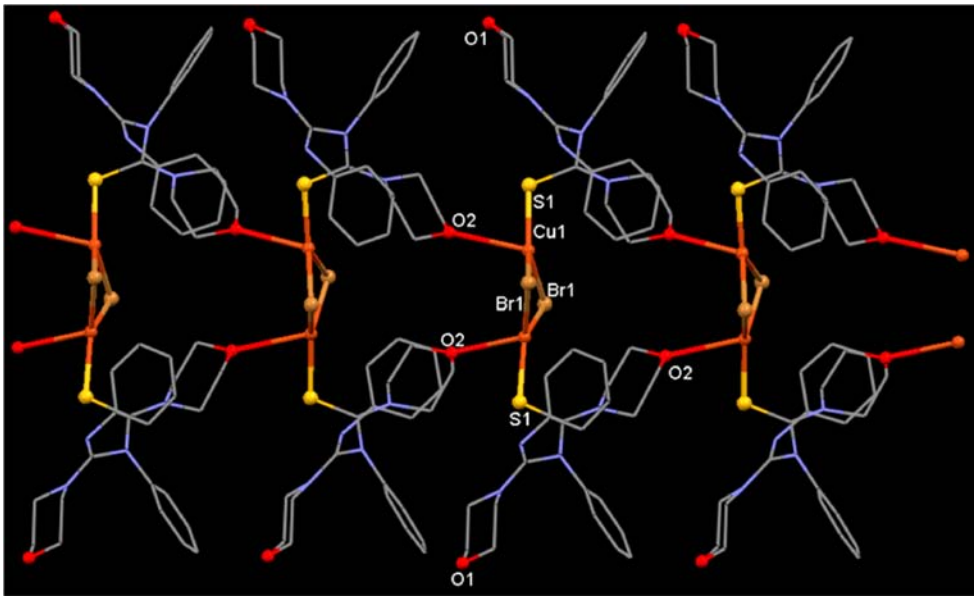

Figure 4. 1D coordination polymer of compound **B**.

equivalent of thiourea **1** (see Supporting Information Figure S1). Encouraged by the presence of an interesting structural motif in complex **A**, the in situ generated thiourea **1** was then treated with $CuBr_2$ instead of CuI_2. Here, also similar observations were noticed. The resultant compound **B** was crystallized from ethanol giving a rod shaped pale yellow crystal. X-ray crystallographic analysis of complex **B** showed an equally interesting structural motif to that of **A** as shown in Figure 2.

A plethora of Cu^I complexes prepared in the literature is by the treatment of various ligands containing soft centers with salts of Cu^I, and there are only few examples where it is prepared from Cu^{II} salts. In the latter case Cu^{II} is reduced in situ to Cu^I in the presence of an external reducing agent.[10] In the present case, the complexes of Cu^I, **A** and **B** are prepared from their respective $Cu^{II}X_2$ (X = I, Br) salts which act as the source for Cu^I generated in situ upon reduction by thiourea (Tu) **1**. The thiourea get transformed to the Tag unit **1a** by an oxidative dimerization (S−S bond formation) followed by an imine-disulfide rearrangement. The Tag unit binds to the in situ generated Cu^I giving complexes **A** and **B**, a process not documented in the literature so far. Due to the presence of soft sulfur atom in thioureas and substituted thioureas, they are effective ligands for Cu^I salts.[11a] Unlike Cu^{II}, generally Cu^I centers can have variable coordination numbers ranging from 2 to 4.[11b]

The isolated thioamidoguanidino (Tag) **1a** ligand has no affinity for $Cu^{II}X_2$ (X = I, Br) salts whereas it has strong affinity toward Cu^I and forms complexes **A** and **B** when treated with CuI and CuBr, respectively. With the reduced form of Cu, i.e Cu^I, no transformation of thiourea (Tu) **1** to thioamidoguanidino (Tag) **1a** was observed thus supporting the redox mechanism. Interestingly, the in situ generated thiourea **1** forms a cluster with a $Cu^I{}_3S_4Br_3$ core **C** as shown in Figure 3 when treated with Cu^IBr. A vast array of Cu^I clusters are known where sulfur atom of thioureas behaves as SAB,[11a,12] but it is often difficult to predict as to when sulfur and halides behave as the SAB and when as monodentate.

Crystal Structure of $[Cu_2^I(\mu\text{-}X)_2Tag_2]_n$ (X = I (A), Br (B)). Compounds **A** and **B** with space group *C*2/*c* and *Pccn* respectively contains a dimeric core of $[Cu_2(\mu\text{-}X)_2]$ in their crystal structure. As shown in Figures 1 and 2, the asymmetric units of compounds **A** and **B** contain a distorted tetrahedral Cu^I center bridged by two halogen atoms via a $Cu_2(\mu\text{-}X)_2$ bridge. A monodentate sulfur atom of a Tag moiety is in the basal plane and one of the morpholine-O atoms of another Tag moiety directed axially in their crystal structures. The axially coordinating morpholine-O atom is nearly perpendicular to the virtual $[Cu_2(\mu\text{-}X)_2Tag_2]$ plane. In compounds **A** and **B**, the distortion from regular tetrahedron geometry is evident from the bond angles around Cu^I center (Table 2). Compound **A** is centrosymmetric due to the trans orientation of two Tag units whereas the compound **B** is ascentric due to its cis orientation. As can be seen from the crystal structures of **A** and **B** despite the presence of several hard nitrogen atoms in the Tag ligand **1a**, only the soft sulfur and halogen atoms are coordinating to the Cu^I centers. Such monodentate sulfur coordination modes are rarely found in the literature.[13] Due to the presence of two or more lone pairs in a single atom, usually halogens (Cl, Br, and I) and sulfur atoms are ideal candidates for single-atom-bridging (SAB), and thus, an efficient contributor to metal−organic networks (MONs). Similar types of four-coordinated Cu^I bridges by a pair of iodide $[Cu_2(\mu\text{-}I)_2]$ and thiocarbonyl sulfur $[Cu_2(\mu\text{-}S_2)]$ atoms each acting as SAB's is reported.[14] In compounds **A** and **B**, comparison of bond angles around the Cu^I centers (Table 2) indicates that the latter is more distorted than the former. In both the complexes **A** and **B**, the central $Cu_2(\mu\text{-}X)_2$ core is rhomboidal with a bridging bond distances of Cu−I (2.59 Å) and Cu−Br (2.45 Å) very close to their terminal Cu−I (2.58 Å) and Cu−Br (2.43 Å) bond distances. The angles in the core of **A** are 65.82(3)° for Cu1−I1−Cu1A and 114.18(4)° for I1−Cu1−I1A. The similar $Cu_2(\mu\text{-}I)_2$ motif exists where the copper is tetra-coordinated; the bond angles are reported to be 56.3° for I1−Cu1−I1(A) and 123.7° for Cu1−I1−Cu1A.[10b] The angles in the core of **B** are 103.14(4)° for Br1−Cu1−Br1A and 74.50(3)° for Cu1−Br1−Cu1A. The similar $Cu_2(\mu\text{-}Br)_2$ core exists where the copper is tetra-coordinated, and the bond angles follow the opposite trend 50.6° for Br1−Cu1−Br1A and 120.4° for Cu1−Br1−Cu1A.[10b] The Cu−S bond distance is 2.259 Å and S1−Cu1−Cu1A

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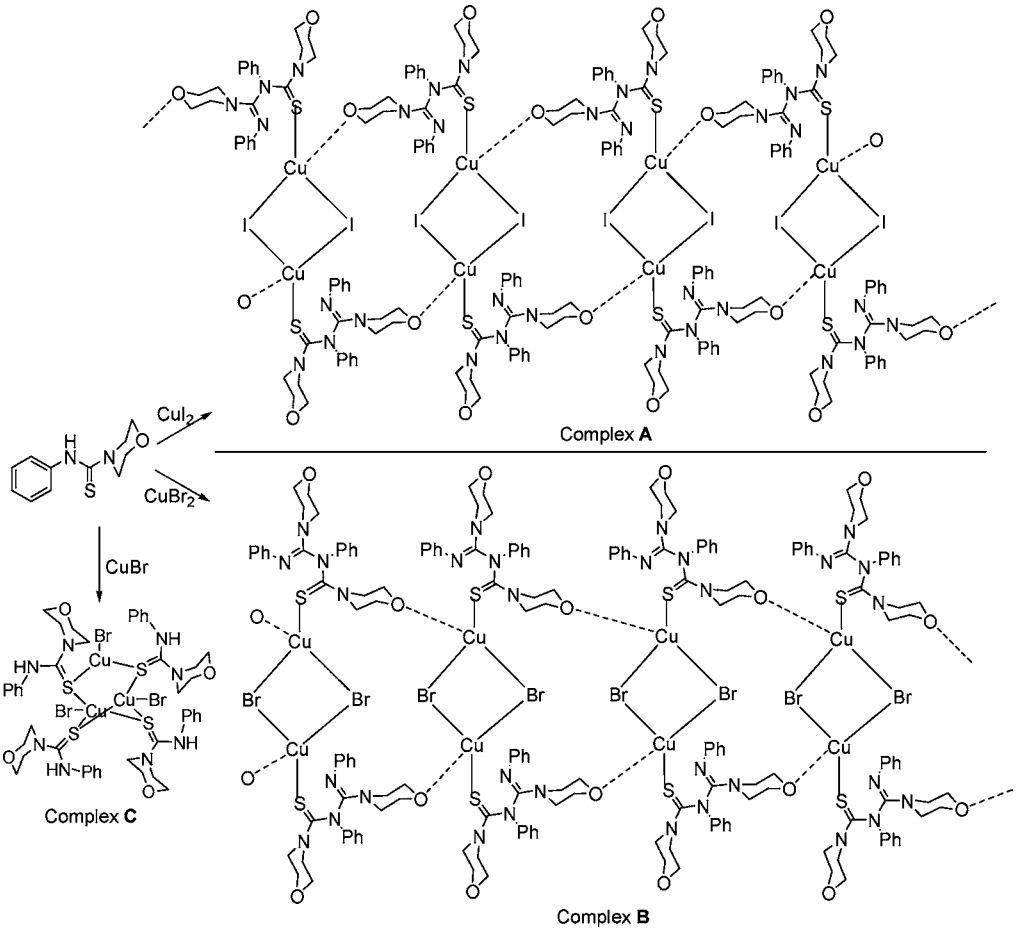
Scheme 2. Schematic Diagram of Coordination Polymer of Complex A and B and Cluster C



atoms are not linear with an angle of 169.80° in **A**, and the Cu_2I_2 core is perfectly rhomboidal in shape (Figure 1). The corresponding Cu_2Br_2 core in **B** is not perfectly rhomboidal; rather, it is bowl shaped. The bromine atoms $(\mu\text{-Br})_2$ are out of the plane by 20.45° and S1−Cu1−Cu1A atoms are nearly linear with an angle of 178.10° (Figure 2). This may be due to the trans orientation of iodine atoms in **A** and cis orientation of bromine atoms in **B**.

In compounds **A** and **B**, the axially coordinating morpholine-O atoms of Tag extends the dimeric $[Cu_2(\mu\text{-X})_2]$ core to a 1D coordination polymer as shown in Figures 3 and 4. In the polymeric unit the centroid−centroid distances between two nearby $Cu_2(\mu\text{-X})_2$ core are 7.37 Å (for compound **A**) and 7.33 Å (for compound **B**), respectively. It is interesting to note that although the Tag moiety contains two morpholine-O atoms, only one of the morpholine-O atoms (O2) extends the network whereas another morpholine-O atom (O1) exhibits C−H···O interactions (Scheme 2). In compound **A**, the hydrogen bonding interactions C4−H4···O1 = 3.45(1) and C6−H6···I1 = 3.82(1) Å between the Tag moieties extending the 1D chain to a 2D ladder along the *bc* plane (see Supporting Information Figure S5). Similarly, in compound **B**, noncovalent interactions such as C15−H15···O1 = 3.37(1), C8−H8···N2 = 3.61(1), and C6−H6···Br1 = 3.65(1) Å extend the 1D chain to a 2D layer along the axis (see Supporting Information Figure S6).

Crystal Structure of $[Cu_3^{I}Br_3(Tu)_4]$ (C). Complex **C** crystallized in the $\bar{P}1$ space group possessing a $Cu^{I}{}_3S_4Br_3$ cluster. As shown in Figure 5, the asymmetric unit of compound **C** consists of a tri- and two tetra-coordinated Cu^{I}

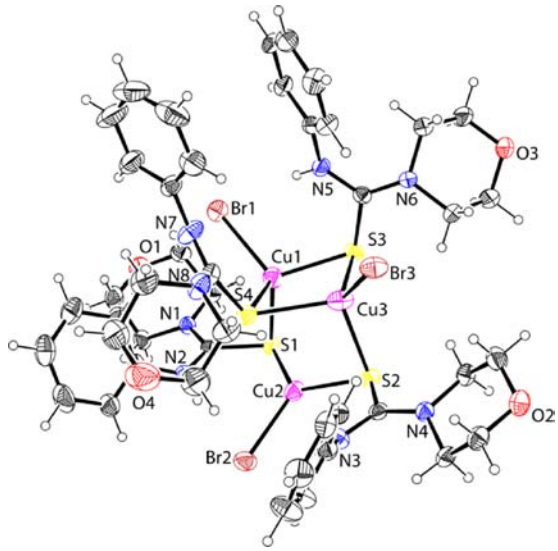


Figure 5. ORTEP view (30% probability ellipsoids) of compound **C**.

centers with four $(\mu_2\text{-S})$ bridging of Tu ligands and three axially coordinating bromine atoms. Unlike in compounds **A** and **B** where the two Cu^{I} centers are μ_2-X bridged and have a μ_1-S linkage, in compound **C**, the linkages are opposite possessing four $(\mu_2\text{-S})$ bridges and three μ_1-Br linkages (Scheme 2). The tri-coordinated Cu^{I} center (Cu_2) form bonds with two S atoms of Tu (Cu2−S1 = 2.245(1) Å, Cu2−S2 = 2.261(1) Å) and one

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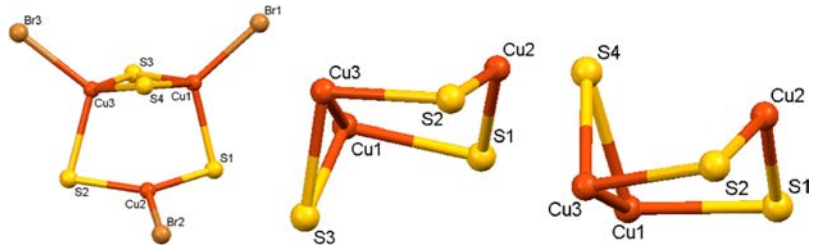

Figure 6. Ball–stick model of $Cu^{I}_{3}S_4Br_3$ cluster core (left) having both chair (middle) and boat form (right) of $Cu^{I}_{3}S_4$ cluster.

Br atom (Cu2–Br2 = 2.397(1) Å). The mean angle at Cu2 center is 119.85(3)° which suggests almost a trigonal planar geometry at the Cu2 center. The coordination environment around the tetra-coordinated Cu1 and Cu3 centers are satisfied by three S atoms of the Tu and one Br atom with a quasi-tetrahedral geometry. The Cu–S bond distances are in the range of (2.322(1)–2.487(1) Å) with an average bond distance of 2.414(1) Å around the Cu1 center and of 2.364(1) Å around Cu3 center. This may be compared with the Cu–S–Cys bonds in the range from 2.145–2.395 Å found in structurally characterized $Cu_8(CysS)_{10}$ and (Cu_8–yeastMT) clusters.[15] The Cu–Br distances are of 2.361(1) and 2.459(1) Å around Cu1 and Cu3 centers respectively. The axially coordinating Br1 atom is nearly perpendicular to the virtual plane containing S1S3S4 atoms, while the Br3 atom is nearly perpendicular to the plane containing S2S3S4 atoms. In compound **C**, comparison of bond angles (Table 3) around Cu1 and Cu3 centers indicates that the former Cu center is more distorted than the latter.

The central plane with $Cu_2(\mu_2\text{-}S)_2$ core contains two tetrahedral copper center which is rhomboidal in shape. The bridging bond distances of Cu1–S3; 2.392(1), Cu1–S4; 2.487(1), Cu2–S3; Cu2–S4; 2.350(1) Å, respectively, are shorter in comparison to those of complexes **A** and **B**. The angles in the $Cu_2(\mu_2\text{-}S)_2$ core respectively are 106.61(4)° for S3–Cu1–S4; 113.72(4)° for S3–Cu3–S4; 70.18(3)° for Cu1–S3–Cu3; and 68.11(3)° for Cu1–S4–Cu3. A closer look at the $Cu^{I}_{3}S_4Br_3$ cluster revealed the existence (Figure 6, left), of both chair (S3Cu3S2Cu2S1Cu1S3, middle) and boat forms (S4Cu3S2Cu2S1Cu1S4, right) within the cluster (Figure 6). The axially bridged Br atoms (Br2 and Br3) exhibit intramolecular H–bonding interactions with NH group of the Tu (Figure 7).[10b] The H–bonding distances are N1–H1···Br2 = 3.34(1), N3–H3···Br2 = 3.36(1), and N7–H7···Br3 = 3.24(1) Å, respectively.

It is interesting to note that despite the presence of four morpholine-O atoms from four Tu, none of them extend the cluster to either 1D, 2D, or 3D structures as was found in compounds **A** and **B**. Compound **C** exhibits different noncovalent interactions such as C6–H6···O1 = 3.18(1), C43–H43···O2 = 3.44(1), C19–H19···O3 = 3.23(1), C8–H8···S3 = 3.70(1), C27–H27···Br1 = 3.76(1), and C31–H31···Br3 = 3.53(1) Å extending the Cu^{I} cluster to a 2D sheet structure along the *bc* plane (see Supporting Information Figure S7).

CONCLUSION

In conclusion we have developed a method where an aryl-*sec*-alkyl thiourea (Tu) undergoes an oxidative rearrangement in the presence of a redox active metal salt $Cu^{II}X_2$ to give a thioaminoguanidino moiety (Tag) and itself gets reduced to Cu^{I}. An interesting bimetallic Cu^{I} complex is formed from the resultant transformed ligand (Tag) and halide ions to form a $[Cu_2^{I}(\mu_2\text{-}X)_2Tag_2]$ complex. However in the presence of Cu^{I}, the thiourea forms a $[Cu^{I}_{3}(\mu_2\text{-}S)_4Tu_4Br_3]$ cluster. Compounds **A** and **B** contain only tetra-coordinated Cu^{I} centers whereas compound **C** contains one tri- and two tetra-coordinated Cu^{I} centers. Compounds **A** and **B** exhibit 1D chain structures with a $Cu_2(\mu_2\text{-}X)_2$ core whereas compound **C** is a $Cu^{I}_{3}S_4Br_3$ cluster. Compound **A** is centrosymmetric, whereas the compound **B** is ascentric. In compound **A**, the Cu_2I_2 core is perfectly rhomboidal, whereas in compound **B**, the Cu_2Br_2 core is bowl shaped. Thus the synergism of the potentially bridging ligands, the effectiveness of the halide ions as SAB and directional nature of noncovalent interactions provide complex connectivity patterns and a remarkable structural diversity. The occurrence of different noncovalent interactions between ligands and halide ions extend the networks to a 2D structure. These complexes are air stable, non–hygroscopic thus might find potential application as catalyst, in the construction of metal organic framework, in light-emitting diode (LED) technology and also understanding of metallothionenes.

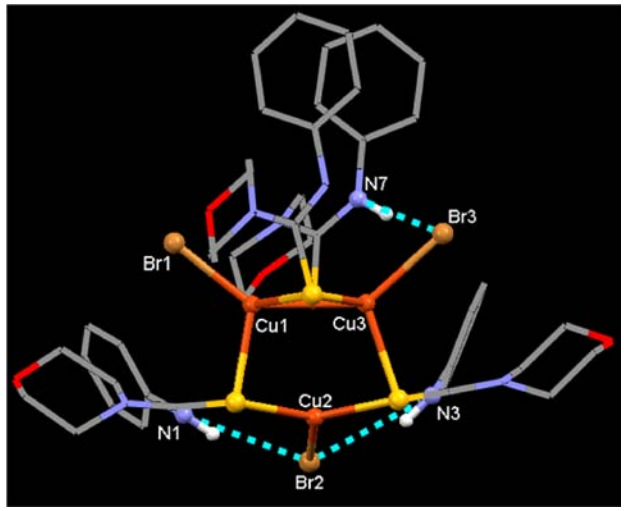

Figure 7. Mercury drawing representing intramolecular H–bonding interactions in compound **C**.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF, ^1H, ^{13}C NMR spectra, and HRMS and EPR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

We dedicate this paper to Prof. Mihir K. Chaudhuri on the eve of his 65th birthday.

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