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Crystal Structures and Vibrational Spectroscopy of Copper(I) Thiourea Complexes

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Several synthetic strategies using copper(I) starting materials or copper(II) compounds and an in situ sulfite reductant have been used to systematically explore the chemistry of copper(I) complexes with thiourea and substituted thiourea ligands. This has resulted in the discovery of several new complexes and methods for the bulk synthesis of some previously reported complexes that had been prepared adventitiously in small quantity. The new complexes are (tu = thiourea, dmtu = *N*,*N*′-dimethylthiourea, etu = ethylenethiourea): $[I_4Cu_4(tu)_6]\cdot H_2O$, $[Cu_4(tu)_{10}](NO_3)\cdot tu\cdot 3H_2O$, $[BrCu(dmtu)_3]$, $[ICu(dmtu)_3]_2$, $[BrCu(etu)_2]_2$, $[ICu(etu)_2]$, $[ICu(etu)_2]_3$. $[I_4Cu_4(tu)_6]\cdot H_2O$ has an adamantanoid structure, with four terminal iodide ligands and six doubly bridging tu ligands. In contrast to this, $[Cu_4(tu)_{10}](NO_3)\cdot tu\cdot 3H_2O$ contains a tetranuclear cluster in which four of the tu ligands are terminal and the other six are doubly bridging. $[BrCu(dmtu)_3]$ is a mononuclear complex with tetrahedral coordination of copper by one bromide and three dmtu ligands, whereas $[Cu(dmtu)_3]_2I_2$ has a centrosymmetric dimeric cation with two uncoordinated iodides, four terminal dmtu and two doubly bridging dmtu ligands, $[(dmtu)_2Cu(\mu\text{-}S\text{-}dmtu)_2Cu(dmtu)_2]I_2$. A reversal of this monomer to dimer trend from bromide to iodide is seen for the etu counterparts: $[BrCu(etu)_2]_2$ is a centrosymmetric dimer with two doubly bridging etu ligands, $[(etu)BrCu(\mu\text{-}S\text{-}etu)_2CuBr(etu)]$, whereas $[ICu(etu)_2]$ is a trigonal planar monomer, although the novel $[I_3Cu_3(etu)_6]$ is also defined. Infrared and Raman spectra of the synthesized complexes were recorded and the metal−ligand vibrational frequencies have been assigned in many cases. The results confirm previously observed correlations between the vibrational frequencies and the corresponding bond lengths for complexes of the unsubstituted tu ligand. A mechanochemical/infrared method was used to synthesize $[I_3Cu_3(etu)_6]$ from CuI and etu, and to demonstrate the polymorphic transition from $[ICu(etu)_2]$ to $[I_3Cu_3(etu)_6]$.

Introduction

A considerable number of complexes of simple copper(I) salts, formed with thiourea and its derivatives, relevant in many biological and pharmaceutical areas,[1,2] and involving a wide variety of compositions and structures, have been reported in the past;[3−59] in these, thiourea behaves as a "soft" ligand, capable of unidentate or diverse bridging modes in its complexes with copper(I) salts, associated "hard" anions usually being excluded from the coordination sphere while "soft" anions such as the heavier halide ions (i.e., not F) may be competitive. In the context of crystallization from diverse solvents, the strong hydrogen-bonding characteristics, capable of modification by

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substitution, may be relevant. Part of the interest in these compounds derives from the many and varied structures that they show. Table 1 presents the array of types already defined structurally for thiourea, unsubstituted or substituted with simple hydrocarbon substituents, and copper(I) salts with simple "hard" or "soft" (halide X = Cl, Br, I; there are other examples for X = SCN, CN in the literature) counterions, but there are also practical interests that derive from the possible role of such complexes in (e.g.) the mechanism of action of thiourea as a leveling agent in copper electroplating,[60−62] or as an inhibitor for copper corrosion in aggressive aqueous environments.[63]

The method of preparation of complexes of copper(I) with thiourea and non-coordinating anions has generally involved the addition of the thiourea ligand to an aqueous solution of the corresponding copper(II) salt. The copper(II) is reduced to copper(I) with concomitant oxidation of a portion of the thiourea ligand. The initial stage of this oxidation process presumably involves formation of the corresponding formamidine disulfide,[64]

$$(\mathrm{RHN})_2\mathrm{CS} \rightarrow {}^1\!/_2[(\mathrm{RN})(\mathrm{RHN})\mathrm{CS}]_2 + \mathrm{H}^+ + \mathrm{e}^- \qquad (1)$$

but the final products vary, depending on the particular thiourea ligand involved and also on the reaction conditions, and in many cases involves the precipitation of elemental sulfur. In many of the previously reported studies, the reaction conditions (e.g., the amounts and concentrations of the reactants) have not been

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Table 1. Structural Types Among Simple Non-coordinating Anion Salts and Adducts of the Copper(I) Halides (CuX; X = Cl, Br, I) with Simple (Hydrocarbon-Substituted) Thiourea Ligands[a]

CuX/L ratio	form	ligand/anion	ref
(a) Monomers, Dimers and One-Dimensional Polymers of Stoichiometry 1:1−4			
1: 4 (no X)	$[\mathrm{CuL}_4]^+\mathrm{X}^-$ (ionic)	tu/$(\mathrm{SiF}_6)_{0.5}$	3−5
		etu/NO_3	6, 7
		phtu/Cl	8
1: 3 (no X)	$[\mathrm{CuL}_3]^+\mathrm{X}^-$ (ionic)	tu/Hphth	9
		etu/$(\mathrm{SO}_4)_{0.5}$	6, 10
		tmtu/BF_4	10
		detu/$(\mathrm{SO}_4)_{0.5}$	11
		atu/NO_3	12
		mimtH/NO_3	13
1: 3 (no X)	$[\mathrm{CuL}{>}_3]^{+}_{(\infty\vert\infty)}\ \mathrm{X}^-$	tu/Cl	14−18
	(ionic, 1-D polymer	tu/Br	17, 18
	$[..\mathrm{CuL}_2(\mu\text{-L})\mathrm{CuL}_2(\mu\text{-L})\cdots]^{+}_{(\infty\vert\infty)})$	tu/I	17
1: 3 (no X)	$[\mathrm{L}_2\mathrm{Cu}(\mu\text{-L})_2\mathrm{CuL}_2]\mathrm{X}_2$	tu/ClO_4	19
	(ionic, binuclear)	tu/BF_4	20
		tu/$(\mathrm{SO}_4)_{0.5}(\cdot\mathrm{H}_2\mathrm{O})$	21
		tu/Cl$(\cdot\mathrm{H}_2\mathrm{O})$	18
		etu/ClO_4	22
		dmtu/BF_4	20
		mmtu/BF_4	20
		atu/$(\mathrm{SiF}_6)_{0.5}$	23
		datu/NO_3	24
		mimtH/BF_4	25
1: 3 (+ X)	$[\mathrm{XCuL}_3]$	dmtu/Cl	26
	(neutral, mononuclear)	detu/I	27
1: $2^1/_2$ (no X)	$[\cdots\mathrm{CuL}_2(\mu\text{-L})\mathrm{CuL}(\mu\text{-L})\cdots]_{(\infty\vert\infty)}\mathrm{X}$	tu/$(\mathrm{SO}_4)_{0.5}$	28
	(ionic, 1-D polymer)		
1: $2^1/_2$ (no X)	$[\mathrm{L}_2\mathrm{Cu}(\mu\text{-L})\mathrm{CuL}_2]\mathrm{X}_2$	mimtH/$(\mathrm{SO}_4)_{0.5}(\cdot\mathrm{H}_2\mathrm{O})$	29
	(ionic, binuclear)		
1: 2 (+X)	$[\mathrm{XCuL}_2]$	metu/Cl	30
	(neutral, mononuclear)	eetu/Cl	31
		petu/Cl	32, 33
		ipetu/Cl	33
		mmetu/Cl	34
		ptu/Cl	35
		eetu/Br	33
		ipetu/Br	33
		ptu/Br	36
		petu/I	33, 37
1: 2 (no X)	$[\mathrm{CuL}_2]^{+}_{(\infty\vert\infty)}\ \mathrm{X}^-$	dmtu/NO_3	38
	(ionic, 1-D polymer)		
	$[\cdots\mathrm{Cu}(\mu\text{-L})_2\mathrm{Cu}(\mu\text{-}\cdots]^{+}_{(\infty\vert\infty)})$		
1: 2 (+ X)	$[\cdots\mathrm{CuLX}(\mu\text{-L})\mathrm{CuLX}(\mu\text{-L})\cdots]_{(\infty\vert\infty)}$	tu/Cl	39
	$[\mathrm{CuL}_2]^{+}_{(\infty\vert\infty)})\ \mathrm{X}^-$ (1-D polymer)		
1: 2 (+ X)	$[\mathrm{L}_2\mathrm{CuX}(\mu\text{-L})\mathrm{CuXL}]$	etu/Cl	7
	(binuclear)		
1: 1 (+ X)	$[\mathrm{XCu}_3(\mu\text{-X})_2(\mu\text{-tu})_3]_{(\infty\vert\infty)}$	etu/Br	40, 41
	(1-D polymer)	etu/I	
	also: $[\mathrm{LCuX}_2]^-$ (NEt_4^+)(ionic)	metu/Br	42
(b) Tetranuclear Forms			
(i) $\mathrm{Cu}_4\mathrm{S}_6$ "adamantanoid" Forms			
4: 6 (no X)	$[\mathrm{Cu}_4(\mu\text{-L})_6]\mathrm{X}_4$	tu/$\mathrm{NO}_3(\cdot\mathrm{H}_2\mathrm{O})$	43
	(ionic, tetranuclear)	tu/$\mathrm{SO}_4(\cdot\mathrm{H}_2\mathrm{O})$	44
		tu/SO_4, $\mathrm{HSO}_4(\cdot\mathrm{H}_2\mathrm{O})$	44, 45
		atu/$\mathrm{O}_3\mathrm{SCF}_3$	46
		ptu/ClO_4	47
4: 6 (+ X)	$[(\mathrm{XCu})_4(\mu\text{-L})_6]$	atu/Cl	48
	(tetranuclear)	ettu/I$(\cdot\mathrm{H}_2\mathrm{O})$	49
4: 7 (no X)	$[\mathrm{LCu}_4(\mu\text{-L})_6]\mathrm{X}_4$	tu/$\mathrm{SO}_4(\cdot\mathrm{H}_2\mathrm{O})$	50
	(ionic, tetranuclear)	tu/NO_3, $\mathrm{SO}_4(\cdot\mathrm{H}_2\mathrm{O})$	51
4: 9 (no X)	$[\mathrm{L}_3\mathrm{Cu}_4(\mu\text{-L})_6]\mathrm{X}_4$	tu/$\mathrm{NO}_3(\cdot\mathrm{H}_2\mathrm{O})$	43
	(ionic, tetranuclear)		
(ii) Nonadamantanoid Forms			
4: 9 (no X)	$[(\mathrm{LCu})_4(\mu\text{-L})_4(\mu\text{-L})]\mathrm{X}_4$	etu/$\mathrm{NO}_3(\cdot\mathrm{H}_2\mathrm{O})$	52
	(ionic, tetranuclear)		
	$[\mathrm{Cu}_4\mathrm{L}_9]_{(\infty\vert\infty)}\mathrm{X}_4$	tu/NO_3	53
	(ionic, 1-D polymer)		
4: 10 (no X)	$[(\mathrm{LCu})_4(\mu\text{-L})_6]\mathrm{X}_4$	bzt/$\mathrm{ClO}_4(\cdot\mathrm{H}_2\mathrm{O})$	54
	(ionic, tetranuclear)		
4: 10 (no X)	$[\mathrm{L}_5\mathrm{Cu}_4(\mu\text{-L})_5]\mathrm{X}_2$	tu/$\mathrm{SiF}_6(\cdot\mathrm{H}_2\mathrm{O})$	55
	(ionic, 1-D polymer)		

Table 1. Continued

CuX/L ratio	form	ligand/anion	ref
4: 12 (no X)	$[(L_2Cu)_4(\mu\text{-}L)_4]X_4(\cdot H_2O)$ (ionic, tetranuclear)	$tu/SO_4(\cdot H_2O)$	56
	(c) Hexanuclear Forms		
6: 14 (no X)	$[L_8Cu_6(\mu_3\text{-}L)_4(\mu_2\text{-}L)_2]X_6$ (ionic, hexanuclear)	tu/ClO_4	57

[a] "+" or "no" X indicating the presence or absence of halide in the coordination sphere. Abbrevations for ligands: tu = thiourea; etu, ptu = $SC(NHCH_2)_2(CH_2)_{0,1}$ respectively; atu, ettu, phtu = $RNHCSNH_2$, R = allyl, ethyl, phenyl; mmtu = $H_2NCSNMe_2$; datu, dmtu, detu = $SC(NHR)_2$, R = allyl, methyl, ethyl; tmtu = $SC(NMe_2)_2$; metu, eetu, petu, ipetu = $SCNR(CH_2)_2NH$, R = methyl, ethyl, propyl, i-propyl; mmetu = $SC(NMeCH_2)_2$; mimtH = $SCNMe(CH)_2NH$; bzt = $SC(NH)_2C_6H_4$. Hphth = hydrogen phthalate.

specified, and the compounds have been characterized by single-crystal X-ray diffraction studies on products that may represent only a small proportion of the material used in the reaction. In two more recent studies the reaction conditions in the copper(II) sulfate/thiourea system have been examined more carefully, resulting in the discovery of the new copper(I) thiourea sulfate complexes $[Cu_4(tu)_7](SO_4)_2\cdot H_2O$[50] and $[Cu_4(tu)_{12}](SO_4)_2\cdot 2H_2O$.[56] It seems likely that further systematic studies will result in a better understanding of copper(I)/thiourea complex chemistry, and we have undertaken a number of such studies, some of which are reported herein.

In the course of these studies, it became clear that the reaction conditions for syntheses involving the reduction of copper(II) by the thiourea ligand are not particularly well defined because of the variable and uncertain nature of the redox processes involved (see above). We have therefore investigated two alternative synthetic procedures in which the amounts and concentrations and oxidation states of the reactants are accurately known, and we have used these to prepare bulk samples of a number of the complexes studied.

We have also investigated the use of spectroscopic methods to characterize the bulk compounds prepared. Previously, we have shown that infrared and Raman spectroscopy yield useful information about the coordination environment in these types of compound.[6,50] In the present study we report the vibrational spectra for a wider range of such complexes supported by the structural characterization of a number of new copper(I)/thiourea compounds (with well-defined syntheses) by single crystal X-ray studies.

Experimental Section

Preparation of Compounds. Hexakis(thiourea)dicopper(I) Sulfate Monohydrate, $[Cu_2(tu)_6](SO_4)\cdot H_2O$ (Cuprous Oxide Method). Copper(I) oxide (1.2 g, 8.5 mmol) and thiourea (3.9 g, 51 mmol) were added to water (70 mL) containing concentrated H_2SO_4 (4.6 mL, 83.5 mmol), and the mixture was set stirring while warming on a hotplate. All of the Cu_2O dissolved after about 15 min. More thiourea (9.0 g, 118 mmol) and water (80 mL) were added, and the mixture was heated and filtered while hot. The filtrate in a 150 mL conical flask was covered with a watch glass and placed in an insulated container and allowed to cool slowly. Large crystals formed, which were collected and washed with ice-cold water. Yield 5.1 g (86.4%).

Hexakis(thiourea)dicopper(I) Sulfate Monohydrate, $[Cu_2(tu)_6](SO_4)\cdot H_2O$ (Sulfite Reduction Method). A solution of sodium sulfite (1.26 g, 10 mmol) in water (20 mL) was added to a solution of copper(II) sulfate pentahydrate (5.0 g, 20 mmol) in water (20 mL). To the resulting mixture was added a solution of thiourea ("tu") (5.0 g, 65.7 mmol) in water (40 mL). A yellow oil and some white crystalline solid separated. The mixture was heated until the oil and solid dissolved, and filtered to remove the remaining cloudiness. Colorless crystalline product separated from the solution as it cooled. The product was collected and washed with water. Yield 4.2 g (59.7%). Large single crystals were grown by dissolving the product in a hot solution of thiourea (0.9 g) in water (300 mL), filtering the resulting solution, and allowing the filtrate to slowly evaporate in an open flask. Fine needle-like crystals form initially, but these redissolve as the solution volume decreases and are replaced by large block-shape crystals. The Raman spectrum of the product was identical to that previously reported.[50]

Pentakis(thiourea)dicopper(I) Sulfate Trihydrate, $[Cu_2(tu)_5](SO_4)\cdot 3H_2O$. This was prepared by a method similar to that described above, but with the use of a smaller amount of thiourea (3.81 g, 50 mmol) in the first step and the omission of excess thiourea in the recrystallization step. The yield from the first step was 5.1 g (78.0%). The Raman spectrum of the product was identical to that previously reported.[50]

Hexakis(thiourea)tetracopper(I) Disulfate Dihydrate, $[Cu_4(tu)_6](SO_4)_2\cdot 2H_2O$. A hot solution of copper(II) sulfate pentahydrate (2.50 g, 10 mmol) in water (15 mL) was rapidly added to a hot solution of sodium sulfite (1.26 g, 10 mmol) and thiourea (1.14 g, 15 mmol) in glacial acetic acid (40 mL). The product separated immediately as a white precipitate, which was collected and washed with water. Yield, 2.3 g (97.2%). Anal. Calcd for $C_6H_{28}Cu_4N_{12}O_{10}S_8$: C, 7.67; H, 3.01; N, 17.90. Found: C, 7.7; H, 3.0; N, 17.7.

Hexakis(thiourea)tetracopper(I) Tetranitrate Tetrahydrate, $[Cu_4(tu)_6](NO_3)_4\cdot 4H_2O$. Water (40 mL) was added to copper(I) oxide (2.0 g, 14 mmol) and thiourea (2.78 g, 36.5 mmol), and the mixture was stirred for a few minutes. To this mixture was added concentrated nitric acid (5 mL of 70%; contains 80 mmol). Some of the copper(I) oxide dissolved, and a dense white precipitate formed. This was dissolved by warming, and the mixture was stirred and heated to dissolve the remaining copper(I) oxide. The solution was filtered while hot to yield a clear, colorless solution, which deposited a colorless crystalline solid upon cooling. Yield 4.67 g (74.0%). Anal. Calcd for $C_6H_{32}Cu_4N_{16}O_{16}S_6$: C, 6.99; H, 3.13; N, 21.74. Found: C, 7.2; H, 2.4; N, 21.7.

Nonakis(thiourea)tetracopper(I) Tetranitrate Tetrahydrate, $[Cu_4(tu)_9](NO_3)_4\cdot 4H_2O$. A warm solution of thiourea (2.28 g, 30 mmol) and sodium sulfite (0.63 g, 5 mmol) in water (20 mL) was added rapidly to a warm solution of copper(II) nitrate trihydrate (2.42 g, 10 mmol) and potassium nitrate (5.0 g, 49.5 mmol) in water (20 mL). On cooling to room temperature the solution yielded a colorless crystalline product, which was collected and washed with water. Yield 2.97 g (94.4%). Anal.

Calcd for $C_9H_{44}Cu_4N_{22}O_{16}S_7$: C, 8.58; H, 3.52; N, 24.47. Found: C, 8.7; H, 3.3; N, 24.3.

Decakis(thiourea)tetracopper(I) Tetranitrate Monothiourea Trihydrate, $[Cu_4(tu)_{10}](NO_3)_4 \cdot tu \cdot 3H_2O$. Concentrated nitric acid (5 mL) was added to a mixture of cuprous oxide (1.43 g, 10 mmol) and thiourea (2.28 g, 30 mmol) in water (40 mL). Most of the cuprous oxide dissolved yielding a sparingly soluble white solid. To this mixture was added a solution of thiourea (2.28 g, 30 mmol) in water (50 mL), and the mixture was stirred and heated until all of the solids had dissolved. The solution was filtered while hot and allowed to stand. The colorless product that crystallized was collected and washed with cold water. Yield 5.68 g (81.5%). Anal. Calcd for $C_{11}H_{50}Cu_4N_{26}O_{15}S_{11}$: C, 9.48; H, 3.62; N, 26.13. Found: C, 9.5; H, 3.5; N, 25.9.

Tris(thiourea)copper(I) Monohydrogenphthalate, $[Cu(tu)_3][C_6H_4(COO)_2H]$. A hot solution of potassium monohydrogenphthalate (1.55 g, 7.6 mmol) in water (10 mL) was rapidly added to a hot solution of pentakis(thiourea)dicopper(I) sulfate trihydrate (2.5 g, 3.8 mmol) and thiourea (0.29 g, 3.8 mmol) in water (30 mL). The product separated immediately as a white precipitate, which was collected and washed with water. Yield, 2.9 g (84%). Anal. Calcd for $C_{11}H_{17}Cu_4N_6O_4S_3$: C, 28.21; H, 3.75; N, 18.39. Found: C, 28.1; H, 3.7; N, 18.2.

Dekakis(thiourea)tetracopper(I) Bis(hexafluorosilicate) Monohydrate, $[Cu_4(tu)_{10}](SiF_6)_2 \cdot H_2O$. Water (40 mL) was added to copper(I) oxide (1.43 g, 10 mmol) and thiourea (3.81 g, 50 mmol), and the mixture was stirred for several minutes. To this mixture was added H_2SiF_6 (5.8 g of 25%; contains 10 mmol). Some of the copper(I) oxide dissolved, and a dense white precipitate formed. This was dissolved by warming, and the mixture was stirred and heated to dissolve the remaining copper(I) oxide. This did not occur rapidly, so a further amount of H_2SiF_6 (2.5 g of 25%; contains 4.3 mmol) was added, resulting in dissolution of nearly all of the copper(I) oxide. The solution was filtered while hot to yield a clear, colorless solution, which deposited a colorless crystalline solid upon cooling. Yield 6.0 g (91.0%). Anal. Calcd for $C_{10}H_{42}Cu_4F_{12}N_{20}OS_{10}Si_2$: C, 9.12; H, 3.21; N, 21.26. Found: C, 9.0; H, 3.2; N, 20.8.

Hexakis(ethylenethiourea)dicopper(I) Dinitrate, $[Cu_2(etu)_6](NO_3)_2$. To a mixture of cuprous oxide (0.145 g, 1 mmol) and ethylenethiourea ("etu" = 1,3-imidazolidine-2-thione) (0.613 g, 6 mmol) in water (5 mL) was added concentrated nitric acid (70%, 6 drops; ca. 0.3 mL, contains about 7 mmol HNO_3). The solids dissolved upon warming to produce a colorless solution which was filtered while hot. A few crystals formed in the filtrate after standing for several days. These were removed, and the main bulk of product that crystallized upon further standing was collected and washed with ice-cold water. Yield 0.54 g (62.2%). Anal. Calcd for $C_{18}H_{36}Cu_2N_{14}O_6S_6$: C, 25.31; H, 4.36; N, 22.95. Found: C, 25.0; H, 4.2; N, 22.7. The small amount of product that crystallized initially was identified by X-ray crystallography as bis(tris(ethylenethiourea)copper(I)) sulfate,[6] presumably formed as a result of oxidation of some of the ligand by the excess nitric acid present in the reaction mixture.

Bis(*N,N′*-dimethylthiourea)copper(I) Nitrate, $[Cu(dmtu)_2](NO_3)$. A solution of concentrated nitric acid (1.0 g of 70%; contains 0.7 g, 11 mmol) in water (20 mL) was added with stirring to a mixture of copper(I) oxide (0.72 g, 5 mmol) and *N,N′*-dimethylthiourea ("dmtu") (2.1 g, 20 mmol). The solids dissolved within a few minutes to yield a colorless solution. After stirring for about 5 min, a colorless microcrystalline solid separated. This was redissolved by heating, and the resulting solution was filtered. The colorless crystalline product that separated upon cooling was collected and washed with a little ice-cold water. Yield, 2.6 g (76.6%). Anal. Calcd for $C_6H_{16}CuN_5O_3S_2$: C, 21.58; H, 4.83; N, 20.98. Found: C, 21.7; H, 4.8; N, 20.8.

Tris(*N,N′*-dimethylthiourea)copper(I) Tetrafluoroborate, $[Cu(dmtu)_3](BF_4)$. A solution of tetrafluoroboric acid (2.4 g of 40%; contains 1.0 g, 11 mmol) in water (20 mL) was added with stirring to a mixture of copper(I) oxide (0.72 g, 5 mmol) and *N,N′*-dimethylthiourea (3.1 g, 30 mmol). The solids dissolved within a few minutes to yield a white precipitate and a colorless solution. The white solid was dissolved by heating, and the resulting solution was filtered. The colorless crystalline product that separated upon cooling was collected and washed with a little ice-cold water. Yield, 3.9 g (83.4%). Anal. Calcd for $C_9H_{24}BCuF_4N_6S_3$: C, 23.35; H, 5.23; N, 18.16. Found: C, 23.5; H, 5.2; N, 18.2.

Tris(thiourea)copper(I) Chloride, $[Cu(tu)_3]Cl$. Water (15 mL) was added to a mixture of copper(I) chloride (0.99 g, 10 mmol) and thiourea (2.28 g, 30 mmol), and the mixture was heated until the solids had dissolved. The slightly cloudy solution was filtered while hot, and the filter was washed with water (5 mL). The filtrate was allowed to stand and evaporate, yielding a viscous glassy product. This yielded a white microcrystalline product upon mixing with a small volume of a 1:1 ethanol/diethyl ether mixture. The product was collected and washed with 1:1 ethanol/diethyl ether. Yield 2.89 g (88.6%). Anal. Calcd for $C_3H_{12}ClCuN_6S_3$: C, 11.01; H, 3.69; N, 25.67. Found: C, 11.0; H, 3.6; N, 25.4.

Tris(thiourea)copper(I) Bromide, $[Cu(tu)_3]Br$. Water (10 mL) was added to a mixture of copper(I) bromide (0.72 g, 5 mmol) and thiourea (1.14 g, 15 mmol), and the mixture was heated until the solids had dissolved. The solution was filtered while hot, and the filter was washed with water (2 mL). The filtrate was allowed to stand and evaporate, yielding large needle-like crystals. The product was collected and washed with a little ice-cold water. Yield 1.40 g (75.7%). Anal. Calcd for $C_3H_{12}BrCuN_6S_3$: C, 9.69; H, 3.25; N, 22.60. Found: C, 9.8; H, 3.4; N, 22.6.

Tris(thiourea)copper(I) Iodide, $[Cu(tu)_3]I$. Water (10 mL) was added to a mixture of copper(I) iodide (0.95 g, 5 mmol) and thiourea (1.14 g, 15 mmol), and the mixture was heated until the solids had dissolved. The slightly cloudy solution was filtered while hot, and the filter was washed with water (2 mL). The filtrate was allowed to stand and evaporate, yielding a viscous glassy product. This yielded a white microcrystalline product upon mixing with diethyl ether (5 mL). The product was collected and washed with diethyl ether. Yield 1.96 g (93.8%). Anal. Calcd for $C_3H_{12}CuIN_6S_3$: C, 8.60; H, 2.89; N, 20.07. Found: C, 8.7; H, 2.7; N, 20.1.

Hexakis(thiourea)tetrakis(iodocopper(I)) Monohydrate, $[I_4Cu_4(tu)_6] \cdot H_2O$. A hot solution of thiourea (0.76 g, 10 mmol) in water (15 mL) was added to a hot solution of copper(I) iodide (0.95 g, 5 mmol) and potassium iodide (10 g, 60 mmol) in water (10 mL). The yellow color of the CuI/KI solution discharged as the thiourea solution was added, to yield a colorless solution. As the solution cooled slightly an oil began to separate, and the warm supernatant solution was decanted from the initially formed oil, which was slightly discolored. Upon further cooling a pale yellow oil separated. The slightly warm supernatant solution was decanted, and this deposited small colorless crystals upon standing, which were collected and washed with a little water. Yield 0.19 g (12.5%). Anal. Calcd for $C_6H_{26}Cu_4I_4N_{12}OS_6$: C, 5.83; H, 2.12; N, 13.59. Found: C, 6.0; H, 1.9; N, 13.8.

Dibromotetrakis(ethylenethiourea)dicopper(I), $[Br_2Cu_2(etu)_4]$. A mixture of copper(I) bromide (0.72 g, 5 mmol) and ethylenethiourea (2.07 g, 20 mmol) and water (25 mL) was heated to boiling. The solution was filtered while hot, and the filtrate was allowed to stand and cool. Large colorless crystals form as the solution evaporates; these were collected after the volume of the solution had reduced by about 25% and washed with a little ice-cold water. Yield 0.93 g (53%). Anal. Calcd for $C_6H_{12}BrCuN_4S_2$: C, 20.72; H, 3.48; N, 16.11. Found: C, 21.0; H, 3.5; N, 16.1.

Iodobis(ethylenethiourea)copper(I), [ICu(etu)$_2$]. Copper(I) iodide (0.39 g, 2 mmol), ethylenethiourea (0.41 g, 4 mmol), and potassium iodide (8.3 g, 50 mmol) were placed in water (10 mL), and the mixture was heated to boiling and filtered while hot to remove some undissolved material. The filtrate was cooled slowly in a hot water bath, and the product separated as small colorless crystals, which were collected and washed with water. Yield 0.12 g (15%). Anal. Calcd for $C_6H_{12}CuIN_4S_2$: C, 18.25; H, 3.06; N, 14.19. Found: C, 18.1; H, 3.0; N, 14.0.

Tris(iodobis(ethylenethiourea)copper(I)), [ICu(etu)$_2$]$_3$. (a) Copper(I) iodide (1.90 g, 10 mmol) and ethylenethiourea (3.06 g, 30 mmol) were placed in water (50 mL), and the mixture was heated to boiling. The supernatant solution was decanted while hot to remove some undissolved material, and the product began to form immediately as small colorless crystals. The product was collected while the mixture was still warm and was washed with water. Yield 1.97 g (50%). Anal. Calcd for $C_6H_{12}CuIN_4S_2$: C, 18.25; H, 3.06; N, 14.19. Found: C, 18.3; H, 3.0; N, 14.1. (b) Copper(I) iodide (0.29 g, 1.5 mmol), ethylenethiourea (0.31 g, 3.0 mmol), and dimethylformamide (5 drops, 0.13 g) were ground together for several minutes using a mortar and pestle. The resulting mixture was placed in the fume cupboard for about 30 min, to allow removal of the dimethylformamide by evaporation, and was then briefly ground again and dried in the fume cupboard for a further 30 min. The product was an off-white powder whose IR spectrum was identical to that of the product crystallized from solution by method (a) above. Yield 0.58 g (99%). (c) Monomeric [ICu(etu)$_2$] (0.04 g, 0.1 mmol) was ground for a few minutes using a mortar and pestle with the minimum amount of water to form a paste, and the product was allowed to dry for several minutes in the fume cupboard. The IR spectrum of the product after two such treatments was identical to those of the products obtained by methods (a) and (b) above.

Chlorotris(dimethylthiourea)copper(I), [ClCu(dmtu)$_3$]. Copper(I) chloride (0.50 g, 5 mmol) was added to a solution of dimethylthiourea (1.6 g, 15.4 mmol) in water (10 mL). All of the CuCl dissolved at room temperature to give a clear solution, which was allowed to stand and evaporate, yielding a viscous glassy product. This crystallized after several days to a mass of colorless crystalline product. This was mixed with a small volume of a 1:1 ethanol/diethyl ether mixture (4 mL), and the product was collected and washed with 1:1 ethanol/diethyl ether (4 mL). Yield 1.94 g (94.3%).

Bromotris(dimethylthiourea)copper(I), [BrCu(dmtu)$_3$]. Copper(I) bromide (0.72 g, 5 mmol) was added to a solution of dimethylthiourea (1.6 g, 15.4 mmol) in water (10 mL). All of the CuBr dissolved at room temperature to give a clear solution, which was filtered. The filter was washed with water (2 mL), and the filtrate allowed to stand and evaporate. This crystallized after several days to a mass of colorless crystalline product. This was mixed with a small volume of a 1:2 ethanol/diethyl ether mixture (6 mL), and the product was collected and washed with diethyl ether. Yield 2.02 g (88.8%). Anal. Calcd for $C_9H_{24}BrCuN_6S_3$: C, 23.71; H, 5.31; N, 18.43. Found: C, 23.9; H, 5.5; N, 18.5.

Hexakis(dimethylthiourea)dicopper(I) Diiodide, [Cu$_2$(dmtu)$_6$]I$_2$. Copper(I) iodide (0.95 g, 5 mmol) and dimethylthiourea (1.62 g, 15.6 mmol) were dissolved in boiling acetonitrile (5 mL) to yield a pale yellow solution. A viscous glass formed upon evaporation of the solvent from this solution at room temperature. Upon treatment with water (5 mL), the product formed as an off-white solid that was ground to a microcrystalline mass with a glass rod. The product was collected and washed with water. Yield 2.35 g (93.6%). Anal. Calcd for $C_9H_{24}CuIN_6S_3$: C, 21.49; H, 4.81; N, 16.71. Found: C, 21.6; H, 4.8; N, 16.6.

Dichlorotetrakis(ethylenethiourea)dicopper(I), [Cl$_2$Cu$_2$(etu)$_4$] was prepared by a literature method.[7]

Structure Determinations. Full spheres of CCD area-detector diffractometer data were measured (ω-scans, monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; T about 153 K) yielding $N_{t(otal)}$ reflections, these merging to N unique (R_{int} cited) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered "observed". Anisotropic displacement parameter forms were refined (full matrix on F^2) for the non-hydrogen atoms, hydrogen atom treatment following a riding model (reflection weights: $(\sigma^2(F^2) + (aP)^2)^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$). Neutral atom complex scattering factors were employed within the SHELXL 97 program.[65] Pertinent results are given below and in Tables 2−9 and the Figures, the latter showing 20% (295 K) or 50% (100, 153 K) probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms, where shown, having arbitrary radii of 0.1 Å. Crystallographic details in CIF format for the eleven structures described in the paper are available free of charge as Cambridge Crystallographic Data Centre depositions CCDC 665777−665782, 665784−665787, 673982.

Vibrational Spectroscopy. Infrared spectra were recorded at 4 cm^{-1} resolution at room temperature as Nujol mulls between KBr plates on a Perkin-Elmer Spectrum 1000 Fourier-transform infrared spectrometer. Far-infrared spectra were recorded with 2 cm^{-1} resolution at room temperature as pressed Polythene disks or petroleum jelly mulls between Polythene plates on a Digilab FTS-60 Fourier-transform infrared spectrometer employing an FTS-60V vacuum optical bench with a 5 lines/mm wire mesh beam splitter, a mercury lamp source and a pyroelectric triglycine sulfate detector.

Raman spectra were recorded at 4.5 cm^{-1} resolution using a Jobin-Yvon U1000 spectrometer equipped with a cooled photomultiplier (RCA C31034A) detector or a Renishaw System 1000 spectrometer with 488.0 nm excitation.

Results and Discussion

Synthesis of Compounds. Two methods of synthesis which do not involve a copper(II)/thiourea redox reaction were used in the case of the non-halide complexes. The first involves prior reduction of a copper(II) salt by sulfite

$$2Cu^{2+} + SO_3^{2-} + H_2O \rightarrow 2Cu^{+} + SO_4^{2-} + 2H^{+} \qquad (2)$$

in the presence of, or followed by, addition of the thiourea ligand. This method is particularly well suited for the preparation of sulfate complexes and was used for the synthesis of $[Cu_2(tu)_5](SO_4)\cdot 3H_2O$, $[Cu_2(tu)_6](SO_4)\cdot H_2O$, $[Cu_4(tu)_6](SO_4)_2\cdot 2H_2O$. It can also be used to prepare complexes with counter-ions other than sulfate, by carrying out the reaction in the presence of an excess of the required anion. This method was used to prepare $[Cu_4(tu)_6](NO_3)_4\cdot 4H_2O$ and $[Cu_4(tu)_9](NO_3)_4\cdot 4H_2O$.

The second method involves the reaction of copper(I) oxide with the acid of the required anion

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(65) Sheldrick, G. M. *SHELXL 97, A Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

$$Cu_2O + 2H^+ \rightarrow 2Cu^+ + H_2O \qquad (3)$$

in the presence of the thiourea ligand. This method was used to synthesize $[Cu_2(tu)_6](SO_4)\cdot H_2O$, $[Cu(tu)_4]_2(SiF_6)$[5], $[Cu_4(tu)_{10}](SiF_6)_2\cdot H_2O$, $[Cu(dmtu)_2](NO_3)$, $[Cu(dmtu)_3](BF_4)$ (dmtu = *N*,*N*′-dimethylthiourea). The second of these has previously only been obtained as the result of an adventitious reaction between BF_4^- and the glass reaction vessel.[3,20]

The above synthetic methods are particularly advantageous in cases where the Cu^{2+}/thiourea redox reaction produces elemental sulfur as a byproduct, often over a long period of time, so that rapid collection of bulk quantities of pure product is difficult. This seems to be the situation for thiourea

Table 2. Crystal/Refinement Data

Compound	$[Cu(tu)_3]Br$[a]	$[Cu(tu)_3]I$[a]	$[Cu_4I_4(tu)_6]\cdot H_2O$[b]	$[Cu_4(tu)_{10}](NO_3)_4\cdot tu\cdot 3H_2O$[c]	$[ClCu(dmtu)_3]$[d]	$[BrCu(dmtu)_3]$[d]
formula	$C_3H_{12}BrCuN_6S_3$	$C_3H_{12}CuIN_6S_3$	$C_6H_{26}Cu_4I_4N_{12}OS_6$	$C_{11}H_{50}Cu_4N_{26}O_{15}S_{11}$	C_9H_{24} $ClCuN_6S_3$	$C_9H_{24}BrCuN_6S_3$
M_r (Dalton)	371.8	418.8	1236.6	1393.6	411.5	456.0
crystal system	tetragonal	tetragonal	triclinic	monoclinic	trigonal	triclinic
space group	$P4_32_12$ (No. 96)	$P4_32_12$ (No. 96)	$P\bar{1}$(No. 2)	$P2_1/n$ (No. 14)	$P3c1$ (No. 158)	$P1$ (No. 1)
a (Å)	13.524(1)	13.836(2)	11.5921(7)	14.2523(7)	14.625(2)	7.6987(8)
b (Å)			14.4772(8)	14.5466(6)		8.677(2)
c(Å)	13.765(1)	14.027(2)	20.319(1)	24.236(2)	14.658(2)	14.561(2)
α (Å)			84.732(1)			88.04(2)
β (Å)			73.898(1)	91.107(6)		83.47(1)
γ (Å)			78.969(1)			75.97(2)
V (Å^3)	2518	2685	3213	5024	2715	$937._5$
D_c (g cm^{-3})	1.96_2	2.07_2	2.55_6	1.84_3	1.51_0	1.61_5
Z	8	8	4	4	6	2
μ_{Mo} (mm^{-1})	5.4	4.4	6.9	2.21	1.7	3.6
specimen (mm)	0.25 × 0.20 × 0.18	0.15 × 0.13 × 0.09	0.45 × 0.30 × 0.20	0.27 × 0.04 × 0.02	0.45 × 0.35 × 0.30	0.20 × 0.16 × 0.082
$'T'_{min/max}$	0.69	0.80	0.50	0.86	0.69	0.67
$2\theta_{max}$ (deg)	75	67	75	50	75	80
N_t	51662	37396	65952	45649	55475	67863
N (R_{int})	6652 (0.054)	5137 (0.047)	32898 (0.045)	8711 (0.11)	9499 (0.041)	23167 (0.041)
N_o	4786	4486	22452	4511	6841	15961
$R1$	0.031	0.049	0.040	0.11	0.028	0.058
$wR2$ (a)	0.063 (0.032)	0.117 (0.030)	0.101 (0.047)	0.35 (0.2)	0.057 (0.032)	0.16 (0.094)
S	0.93	1.12	1.03	1.12	0.93	1.04
x_{abs}	−0.002(6)	0.00(3)			0.011(5)	0.022(7)

Compound	$[\{Cu(dmtu)_3\}_2]I_2$	$[\{Cu(etu)_3\}_2](NO_3)_2$[e]	$[BrCu(etu)_2]_2$	$[ICu(etu)_2]$[f]	$[ICu(etu)_2]_3$[f]
formula	$C_{18}H_{48}Cu_2I_2N_{12}S_6$	$C_{18}H_{36}Cu_2N_{14}O_6S_6$	$C_{12}H_{24}Br_2Cu_2N_8S_4$	$C_6H_{12}CuIN_4S_2$	$C_{18}H_{36}Cu_3I_3N_{12}S_6$
M_r (Dalton)	1006.0	864.0	695.5	394.8	1184.3
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$(No. 2)	$P2_1$ (No. 4)	$C2/c$ (No. 15)	$P2_1/m$ (No. 11)	$P2_1/c$ (No. 14)
a (Å)	7.7000(4)	6.4502(1)	19.538(2)	7.469(4)	12.580(5)
b (Å)	10.2597(6)	23.0260(4)	7.7273(7)	14.669(5)	16.925(9)
c(Å)	12.7568(7)	11.3724(2)	16.825(2)	11.726(4)	17.025(8)
α (Å)	69.449(1)				
β (Å)	81.853(1)	100.364(2)	116.083(1)	101.73(3)	96.56(4)
γ (Å)	83.925(1)				
V (Å^3)	932_4	1661	2281	1258	3601
D_c (g cm^{-3})	1.79_1	1.72_7	2.02_5	2.08_4	2.18_4
Z	1	2	4	4	4
μ_{Mo} (mm^{-1})	3.3	1.72	5.8	4.5	4.7
specimen (mm)	0.17 × 0.13 × 0.09	0.31 × 0.19 × 0.12	0.47 × 0.36 × 0.25	0.33 × 0.14 × 0.25	0.08 × 0.28 × 0.28
$'T'_{min/max}$	0.76	0.92	0.60	0.53	0.60
$2\theta_{max}$ (deg)	75	82	58	50	50
N_t	19376	54915	12919	4587	(5805)
N (R_{int})	9596 (0.022)	20915 (0.027)	2833 (0.028)	2293 (0.066)	5805
N_o	7860	15689	2618	1673	3385
$R1$	0.024	0.028	0.021	0.044	0.061
$wR2$ (a)	0.058 (0.030)	0.070 (0.050)	0.054 (0.029)	0.14 (0.037)	0.21 (0.121)
S	1.02	0.87	1.11	1.12	1.17
x_{abs}		0.5(1)			

[a] These structures on the relevant specimens are established as $P4_32_12$ (cf. the chloride,[15−18] recorded as $P4_12_12$ or $P4_32_12$, and a contemporaneous determination of the isomorphous bromide, $P4_32_12$.[18]). In the iodide, anion displacement amplitudes were appreciably larger than in the remainder of the structure in an initial room-temperature study; attempted modeling in terms of disorder was inauspicious, as also attempted resolution at 153 K and in the latter (presented) study a single envelope model was adopted. In the bromide, the anion amplitude was comparable with the average of those of the other non-hydrogen atoms in the structure (U_{eq} 0.030 Å^2). [b] tu(22) was modeled with a disordered $C(NH_2)_2$ component, site occupancies of the two fragments set at 0.5 after trial refinement; the residues modeled as water molecule oxygen atoms were modeled as disordered in concert. [c] *T* was 100 K. Even for the "best" specimen selected, data were weak and limited (the structure is quasi *C*2/*c*), and would support meaningful anisotropic displacement parameter refinement for Cu, S only. Associated hydrogen atoms were not located for the residues assigned as water molecule oxygen atoms, one being modeled as disordered over two sites of equal occupancy (0.5) (separation O(3)···O(4) 0.85(3) Å). Nitrates 4, 5 were modeled as disordered about crystallographic inversion centers. [d] Whereas the chloride was unproblematic, the bromide presents a frustrating composite of difficulties arising from pseudosymmetry/disorder/twinning. The most satisfying determination, presented here, is derivative of very extensive data, measured at 100 K, all six ligands being modeled as disordered at the nitrogen atoms and beyond (ligand 6 also at the central carbon), occupancies being set at 0.5 after trial refinement. [e] *T* was 100 K. [f] Data were measured at about 295 using a single counter instrument (a hemisphere for the monomer (analytical absorption correction), a unique set for the trimer (Gaussian correction)). For the trimer, using data acquired using a CCD instrument at 100 K, numerous components became disordered, with associated modeling yielding geometries of no better precision that those obtained for the room temperature ordered model.

Table 3. Selected Molecular Geometries, $[XCu(dmtu)_3]$

$X = Cl$[a]

atoms	parameters
Distances (Å)	
Cu(n)−X(n)	2.4026(7), 2.4238(7), 2.3822(7) (2.40(2))
Cu(n)−S(n)	2.3499(4), 2.3476(4), 2.3615(4) (2.353(8))
X(n)···H(n1)	2.3, 2.3, 2.4
X(n)···N(n1)	3.136(1), 3.158(1), 3.148(2) (3.147(11))
Angles (degree)	
X(n2)−Cu(n)−S(n)	112.04(1), 112.12(1), 111.77(1) (112.0(2))
S(n)−Cu(n)−S(n′)	106.78(1), 106.70(1), 107.08(1) (106.9(2))
Cu(n)−S(n)−C(n)	111.88(4), 111.19(5), 111.53(4) (111.6(3))

$X = Br$[b]

atoms	parameters	atoms	parameters
Distances (Å)			
Cu(n)−Br(n)	2.5514(6), 2.4646(6)	Cu(n)−S(n1)	2.327(1), 2.322(1)
Cu(n)−S(n2)	2.354(1), 2.333(1)	Cu(n)−S(n3)	2.348(1), 2.340(1)
⟨Cu−Br⟩	2.51(6)	⟨Cu−S⟩	2.337(12)
Angles (degree)			
Br(n)−Cu(n)−S(n1)	115.30(4), 116.05(4)	S(n1)−Cu(n)−S(n2)	104.51(5), 101.58(5)
Br(n)−Cu(n)−S(n2)	114.22(3), 116.73(3)	S(n1)−Cu(n)−S(n3)	105.90(5), 99.54(5)
Br(n)−Cu(n)−S(n3)	113.49(3), 115.41(3)	S(n2)−Cu(n)−S(n3)	102.11(5),105.22(5)
av	115.2(12)	av	103(2)
Cu(n)−S(n1)−C(n1)	114.8(2), 114.4(1)	Cu(n)−S(n2)−C(n2)	112.5(2), 113.5(2)
Cu(n)−S(n3)−C(n3)	113.4(2), 113.9(3)/112.7(2)	av	113.7(8)

[a] Values are for the three independent molecules n = 1,2,3 (av) respectively. The copper atoms lie 0.125(2), 0.128(2), 0.724(2) Å out of their associated SCN_2 planes [b] Values are for the two independent molecules n = 1, 2 (in molecule 2, read 4−6 for n1−n3). For the pair of components of the full $SC(NC)_2$ ligand skeletal planes χ^2 are 402/193; 99/222; 530/280 (molecule 1); 168/164; 146/397; 448/798 (molecule 2), with Cu deviations 0.432(10)/0.383(7); 0.579(8)/0.186(8); 0.282(10)/0.639(7) (molecule 1); 0.275(8)/0.203(7); 0.422(7)/0.441(9); 0.436(8)/0.395(9) Å (molecule 2). In Figure 1 read S(1−6) for S(11,12,21,22,31,32) in the above table.

and dmtu in particular. Bulk quantities of copper(I) complexes of the substituted thioureas *N*,*N*,*N*′,*N*′-tetramethylthiourea (tmtu) and “ethylenethiourea” (imidazolidine-2-thione; etu) were conveniently prepared by literature methods, involving Cu^{2+}/thiourea redox reactions,[6,10,50,59] although they could also be prepared by the above new methods if required. Additional advantages of the cuprous oxide method are (1) that the copper reagent involved is the same in all cases, and (2) that the complexes are formed from solutions that contain only the components of the complex, thus reducing the number of variables in the reaction.

The copper(I) halide complexes were most conveniently prepared by reaction of copper(I) halide with the appropriate thiourea ligand. This resulted in the preparation of the compounds $[Cu(tu)_3]X$ (X = Br, I), $[Br_2Cu_2(etu)_4]$, $[BrCu(dmtu)_3]$ and $[Cu_2(dmtu)_6]I_2$, $[ICu(etu)_2]/[I_3Cu_3(etu)_6]$, and $[I_4Cu_4(tu)_6]\cdot H_2O$, which had not previously been structurally characterized, and the crystal structures of these are discussed below. A surprising aspect of this work was the relative difficulty encountered in preparing complexes of 1:2 CuX/thiourea ligand stoichiometry, which are abundant in the literature for substituted thiourea ligands (see Table 1). In an attempted synthesis of CuI/tu (1:2), a complex of 2:3 stoichiometry was obtained (see Experimental Section) and was shown by an X-ray study (see below) to be $[I_4Cu_4(tu)_6]\cdot H_2O$ with an adamantane Cu_4S_6 core similar to that observed in previously reported $[Cu_4(tu)_6]^{4+}$ complexes.[43,44] There has been one previous report of a similar complex $[I_4Cu_4($*N*-ethylthiourea$)_6]$ with an adamantane-like structure.[49] It appears that this structure, which is quite common in copper/thiourea complexes involving non-coordinating anions, might be more prevalent than previously observed in the corresponding halide complexes. While there have been several reports of the structures and spectroscopic properties of trigonal monomeric CuI/xtu (1:2) complexes with xtu = substituted ethylenethiourea,[33,37] there have been no reports of the parent etu complex. In the present work we report the preparation and properties of trigonal monomeric $[ICu(etu)_2]$ and of a highly novel cyclic trimer polymorph $[ICu(etu)_2]_3$. The latter compound was prepared by conventional solution methods and also by the recently developed method of solvent-assisted mechanochemical synthesis.[66,67] Mechanochemical conversion of the trigonal monomer to the cyclic trimer shows that the latter is the more stable phase. This is consistent with the observation of a slow transformation of some samples of the trigonal monomer to the cyclic trimer phase upon standing for long periods. Conventional solution-based syntheses were not particularly reliable in producing one or other of the two polymorphs, but mechanochemical synthesis always produced the cyclic trimer phase in essentially quantitative yield (see Experimental Section).

Single Crystal X-ray Studies. The crystal structure of the array of maximum 1:4 stoichiometry, exemplified by the compound $[Cu(tu)_4]_2(SiF_6)$, which has been the subject of previous studies at room-temperature,[3,4] has been recently redetermined,[5] the results offering the enhanced precision

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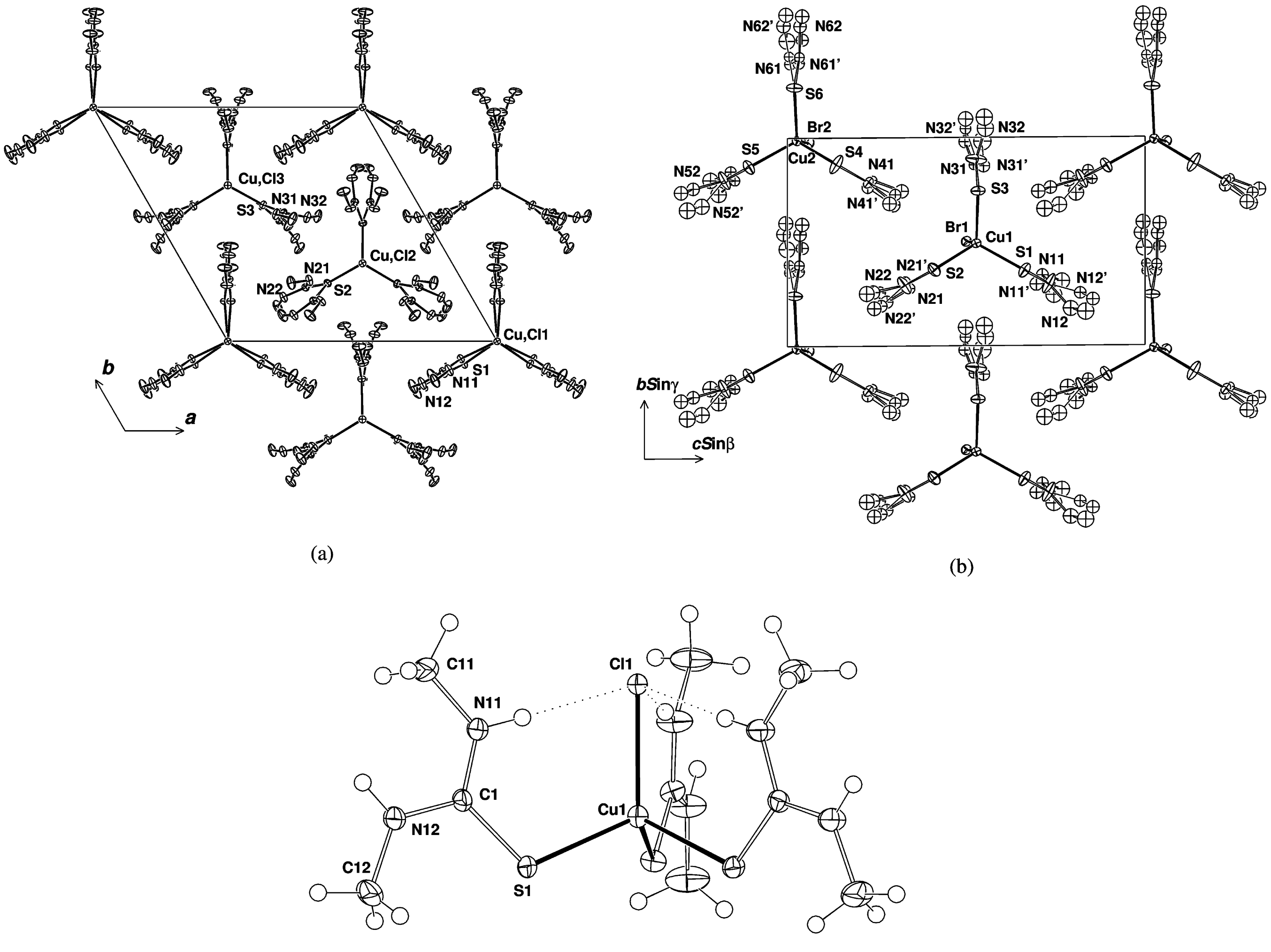
(66) Bowmaker, G. A.; Chaichit, N.; Pakawatchai, C.; Skelton, B.W.; White, A. H. *Dalton Trans.* **2008**, 2926–2928.

(67) Bowmaker, G. A.; Hanna, J. V.; Hart, R. D.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2008**, 5290–5292.



(a)

(b)

(c)

Figure 1. (a) Unit cell contents of [ClCu(dmtu)$_3$], projected down *c*. (b) Unit cell contents of [BrCu(dmtu)$_3$], projected down *a*. (c) Molecule 1 of the chloride complex.

consequent upon the use of a CCD instrument with extensive data measured at low temperature. The results are harmonious with those of the previous studies but greatly extend our appreciation of its elegant hydrogen-bonding scheme. In the two independent cations, Cu−S range between 2.3173(8)−2.3433(8), av 2.336(11) Å, with S−Cu−S 92.72−117.16(3)°. The [Cu(etu)$_4$]$^+$ cation has also been structurally characterized (in the nitrate salt) in refs. 6, 7 exhibiting similar distortions in the CuS$_4$ environment. There is also, perhaps remarkably, a further example with the phenylthiourea ligand, [Cu(phtu)$_4$]$^+$ with a chloride counterion, preferentially uncoordinated, the cation having $\bar{4}$ symmetry, with Cu−S 2.3313(5) Å and S−Cu−S 105.67(1), 117.38(2)°.[8]

Structurally authenticated complexes of 1:3 CuX/(x)tu ligand stoichiometry in which the three (x)tu ligands are coordinated to the copper atom, with or without X, in a mononuclear array are few in number, comprising trigonal planar CuS$_3$ arrays in [Cu(tu)$_3$]$^+$ hydrogen *o*-phthalate,[9] (⟨Cu−S⟩ 2.238(9) Å), [Cu(etu)$_3$]$_2$(SO$_4$)[6,10] (⟨Cu−S⟩ ca. 2.28 Å), [Cu(tmtu)$_3$](BF$_4$)[10] (⟨Cu−S⟩ 2.244(12) Å), [Cu(detu)$_3$]$_2$(SO$_4$),[11] (Cu−S 2.241(1) Å), [Cu(atu)$_3$](NO$_3$)[12] (2.2411(8) Å), [Cu(mimtH)$_3$](NO$_3$)[13] (⟨Cu−S⟩ 2.249(12) Å). Approaching halide ions engendering four-coordination are observed in [ClCu(dmtu)$_3$][26] (Cu−Cl, S 2.406(5), 2.360(1) Å (room temperature, space group *R*3*m*), and [ICu(detu)$_3$][27] (Cu−I, S 2.656(1), 2.350(1) Å. These are augmented in the present work by the pair of four-coordinate mononuclear complexes, with quasi-tetrahedral XCuS$_3$ metal atom environments, found for [XCu(dmtu)$_3$], X = Cl, Br (Table 3(a,b), Figure 1). (The iodide is different; see below). In the present study of the chloro complex at 153 K, the Cl−Cu bonds of three independent molecules are now elegantly disposed on the crystallographic 3-axes of a *P*3*c*1 cell; the non-hydrogen atoms of each ligand present as essentially planar (χ^2(C$_3$N$_2$S) 7.4, 240, 415), with the methyl substituents disposed one *trans*, one *cis* to the sulfur about each C−N bond, concomitant with the NH hydrogen atom associated with the former being hydrogen-bonded intermolecularly to the associated chlorine atom. The copper atom of molecule 3 lies much further out of the ligand plane than is the case with molecules 1, 2, a feature reflected in longer Cu−S and shorter Cu−Cl distances. The bromide is modeled in a *P*1 array with two independent molecules in the asymmetric unit, their dispositions indicating perturbations from incipient higher symmetry (see Figure 1b, cf. Figure 1a), the ligand conformations/dispositions being similar to those found in the chloride. The

Table 4. Selected Geometries, CuI:etu $(1:2)_{1,3}$

(a) monomeric phase[a]

atoms	parameters	atoms	parameters
	Distances (Å)		
Cu(n)−I(n)	2.552(2), 2.555(2)	Cu(n)−S(n)	2.231(2), 2.239(2)
	Angles (degree)		
I(n)−Cu−S(n)	121.88(6), 121.25(6)	Cu(n)−S(n)−C(n)	110.6(3), 109.8(3)
S(n)−Cu−S(n′)	116.2(1), 117.4(1)		
	Out-of-(SCN_2) Plane Copper Atom Deviations (δÅ)		
δCu(n)/n	0.28(1), 0.04(1)		
	Dihedral Angles of the SCN_2 Planes to the $ICuS_2$ Planes (χ^2 64,343)		
SCN_2 plane	8.8(2), 12.9(2)		
	Intramolecular Hydrogen-Bonds		
I(n)•••N(n5)	3.494(3), 3.547(8)	I(n)•••H(n5)	2.7, 2.7 (est.)

(b) trimeric phase[b]

	n = 1	n = 2	n = 3
	Distances (Å)		
Cu(n)−S(n)	2.381(4)	2.340(4)	2.334(3)
Cu(n)−S(n−1)	2.325(3)	2.330(3)	2.430(4)
⟨Cu−(μ-S)⟩	2.36(4)		
Cu(n)−S(n+3)	2.310(3)	2.306(4)	2.302(4)
⟨Cu(n)−S(n+3)⟩	2.306(4)		
Cu(n)•••Cu(n+1)	4.319(3)	4.525(4)	4.127(3)
S(n)•••S(n+1)	3.437(5)	3.684(3)	3.795(5)
Cu(n)−I(n)	2.631(2)	2.638(2)	2.617(2)
⟨Cu(n)−I(n)⟩	2.629(11)		
	Angles (degree)		
S(n−1)−Cu(n)−S(n)	107.5(1)	94.8(1)	101.3(1)
S(n−1)−Cu(n)−I(n)	117.7(1)	110.7(1)	102.6(1)
S(n)−Cu(n)−I(n)	105.1(1)	115.2(1)	117.9(1)
S(n−1)−Cu(n)−S(n+3)	108.5(1)	111.3(1)	109.6(2)
S(n)−Cu(n)−S(n+3)	112.5(1)	113.7(1)	106.6(1)
I(n)−Cu(n)−S(n+3)	105.1(1)	110.3(1)	117.4(1)
Cu(n)−S(n)−Cu(n+1)	132.0(1)	143.1(2)	124.7(2)
Cu(n)−S(n)−C(n1)	106.8(4)	105.4(5)	110.1(3)
Cu(n+1)−S(n)−C(n1)	106.7(4)	106.6(5)	113.7(3)
Cu(n)−S(n+3)−C(n+3)	106.8(4)	112.7(4)	111.2(4)
	Copper Atom Deviations from etu(n) C_2N_2S Planes (δÅ)		
δCu(n)	0.60(2)	0.55(3)	0.92(2)
δCu(n+1)	0.67(2)	0.13(4)	0.35(2)
δCu(n) (plane n+3)	0.22(2)	0.79(2)	0.59(2)
	"Other atom" Deviations from the Cu_3 Plane (Å)		
δI(n)	1.369(3)	1.850(3)	1.751(3)
δS(n)	0.423(4)	0.142(4)	0.500(4)
δS(n+3)	−2.206(4)	−2.092(4)	−2.184(4)
	Hydrogen-Bonding Contacts (Å)		
Intramolecular hydrogen-bonds			
I(1)•••N,H(15)	3.66(1), 2.9	I(3)•••N,H(35)	3.57(1), 2.9
I(1)•••N,H(32)	3.63(1), 2.8	I(3)•••N,H(65)	3.55(1), 2.6
I(2)•••N,H(55)	3.66(1), 2.8		
Intermolecular hydrogen-bonds			
I(1)•••N,H(62^i)	3.63(1), 2.9	I(3)•••N,H(42^i)	3.83(1), 3.0
I(2)•••N,H(52^i)	3.71(1), 2.7		

[a] Primed atoms are related by the intramolecular 2-axis in each of the two independent molecules. Intermolecular hydrogen-bonds found are: N,H(12)•••S(2) $(1 - x, 1 - y, 1 - z)$ 3.393(8), 2.5; N,H(22•••S(1) $(1 - x, 1 - y, 1 - z)$ 3.431(6), 2.6 Å. [b] S($n \pm 1$) are ring atoms; S($n + 3$) the pendant. Transformation i is: $x, {}^1/_2 - y, z - {}^1/_2$.

$(S{-}Cu{-}S)_3$ angle array is slightly more "closed" in the bromide, with the Cu−S distances in the two complexes being incremented by about 0.1 Å, compare the above planar three-coordinate counterparts. This increment is perhaps slightly greater than those found in CuX/PR_3 (1:3) systems on passing from $[Cu(PPh_3)_3]^+$ arrays (Cu−P ca. 2.3_0 Å) to $[XCu(PPh_3)_3]$ (ca. 2.3_5 Å).[68] In the latter, Cu−Cl, Br, I are typically about 2.3_5, 2.5_0, 2.6_7 Å, compare the $[XCu((x)tu)_3]$ counterpart values of (ca.) 2.4_0, 2.5_1 (this work), 2.6_6 Å.[27]

For 1:2 CuX/(x)tu stoichiometry, no mononuclear adducts of the form $[Cu((x)tu)_2]X$ have yet been structurally defined,

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(68) Effendy; Kildea, J. D.; White, A. H. *Aust. J. Chem.* **1997**, *50*, 587–604.

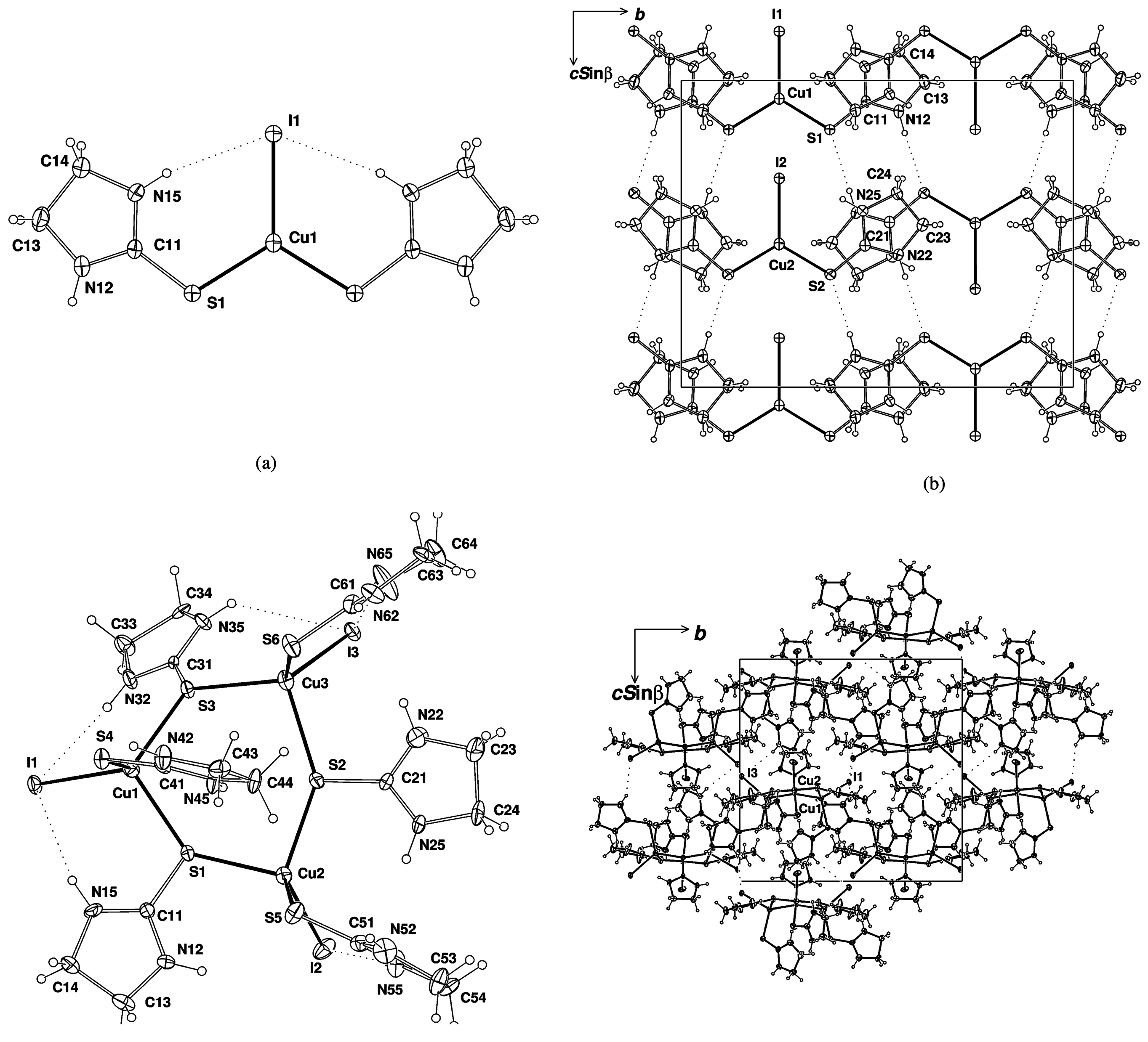

Figure 2. (a) Projection of [ICu(etu)$_2$] (molecule 1), normal to the ICuS$_2$ plane. (b) Unit cell contents, projected down *a*. (c) The CuI/etu (1:2) trimer projected normal to the Cu$_3$S$_3$ "plane". (d) Unit cell contents, projected down *a*, showing the hydrogen-bonded interaction of successive/adjacent glide-related trimers.

all mononuclear adducts taking the form [XCuL$_2$], (quasi-)trigonal planar). These have been defined exclusively for ligands of the form (*N*-substituted) SCNH(CH$_2$)$_{2,3}$.

The mononuclear CuI/etu adduct crystallizes with one-half of each of a pair of [ICu(etu)$_2$] molecules, each with its Cu−I bond disposed on a crystallographic 2-axis, comprising the asymmetric unit of the structure (Table 4a, Figure 2a,b). As in the preceding examples one of the NH components of each ligand hydrogen-bonds to the iodide atom, the other hydrogen-bonding intermolecularly to the sulfur atom of an adjacent alternate molecule. The Cu−I,S distances are similar to those found in the trigonal planar CuS$_3$ arrays noted above, with S−Cu−S not greatly perturbed from the trigonal value. The total array of each molecule is quite closely planar, despite which Cu−S−C angles closely resemble the values in the [XCu(tu)$_3$] arrays. In greater detail, Cu−I, S are similar to the values found in other ICuS$_2$ mononuclear arrays in Table 1 [33,37] in which Cu−S are slightly longer than the values found in the BrCuS$_2$ arrays,[33,36] these in turn being greater than in the ClCuS$_2$ arrays (the latter typically being ca. 2.2_0 Å); S−Cu−S concomitantly diminish on passing from the X = Cl to X = I examples, but the values are much more erratic: for example, those for the X = I systems are 111.4(7) (x2),[33,37] compare the present 116.2(1), 117.4(1)°. In the XCu((x)tu)$_2$ arrays, Cu−Cl, Br, I are typically 2.2_7[30−35] (with a wide spread), 2.3_7,[33,36] 2.5_2 Å,[33,37] compare [XCu(PPh$_3$)$_2$] 2.2_1, 2.3_5, 2.5_2 Å.[69]

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[69] Bowmaker, G.A.; Effendy; de Silva, E. N.; White, A. H. *Aust. J. Chem.* **1997**, *50*, 641–651.

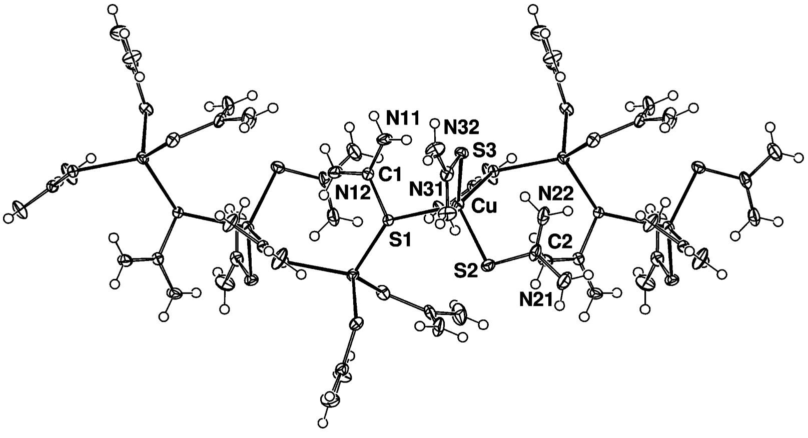

Figure 3. Single strand of the cationic polymer of $[Cu(tu)_3]_{(\infty|\infty)}$ I.

In the trimeric phase of this adduct a single trinuclear $[I_3Cu_3(etu)_6]$ molecule, Figure 2c, devoid of crystallographic symmetry, forms the asymmetric unit for the structure. The three copper atoms of the trimer, the first so defined for any CuX/(x)tu array, form alternate members of a six-membered ring, the other members of which are the sulfur atoms of three etu ligands, each of which function in a bridging capacity, that is, $Cu_3(\mu$-*S*-etu$)_3$. The Cu_3S_3 ring, although nonplanar, is rather flat, the three sulfur atoms lying to the same side of the Cu_3 plane, so that it may effectively be regarded as a flattened "chair" (Table 4b). The rather erratic nature of these deviations is typical of the molecular conformation more widely with the dispositions of individual moieties widely divergent from the potential *3m*-symmetry of the overall aggregate (Table 4b). Each of the copper atoms is four-coordinate, the additional components of the coordination sphere of each being a terminally bound iodide atom and a terminally *S*-bound etu ligand; all three of the latter lie to the same side of the ring. The coordination of the iodide atoms may be regarded as "equatorial" about the six-membered ring, that of the etu ligands "axial". The dispositions of the latter comprise the most extreme manifestation of the departures from *3*-symmetry; among the bridging etu ligands, two (1,2) have their planes quasi-parallel to the Cu_3S_3 ring plane (dihedral angles: 16.7(2), 17.3(4)°) while the other (3) is bent well out of coplanarity (dihedral: 64.0(2)°) but not twisted substantially (τ Cu(1)−S(3)−C(31)−N(32,35), 9(1), −28(1)°). The planes of the three terminally bound etu ligands lie with their associated iodine atoms quasi-coplanar in two cases, presumably a consequence of NH···I hydrogen bonding (H···I $2._7$, $2._6$ Å for ligands 5, 6); the direction of ring $n = 4$ is reversed, however, the relevant hydrogen atom lying toward the center of the Cu_3S_3 ring. A further determinant of the etu ring dispositions, however, appears to be hydrogen-bonding from the set of three outwardly directed NH hydrogen atoms which neatly contact the three iodine atoms of the adjacent glide related molecule at (x, $^1/_2 - y$, $^1/_2 + z$) (H(42)···I(3) $3._0$; H(52)···I(2), $3._0$; H(62)···I(1), $2._9$ Å). The six-membered Cu_3S_3 ring is also found as a basic motif in many other polynuclear arrays, most relevantly in the polymeric CuI/etu (1:1) adduct.[40]

The remainder of the structurally characterized arrays are also oligo- or poly- meric, in the main of familiar types. The adducts CuX/tu (1:3) have been previously defined, the chloride long ago,[14−17] with a more recent redetermination of its bromide counterpart with which it has been shown to be isomorphous.[18] We have cosynchronously studied the bromide, recording it here with the added benefit of extensive low-temperature CCD data in company with the iodide. The arrays are polymeric and ionic, the single-stranded polymeric cation being of the form $\cdots Cu(tu)_2(\mu$-S-tu$)Cu(tu)_2(\mu$-S-tu$)\cdots$ (Figure 3), with the halide ions uncoordinated. While, as expected, the broad features of the two structures are similar, there are some quite substantial differences in the individual geometries within the series (Cl, Br, I) (Table 5), perhaps indicative of the impact of the variation in hydrogen-bonding between the two, at the different temperatures of the two studies. Thus, for example, Cu···Cu differ by about 0.05 Å as do Cu−S(1) ($y - {}^1/_2$, ${}^1/_2 - x$, ${}^1/_4 + z$), with associated differences of up to 5° in the counterpart S−Cu−S angles about the copper atom.

Binuclear forms have been described previously for adducts of both CuX/(x)tu (1:3) and (1:2) stoichiometries. In the diverse examples of Table 1, of 1:3 stoichiometry, with feebly coordinating/"hard" counterions, cations of the form $[(tu)_2Cu(\mu$-*S*-tu$)_2Cu(tu)_2]^{2+}$ are found (it is interesting to note a parallel scorpionate, not discussed here[70]), the anions not being coordinated. There is, however, an example with L = tu, X = Cl in which an uncoordinated halide ion is found;[18] this is paralleled in the present work by a further example with L = dmtu, X = I: $[Cu_2(dmtu)_6]I_2$, contrasting with the above mononuclear $[ICu(detu)_3]$. In the present structure, one-half of the binuclear formula unit comprises the asymmetric unit of the structure, the cation being centrosymmetric, as is the case in the most of the other similar binuclear 1:3 forms also. Three of the NH hydrogen atoms (one from each ligand) are involved in intradimer hydrogen-bonds to sulfur atoms of other ligands, presumably accounting for the considerable excursions in geometries between "equivalent" parameters (Table 6, Figure 4); the others are involved in interactions with the uncoordinated iodide ions. A similar example, albeit not crystallographically centrosymmetric, is found in the etu/NO_3 complex (Table 6).

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(70) Dodds, C. A.; Garner, M.; Reglinski, J.; Spicer, M. D. *Inorg. Chem.* **2006**, *45*, 2733–2741.

Table 5. Selected Geometries, CuX·3tu (one-dimensional polymeric cation)[a]

atoms	parameter	atoms	parameter
	Distances (Å)		
Cu−S(1)	2.3772(6); 2.3784(6); 2.357(1)	Cu−S(2)	2.2807(7); 2.2876(6); 2.287(2)
Cu−S(3)	2.3458(8); 2.3506(6); 2.349(2)	Cu−S(1^{i})	2.4355(7); 2.4073(6); 2.394(1)
Cu···Cu	4.4366(3); 4.4144(4); 4.379(1)		
	Angles (degree)		
S(1)−Cu−S(2)	107.40(2); 106.36(2); 105.62(5)	S(2)−Cu−S(3)	115.54(3); 115.80(2); 116.65(6)
S(1)−Cu−S(3)	109.25(2); 108.93(2); 109.84(5)	S(2)−Cu−S(1^{i})	110.83(2); 112.58(2); 113.02(5)
S(1)−Cu−S(1^{i})	113.87(2); 114.86(2); 116.24(5)	S(3)−Cu−S(1^{i})	100.04(3); 98.46(2); 95.73(5)
	Close Hydrogen-Bonding Contacts (H···X; S estimated) (Å)		
N(11)···X^{ii}	3.305(2); 3.300(2); 3.482(6)	N(12)···X^{ii}	3.216(2); 3.421(2); 3.600(6)
S(3)	−; 3.328(2); 3.313(6)	S(1^{iii})	3.969(2); 3.408(2); 3.426(6),
H(11a)···X^{ii}	2.5; 2.5; 2.6	H(12a)···X^{ii}	2.4; 2.6; 2.8
H(11b)···S(3)	−; 2.5; 2.4	H(12b)···S(1^{iii})	3.6; 2.6; 2.6
N(21)···X^{iv}	3.435(3); 3.620(2); 3.832(2)	N(22)···X^{iv}	3.298(3); 3.408(2); 3.620(6)
H(21a)···X^{iv}	2.7; 2.8; 3.0	H(22a)···X^{iv}	2.5; 2.6; 2.8
N(31)···X^{v}	3.436(3); 3.492(2); 3.651(6)	N(32)···X^{v}	3.242(3); 3.394(2); 3.589(7)
S(2)	3.508(3); 3.473(2); 3.565(6)		
H(31a)···X^{v}	2.7; 2.7; 2.9	H(32a)···X^{v}	2.4; 2.6; 2.8
H(31b)···S(2)	2.7; 2.6; 2.7		

[a] The values in each entry are for X = Cl (ref 19); Br (present study, also see footnote [b]); I (present study). [b] The bromide structure is contemporaneously reported in ref 18 at 295 K showing significant differences in the polymer geometry to the present study, which we have essentially corroborated by a room-temperature study also. Two studies of the chloride are recorded in refs.,[16,18] both at room-temperature; the full report of ref.[18] being the more accessible, that is cited here (CCDC: CUTHIC02). Transformations of the asymmetric unit: (i) $y - {}^{1}/_{2}$, ${}^{1}/_{2} - x$, ${}^{1}/_{4} + z$; (ii) $1 - y$, $1 - x$, $1{}^{1}/_{2} - z$; (iii) ${}^{1}/_{2} - y$, ${}^{1}/_{2} + x$, $z - {}^{1}/_{4}$; (iv) $x - {}^{1}/_{2}$, $1{}^{1}/_{2} - y$, $2{}^{1}/_{4} - z$; (v) ${}^{1}/_{2} - x$, ${}^{1}/_{2} + y$, $1{}^{3}/_{4} - z$. Out-of-(S_2CN) plane deviations of the copper atoms are (Cu) 0.995(6), 0.773(4), 0.724(3); 0.856(4), 0.671(10), 0.673(9); (Cu^{i}, plane 1) 0.291(4); 0.254(4) Å, for X = Br; I.

Table 6. Selected Geometries, CuX: xtu (1:3) (binuclear cation)[a]

	tu		dmtu		etu
	ClO_4[b]	BF_4[c]	BF_4[c]	I[d]	NO_3[d]
			Distances (Å)		
Cu−S(1)	2.460(4)	2.429(3)	2.461(3)	2.4737(3)	2.4715(3),2.4675(4)
Cu−S(1′)	2.395(4)	2.367(3)	2.328(3)	2.3154(3)	2.3487(4),2.3411(4)
Cu−S(2)	2.326(5)	2.295(3)	2.325(3)	2.3118(4)	2.3228(4),2.3302(4)
Cu−S(3)	2.321(4)	2.313(3)	2.301(3)	2.2987(4)	2.3094(3),2.3082(3)
Cu···Cu′	2.862(3)	2.840(3)	2.828(3)	2.8797(3)	3.0746(2)
S(1)···S(1′)	3.924(2)	3.865(5)	3.868(5)	3.8297(5)	3.7067(5)
			Angles (degree)		
Cu−S(1)−Cu′	72.2(1)	72.6(1)	72.3(1)	73.84(1)	79.36(1).79.30(1)
S(1)−Cu−S(1′)	107.8(1)	107.4(1)	107.7(1)	106.16(1)	100.50(1).100.83(1)
S(1)−Cu−S(2)	98.3(2)	98.6(1)	97.8(1)	97.60(1)	105.14(1),103.55(1)
S(1)−Cu−S(3)	104.1(1)	105.0(1)	112.7(1)	110.88(1)	106.61(1),106.70(1)
S(1′)−Cu−S(2)	116.5(2)	116.8(1)	120.3(1)	123.60(2)	119.00(0),119.76(1)
S(1′)−Cu−S(3)	102.4(2)	102.6(1)	101.8(1)	100.55(1)	108.31(1),109.25(1)
S(2)−Cu−S(3)	125.9(2)	124.8(1)	116.6(1)	117.51(1)	115.41(1),114.75(1)
Cu−S(2)−C	111.9(7)	113.4(5)	106.4(3)	108.46(4)	103.74(5),104.16(5)
Cu−S(3)−C	109.5(7)	110.1(4)	107.1(4)	106.26(4)	108.21(5).106.47(4)
Cu−S(1)−C	111.0(5)	105.7(3)	101.5(3)	102.18(4)	95.65(4),107.28(3)
Cu′−S(1)−C	106.4(5)	114.7(4)	110.2(3)	109.53(4)	107.95(5),96.26(4)

[a] Geometries within the binuclear cation are given, together with counterpart values, comparatively, for the BF_4 and the parent tu systems. Primed atoms are centrosymmetrically related. [b] Ref 19. [c] Ref 20 (note that the two tu ligand adduct salts are isomorphous). [d] This work. In the iodide the copper(I) atom lies 2.299(2), −0.163(2), 0.221(2), 1.030(2) Å out of the planes of ligands 1, 1′, 2, 3. The iodide ion has close contacts (<3 Å) to H(n2), thus: I···N,H(12) 3.629(1), 2.8; N,H(22)($1 - x, \bar{y}, 1 - z$) 3.652(1), 2.9; N,H(32) 3.691(2), 3.1 Å. H(n1) contact sulfur atoms of adjacent ligands within the dimer: S(2)···N,H(11)($\bar{x}, 1 - y, 1 - z$) 3.446(1), 2.6; N,H(31) 3.562(1), 2.7; S(3)···N,H(21) 3.610(1), 2.80(1) Å.

For the CuX/(x)tu system, mononuclear arrays have been described above; a polymeric form has also been described for $CuNO_3$/dmtu (1:2), again with the anion discrete, that is, not bonded to the cation, which is a one-dimensional polymer in which all ligand sulfur atoms are bridging.[38] The adduct formed between CuBr and etu, of 1:2 stoichiometry (Table 7, Figure 5), is binuclear, $[Br_2Cu_2(etu)_4]$, of similar aspect to the $[Cu_2((x)tu)_6]^{2+}$ cations described above in the 1:3 complexes, except that, about each copper atom, one of the terminally bound xtu ligands has been replaced by the halide ion, thus $[LXCu(\mu\text{-}L)_2CuXL]$, augmenting the previously defined etu/Cl adduct.[7] The latter, however, takes the form $[L_2ClCu(\mu\text{-}L)CuClL]$, with both three- and four-coordinate copper(I) atoms, the Cu-(μ-)S distance in the latter being long (2.631(3) Å). Again, intradimer hydrogen-bonding, this time from an NH group on each ligand to the bromide, is significant; there is also an interdimer hydrogen-bond to one of the sulfur atoms, these linking the layers of the structure which lie normal to c^* (Figure 5b). We finally note an adduct of stoichiometry intermediate between 1:2 and 1:3 forms, Cu_2SO_4/tu (1:5),[28] in which polymeric chains of alternating trigonal and tetrahedral copper atoms are found

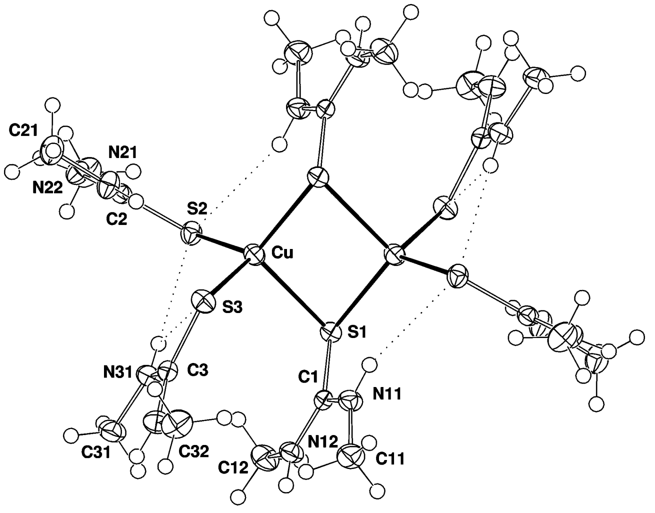


Figure 4. Dimeric $[Cu_2(dmtu)_6]^{2+}$ cation of CuI/dmtu (1:3), projected normal to the Cu_2S_2 plane, showing the intradimer hydrogen-bonds. The cation of the nitrate is similar, with a similar hydrogen-bonding pattern.

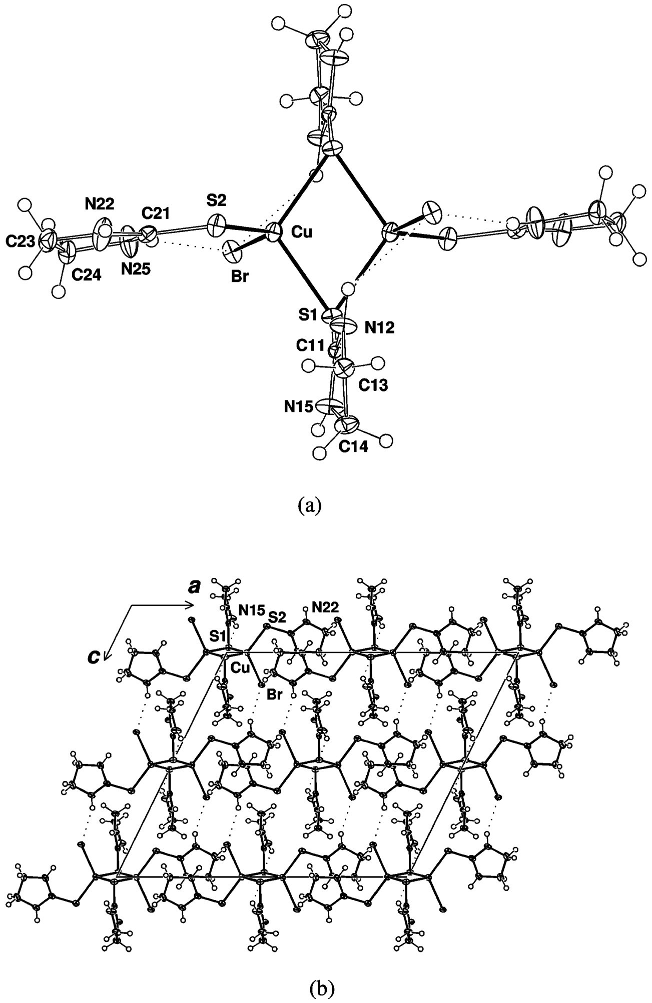


Figure 5. (a) $[Br_2Cu_2(etu)_4]$ dimer (ca. 153 K), projected normal to the Cu_2S_2 plane, showing the intradimer hydrogen-bonds. (b) Unit cell contents, projected down *b*, showing the interdimer hydrogen-bonds between the layers of the structure.

(the sulfate counterions being uncoordinated), with a further adduct of the same stoichiometry (L = mimtH; X = SO_4) taking the form $[L_2Cu(\mu\text{-}L)CuL_2](SO_4)$.

Oligomers of higher nuclearity hitherto recorded are (with one (hexanuclear) exception) all based on tetrameric units, mostly not adamantanoid. The "naked" $[Cu_4L_6]^{4+}$ form, containing three-coordinate copper(I) atoms, has been recorded in the nitrate tetrahydrate, $[Cu_4(tu)_6](NO_3)_4 \cdot 4H_2O$[43] and $[Cu_4(tu)_6](SO_4)(HSO_4)_2 \cdot H_2O$[44,45] and $(SO_4)_2 \cdot 2H_2O$ salts;[44] some or all of the copper(I) atoms achieve four-coordination with additional terminal or (μ_2-*S*-tu) groups (the latter bridging clusters) in $[Cu_4(tu)_7](SO_4)_2 \cdot H_2O$ and $[Cu_4(tu)_9](NO_3)_4$ (*I*2/*c* form; tetrahydrate). In a pair of adducts, one with ethylthiourea ("ettu") as ligand, the other with allylthiourea ("atu"), however, the fourth coordination sites are occupied by terminally bound iodide ions, thus $[(ICu)_4((x)tu)_6] \cdot H_2O$.[49] A similar array has been achieved in the present exercise with the parent tu ligand, which may be represented as $[(ICu)_4(\mu\text{-}S\text{-}tu)_6] \cdot H_2O$; two such formula units, devoid of crystallographic symmetry, comprise the asymmetric unit of the structure (one such unit in the ettu structure) (Table 8, Figure 6). As in the less complicated

Table 7. Selected Geometries, CuBr/etu (1:2)[a]

atoms	parameters	atoms	parameters
Distances (Å)			
Cu−Br	2.4987(3)	Cu−S(1)	2.3819(5)
Cu−S(2)	2.2841(6)	Cu−S(1′)	2.3851(5)
Cu···Cu′	2.7238(5)	S(1)···S(1′)	3.9122(7)
Angles (degree)			
Br−Cu−S(2)	121.39(2)	S(1)−Cu−S(2)	112.75(2)
Br−Cu−S(1)	94.02(1)	S(1′)−Cu−S(2)	106.16(2)
Br−Cu−S(1′)	111.72(2)	S(1)−Cu−S(1′)	110.31(2)
Cu−S(1)−C(11)	114.14(6)	Cu−S(2)−C(21)	107.46(7)
Cu′−S(1)−C(11)	110.72(6)	Cu−S(1)−Cu′	69.69(2)
Out-of-(SCN_2) Plane Copper Atom Deviations (δÅ)			
δCu/1	1.549(3)	δCu/2	0.067(4)
δCu′/1	−1.361(5)		
Dihedral Angles of the SCN_2 Planes to the Central Cu_2S_2 Plane (degree)			
Plane 1	83.81(6))	Plane 2	83.75(9)
(Intramolecular) Hydrogen-Bonds (Å)			
N(12)···Br′	3.382(2)	H(12)···Br′	2.7
N(25)···Br	3.376(3)	H(25)···Br	2.5

[a] Primed atoms are centrosymmetrically related. N,H(15) are hydrogen-bonded intermolecularly to S(1)($\bar{x}$, $\bar{y}$, $\bar{z}$) 3.366(2), 2.6; S(1)···S(1)($\bar{x}$, $\bar{y}$, $\bar{z}$) are 3.9375(5) Å. Also N,H(22)···Br (x, $1 - y$, $z - {}^1/_2$) are 3.386(2), 2.6 Å.

Table 8. Selected Geometries, $[I_4Cu_4(tu)_6](\cdot H_2O)$[a]

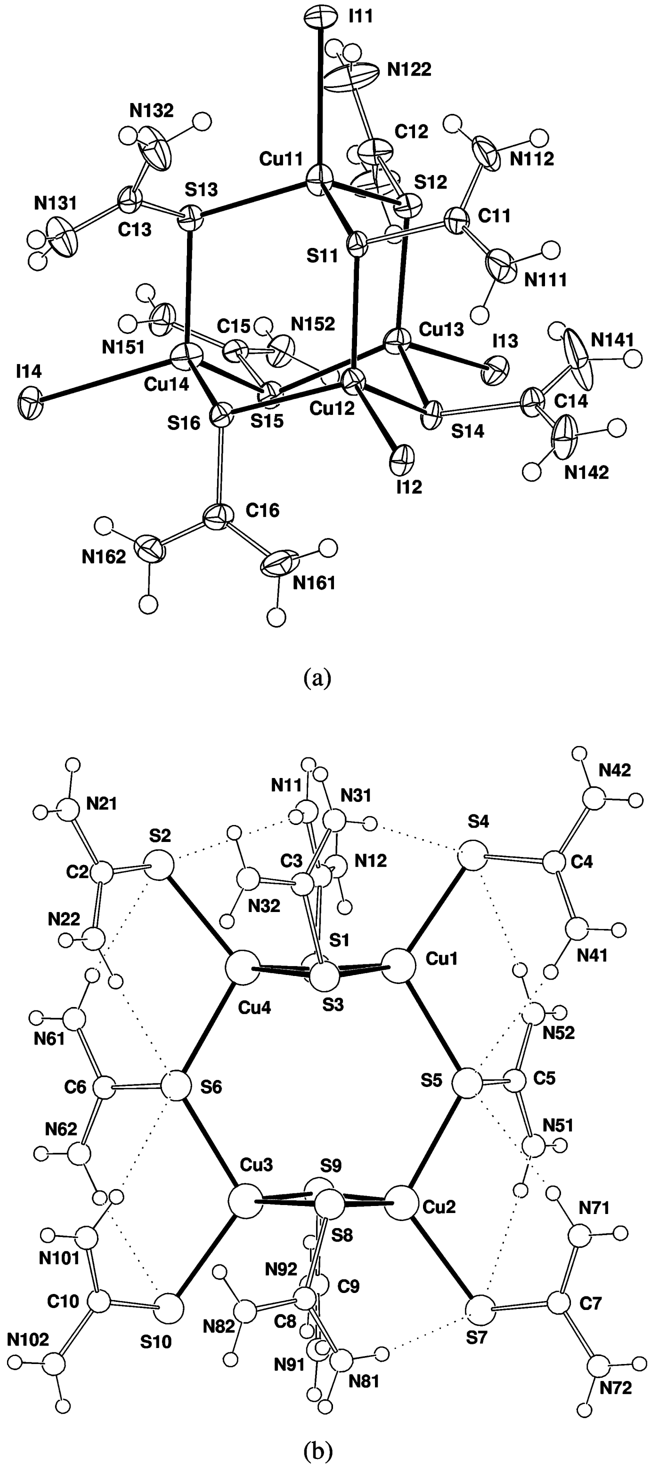
atoms	parameter	atoms	parameter
Distances (Å)			
Cu(n1)−I(n1)	2.7685(5), 2.7137(6)	Cu(n2)−I(n2)	2.6691(4), 2.6623(5)
Cu(n3)−I(n3)	2.7325(5), 2.5988(7)	Cu(n4)−I(n4)	2.7632(6), 2.7269(5)
Cu(n1)−S(n1)	2.2989(8), 2.3087(9)	Cu(n2)−S(n1)	2.3129(9), 2.3557(12)
Cu(n1)−S(n2)	2.2850(9), 2.3123(12)	Cu(n2)−S(n4)	2.3363(8), 2.3078(9)
Cu(n1)−S(n3)	2.3000(11), 2.3073(11)	Cu(n2)−S(n6)	2.2899(11), 2.3227(9)
Cu(n3)−S(n2)	2.2961(10), 2.5185(13)	Cu(n4)−S(n3)	2.3263(10), 2.3266(13)
Cu(n3)−S(n4)	2.2917(8), 2.2709(9)	Cu(n4)−S(n5)	2.2924(9), 2.3287(12)
Cu(n3)−S(n5)	2.3291(11), 2.3012(10)	Cu(n4)−S(n6)	2.3217(8), 2.3583(9)
Cu(n1)···Cu(n2)	3.7686(6), 3.9250(7)	Cu(n2)···Cu(n3)	3.8297(6), 3.8767(7)
Cu(n1)···Cu(n3)	3.6413(6), 4.1018(9)	Cu(n2)···Cu(n4)	3.7055(6), 3.8448(6)
Cu(n1)···Cu(n4)	3.7704(7), 3.7808(6)	Cu(n3)···Cu(n4)	3.7226(7), 3.9394(9)
Angles (degree)			
I(n1)−Cu(n1)−S(n1)	106.72(3), 115.36(3)	I(n2)−Cu(n2)−S(n1)	111.29(3), 113.61(3)
I(n1)−Cu(n1)−S(n2)	109.21(3), 107.23(3)	I(n2)−Cu(n2)−S(n4)	111.16(3), 108.44(3)
I(n1)−Cu(n1)−S(n3)	109.00(2), 111.36(4)	I(n2)−Cu(n2)−S(n6)	108.33(3), 111.37(2)
I(n3)−Cu(n3)−S(n2)	105.37(3), 102.30(3)	I(n4)−Cu(n4)−S(n3)	109.15(3), 107.30(4)
I(n3)−Cu(n3)−S(n4)	112.61(2), 117.72(3)	I(n4)−Cu(n4)−S(n5)	109.87(4), 112.79(3)
I(n3)−Cu(n3)−S(n5)	108.53(3), 121.53(3)	I(n4)−Cu(n4)−S(n6)	106.99(3), 109.72(3)
S(n1)−Cu(n1)−S(n2)	111.22(3), 107.67(4)	S(n1)−Cu(n2)−S(n4)	109.44(3), 111.95(4)
S(n1)−Cu(n1)−S(n3)	108.70(3), 109.01(4)	S(n1)−Cu(n2)−S(n6)	107.07(3), 102.73(4)
S(n2)−Cu(n1)−S(n3)	111.83(4), 105.68(4)	S(n4)−Cu(n2)−S(n6)	109.45(4), 108.59(3)
S(n2)−Cu(n3)−S(n4)	111.87(3), 103.51(4)	S(n3)−Cu(n4)−S(n5)	110.84(3), 107.85(5)
S(n2)−Cu(n3)−S(n5)	118.80(3), 102.16(5)	S(n3)−Cu(n4)−S(n6)	107.45(4), 114.93(4)
S(n4)−Cu(n3)−S(n5)	99.83(3), 106.65(4)	S(n5)−Cu(n4)−S(n6)	112.40(3), 104.37(4)
Cu(n1)−S(n1)−C(n1)	108.6(1), 113.4(1)	Cu(n1)−S(n2)−C(n2)	106.8(1), 115.3(5)/103.4(4)
Cu(n2)−S(n1)−C(n1)	106.4(1), 112.1(2)	Cu(n3)−S(n2)−C(n2)	110.8(2), 110.5(4)/105.3(4)
Cu(n1)−S(n1)−Cu(n2)	109.60(4), 114.59(4)	Cu(n1)−S(n2)−Cu(n3)	105.28(5), 116.16(4)
Cu(n1)−S(n3)−C(n3)	107.4(1), 111.5(1)	Cu(n2)−S(n4)−C(n4)	110.6(1), 112.3(1)
Cu(n4)−S(n3)−C(n3)	105.1(1), 114.6(2)	Cu(n3)−S(n4)−C(n4)	109.8(1), 110.6(2)
Cu(n1)−S(n3)−Cu(n4)	109.17(3), 109.35(6)	Cu(n2)−S(n4)−Cu(n3)	111.68(3), 115.71(5)
Cu(n3)−S(n5)−C(n5)	107.3(1), 107.2(1)	Cu(n2)−S(n6)−C(n6)	107.5(1), 107.5(1)
Cu(n4)−S(n5)−C(n5)	107.9(1), 105.6(2)	Cu(n4)−S(n6)−C(n6)	104.6(1), 103.1(1)
Cu(n3)−S(n5)−Cu(n4)	107.31(4), 116.61(4)	Cu(n2)−S(n6)−Cu(n4)	106.93(4), 110.44(3)
Out-of-(SCN_2) Plane Deviations, δÅ, of Associated Copper Atoms			
δCu(n1)/n1	0.834(7), 0.868(5)	δCu(n2)/n1	1.408(5), 0.879(5)
δCu(n1)/n2	1.469(5), −0.33(2)/−0.32(2)	δCu(n3)/n2	0.857(6), 1.92(1)/2.226(8)
δCu(n1)/n3	0.792(6), 0.634(6)	δCu(n4)/n3	1.524(5), 1.293(5)
δCu(n2)/n4	1.751(5), 0.997(7)	δCu(n3)/n4	0.113(8), 0.735(8)
δCu(n3)/n5	1.723(3), 1.000(6)	δCu(n4)/n5	0.510(5), 1.042(6)
δCu(n2)/n6	0.404(6), 0.512(6)	δCu(n4)/n6	1.850(4), 1.754(4)
Intramolecular Hydrogen-Bonds (Å)			
I(n1)···N(n12)	3.778(4), 3.702(5)	I(n2)···N(n11)	3.702(4), 3.674(3)
H(n1d)	3.0, 2.8	H(n1b)	2.8, 2.8
N(n22)	3.641(4), 3.814(13)	N(n42)	3.787(3), 3.611(6)
H(n2d)	2.8, 3.2	H(n4d)	3.0, 2.7
N(n32)	3.732(4), 3.717(3)	N(n61)	3.738(4), 3.993(4)
H(n3d)	2.9, 2.9	H(n6b)	3.0, 3.2
I(n3)···N(n21)	3.703(3), 3.546(12)	I(n4)···N(n31)	3.694(4), 3.626(5)
H(n2b)	2.9, 2.8	H(n3b)	2.8, 2.8
N(n41)	3.827(5), 3.572(4)	N(n51)	3.707(3), 3.762(4)
H(n4b)	3.1, 2.7	H(n5b)	2.9, 2.9
N(n52)	3.672(3), 3.728(4)	N(n62)	3.636(3), 3.688(3)
H(n5d)	2.9, 2.9	H(n6d)	2.8, 2.9

[a] The two values in each entry are for tetramers 1, 2.

adducts, hydrogen-bonding is an essential ingredient in the overall picture of bonding, perhaps contributing significantly to the stability of this and the other above species; here the six HN−C−NH units tidily bridge pairs of iodine atoms on each of the six edges of the I_4 tetrahedron, conforming to the overall symmetry. Intercluster hydrogen-bonding is less pronounced, with some tendency for pairwise interaction by the remaining outwardly directed "a,c" hydrogen atoms of each ligand with nearby iodine atoms.

Comparison with the "naked" $[Cu_4(tu)_6]^{4+}$ clusters is of interest: in the "naked" species, the geometry about the copper(I) atom approaches trigonal planarity, the sum of the three angles at each copper atom subtended by the sulfur atoms approaching 360°, whereas in the pair of present (and related) arrays those sums are nearer 330°. Cu−S in the present arrays lie about 2.3 Å with a considerable divergence, Cu(23)−S(22) is as high as 2.519(1) Å, whereas in the naked clusters Cu−S distances are disposed about 2.2_5 Å. The Cu−S−Cu angles at the sulfur atoms in the present are distributed around 105°; in the "naked" clusters, the mode is more nearly 80°.

The present study also defines structurally, for the first time, a compound of CuX/tu (4:11) stoichiometry, for X = NO_3; in detail; however, the compound is shown to be of



(a)

(b)

Figure 6. (a) Adamantanoid tetramer (1) of $[I_4Cu_4(tu)_6]\cdot H_2O$. (Tetramer 2 is similar). (b) The nonadamantanoid tetrameric cation of $[Cu_4tu_{10}](NO_3)_4\cdot tu\cdot 3H_2O$.

the form $[Cu_4(tu)_{10}](NO_3)_4\cdot tu\cdot 3H_2O$, one of the thiourea components, unusually, being uncoordinated, with the full formula unit, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. (Note (Table 1) that this seems to be the first copper(I)/thiourea compound of 4:11 stoichiometry (even if it is only a 4:10 complex)). The tetranuclear cation is unusual and not of the adamantanoid form, although it is related to that by two bond switches: Cu(1)−S(3) → Cu(2)−S(3); Cu(2)−S(9) → Cu(1)−S(9)): two pairs of $[(tu)_2Cu(\mu\text{-}S\text{-}tu)_2Cu(tu)_2]^{2+}$ units are bridged by common terminal tu units to form the tetrameric cation shown in Figure 6b). The Cu_4S_{10} array approaches *mmm* symmetry, which is degraded to more nearly *mm* (both planes normal to the plane of the page in the Figure) by the dispositions of the tu units which link the binuclear pairs, that in turn being obviated by the dispositions of the bridging tu groups of the pairs. As elsewhere, the stability of the array appears to be considerably enhanced by the hydrogen-

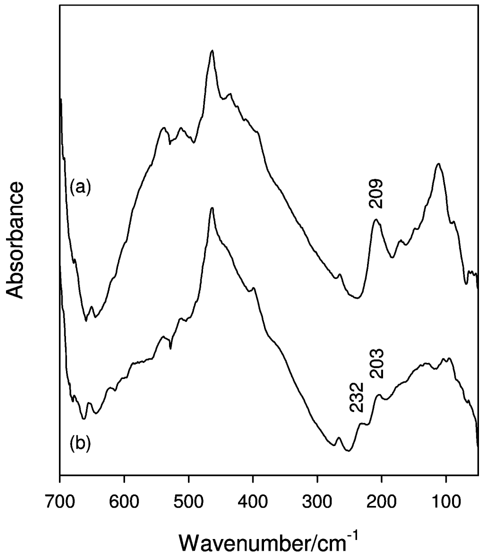


Figure 7. Far-IR spectra of (a) $[Cu(tu)_4]_2(SiF_6)$ and (b) $[Cu_4(tu)_{10}](SiF_6)_2$. Bands assigned to ν(CuS) are labeled with their wavenumbers.

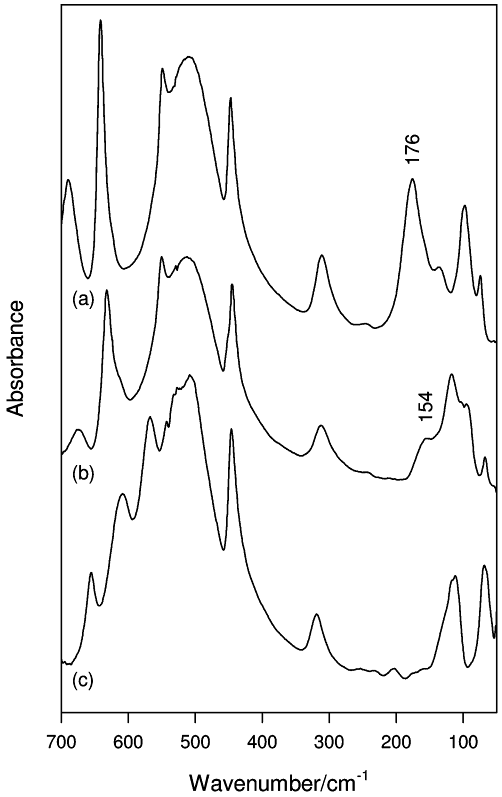


Figure 8. Far-IR spectra of (a) $[ClCu(dmtu)_3]$, (b) $[BrCu(dmtu)_3]$, and (c) $[Cu_2(dmtu)_6]I_2$. Bands assigned to ν(CuX) are labeled with their wavenumbers.

bonding within the cation. The hydrogen atoms designated "B" of all NH_2 groups contact nearby sulfur atoms (Table 9), with the exception of those of the four groups 21, 42, 72, 102 at the periphery; the "B" atoms of these groups, together with all of the other "A"-hydrogen atoms interact with anions or residues assigned as water molecule oxygen atoms, the latter and the anions lying in tunnels through the lattice parallel to *a*. The perturbation of the groups 1,3,8,9 from the higher symmetry is associated with the disposition of the hydrogen bonds, and although geometries are somewhat erratic throughout the cation in consequence of the hydrogen-bonding array, lengthening of the associated Cu(1)−S(1), Cu(4)−S(3), Cu(2)−S(9), Cu(3)−S(8) bonds is consistent with the local quasi-2-axis (lying vertical in the page) thereby imposed (Table 9). A similar structure has been defined in ref 54 with the ligand benzimidazole-2-thione, which preserves the "B"-hydrogen atoms, the "A" being lost by fusion of the aromatic ring. That cation is disposed about a crystallographic inversion center, and, although hydrogen-bonding plays a significant role in component dispositions and core geometries therein, other imperatives are imposed by the large planar components of the ligands. The present $[Cu_4(tu)_{10}]^{4+}$ species is precursive of the $[Cu_4(tu)_{12}]^{4+}$ cationic form found in the hydrated sulfate of ref 56; in that we find that the incorporation of two further tu ligands results in all copper atoms now having $[(\text{terminal-tu})_2Cu(\text{bridging-tu})_2]$ environments, resulting in a single eight-membered ring of "equivalent", alternating copper and sulfur atoms. By contrast, the present structure may be augmented to the previously described $[Cu_6(tu)_{14}]^{6+}$ array (as its perchlorate; ref 57) by the further incorporation of a pair of $[Cu(tu)_2]^+$ components between the sulfur atoms of the pair of $[Cu(\mu\text{-}S\text{-tu})_2Cu]^{2+}$ rhombs. In view of the readiness whereby such additional components may augment the present structure, despite the stability endowed by the hydrogen-bonding, it is of interest to note the uncoordinated thiourea ligand in the present lattice.

Vibrational Spectroscopy. The far-IR spectra of several sets of complexes rendered accessible by the present study are shown in Figures 7−9. The spectra of the unsubstituted thiourea complexes can be interpreted on the basis of the principles established in a previous study.[50] The ν(CuS), ν(CuX), and ν(CS) assignments are summarized in Table 10.

The spectrum of $[Cu_4(tu)_{10}](SiF_6)_2 \cdot H_2O$ is compared with that previously determined for $[Cu(tu)_4]_2(SiF_6)$[5] in Figure 7. It shows two bands attributable to ν(CuS) at 203, 232 cm^{-1} (Figure 7b). There are corresponding bands in the Raman spectrum at 202, 234 cm^{-1}. This compound consists of six-membered rings of alternating Cu and S atoms connected by sulfur bridges to form chains, which are in turn interconnected via a Cu_2S_2 four-membered ring to form a three-dimensional polymer with *d*(CuS) in the range 2.27−2.43 Å (av 2.34 Å).[55] According to a previously established relationship between *d*(CuS) and ν(CuS),[50] this corresponds to a ν(CuS) range of 160−239 cm^{-1} (av 201 cm^{-1}). While the average *d*(CuS) in both of the above compounds are very similar, the range is considerably wider in $[Cu_4(tu)_{10}](SiF_6)_2$, leading to a greater spread of vibrational frequencies and to a splitting of the ν(CuS) band.

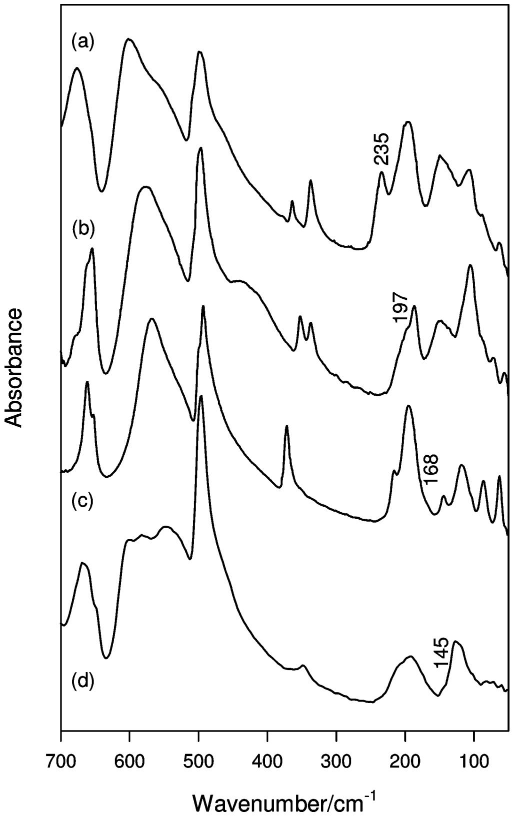


Figure 9. Far-IR spectra of (a) $[Cl_2Cu_2(etu)_4]$, (b) $[Br_2Cu_2(etu)_4]$, (c) $[ICu(etu)_2]$, and (d) $[ICu(etu)_2]_3$. Bands assigned to ν(CuX) are labeled with their wavenumbers.

The far-IR and Raman spectra of the ionic $[Cu(tu)_3]^{+}_{(\infty|\infty)}X^-$ (X = Cl, Br, I;) show ν(CuS) bands in the range 202−217 cm^{-1} (Table 10). No strongly halogen-dependent bands are present, consistent with the fact that all three compounds contain unbound ionic halide. However, a small upward shift in ν(CuS) from X = Cl to X = Br, I is observed, and this is consistent with a corresponding slight decrease in the mean *d*(CuS) in this series (see crystal structure results above). The far-IR and Raman spectra of the adamantanoid $[I_4Cu_4(tu)_6]\cdot H_2O$ show ν(CuS) bands at 227, 217 cm^{-1}, respectively (Table 10). The further increase relative to the values for $[Cu(tu)_3]^{+}_{(\infty|\infty)}X^-$ is consistent with the lower mean *d*(CuS) found in this compound. The Raman spectrum shows a strong band at 143 cm^{-1} with a weak IR counterpart at 139 cm^{-1}, assigned to ν(CuI) of the terminal CuI bonds in the structure. There is no corresponding strong band in the Raman spectra of the other thiourea complexes discussed above, and the assignment is consistent with the ν(CuI) wavenumbers observed in a range of copper iodide complexes with amine, phosphine, and arsine ligands.[71,72]

The far-IR spectra of $[XCu(dmtu)_3]$ (X = Cl, Br) show ν(CuX) at 176, 154 cm^{-1}, respectively (Figure 8a,b), with closely corresponding bands in the Raman spectra (Table

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(71) Bowmaker, G. A.; Healy, P. C.; Kildea, J. D.; White, A. H. *Spectrochim. Acta* **1988**, *44A*, 1219–1223.

(72) Bowmaker, G. A.; Hart, R. D.; de Silva, E. N.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1997**, *50*, 553–566.

Table 9. Selected Cation Geometries, $[Cu_4tu_{10}](NO_3)_3 \cdot tu \cdot 3H_2O$[a]

atoms	parameter	atoms	parameter	atoms	parameter	atoms	parameter
			Distances (Å)				
S(5)−Cu(1)	2.336(3)	S(5)−Cu(2)	2.344(3)	S(6)−Cu(3)	2.321(3)	S(6)−Cu(4)	2.335(3)
Cu(1)−S(4)	2.305(3)	Cu(2)−S(7)	2.313(3)	Cu(3)−S(10)	2.270(3)	Cu(4)−S(2)	2.277(4)
Cu(1)−S(3)	2.315(4)	Cu(2)−S(8)	2.334(4)	Cu(3)−S(9)	2.359(4)	Cu(4)−S(1)	2.325(4)
Cu(1)−S(1)	2.438(4)	Cu(2)−S(9)	2.418(4)	Cu(3)−S(8)	2.423(4)	Cu(4)−S(3)	2.415(4)
Cu(1)···Cu(2)	4.061(2)			Cu(3)···Cu(4)	3.999(2)		
Cu(1)···Cu(4)	2.668(2)			Cu(2)···Cu(3)	2.671(2)		
S(1)···S(3)	3.922(5)			S(8)···S(9)	3.947(5)		
S(1)···S(9)	3.836(4)			S(3)···S(8)	3.905(4)		
			Angles (degree)				
Cu(1)−S(5)−Cu(2)	120.4(2)			Cu(3)−S(6)−Cu(4)	118.4(2)		
S(5)−Cu(1)−S(4)	114.6(1)	S(5)−Cu(2)−S(7)	113.9(1)	S(6)−Cu(3)−S(10)	113.4(1)	S(6)−Cu(4)−S(2)	110.7(1)
S(5)−Cu(1)−S(1)	102.8(1)	S(5)−Cu(2)−S(8)	107.9(1)	S(6)−Cu(3)−S(8)	104.3(1)	S(6)−Cu(4)−S(1)	110.5(1)
S(5)−Cu(1)−S(3)	105.3(1)	S(5)−Cu(2)−S(9)	100.1(1)	S(6)−Cu(3)−S(9)	107.8(1)	S(6)−Cu(4)−S(3)	98.0(1)
S(4)−Cu(1)−S(1)	102.9(1)	S(7)−Cu(2)−S(8)	115.6(1)	S(10)−Cu(3)−S(8)	111.3(1)	S(2)−Cu(4)−S(1)	113.0(1)
S(4)−Cu(1)−S(3)	119.0(1)	S(7)−Cu(2)−S(9)	105.9(1)	S(10)−Cu(3)−S(9)	108.8(1)	S(2)−Cu(4)−S(3)	112.1(1)
S(1)−Cu(1)−S(3)	111.2(1)	S(8)−Cu(2)−S(9)	112.3(1)	S(8)−Cu(3)−S(9)	111.3(1)	S(1)−Cu(4)−S(3)	111.7(1)
Cu(1)−S(4)−C(4)	108.0(4)	Cu(2)−S(7)−C(7)	107.4(4)	Cu(3)−S(10)−C(10)	108.0(5)	Cu(4)−S(2)−C(2)	110.0(5)
Cu(1)−S(5)−C(5)	105.6(4)	Cu(2)−S(5)−C(5)	106.6(4)	Cu(3)−S(6)−C(6)	106.1(4)	Cu(4)−S(6)−C(6)	106.5(4)
Cu(1)−S(1)−Cu(4)	68.1(1)	Cu(1)−S(3)−Cu(4)	68.6(1)	Cu(2)−S(8)−Cu(3)	68.3(1)	Cu(2)−S(9)−Cu(3)	68.0(1)
Cu(1)−S(1)−C(1)	106.5(5)	Cu(1)−S(3)−C(3)	110.0(5)	Cu(2)−S(8)−C(8)	111.4(5)	Cu(2)−S(9)−C(8)	108.2(5)
Cu(4)−S(1)−C(1)	110.6(5)	Cu(4)−S(3)−C(3)	95.9(5)	Cu(3)−S(8)−C(8)	95.1(5)	Cu(3)−S(9)−C(9)	108.5(5)

Atoms	Parameter	Atoms	Parameter
	Hydrogen-Bonds (Intramolecular) (Å)		
N(51),H(51B)···S(7)	3.52(1), 2.6	N(61),H(61B)···S(2)	3.35(1), 2.5
N(52),H(52B)···S(4)	3.50(1), 2.6	N(62),H(62B)···S(10)	3.36(1), 2.5
N(41),H(41B)···S(5)	3.52(1), 2.7	N(71),H(71B)···S(5)	3.51(1), 2.7
N(101),H(10B)···S(6)	3.41(1), 2.6	N(22),H(22B)···S(6)	3.45(1), 2.6
N(11),H(11B)···S(2)	3.35(1), 2.7	N(31),H(31B)···S(4)	3.41(1), 2.5
N(81),H(81B)···S(7)	3.42(1), 2.6	N(91),H(91B)···S(10)	3.31(1), 2.9
	Hydrogen-Bonds (Uncoordinated Thiourea) (Å)		
N(111),H(11C)···O(33^{i})	3.05(2), 2.3	N(112),H(11E)···O(32^{i})	3.04(2), 2.2
(11D)···O(13^{ii})	3.04(2), 2.2	H(11F)···O(3^{iii})	3.04(2), 2.2
		H(11F)···O(4^{iii})	3.00(3), 2.2

[a] Note that NH_2 hydrogen atoms are labelled A, B, the latter nearer the associated sulfur (exception: those associated with N(102)(H(10C,D)) and N(111)(H(11C,D)) and N(112)(H(E,F))). Coordinate transformations: (i) $^1/_2 - x$, $y - {}^1/_2$, $1^1/_2 - z$; (ii) $x - 1$, y, z; (iii) x, $y - 1$, z.

Table 10. Copper−Sulfur, Copper−Halogen, and Carbon−Sulfur Vibrational Wavenumbers (cm^{-1}) from IR and Raman Spectra

	ν(CuS)		ν(CuX)		ν(CS)	
Compound[a]	IR	Raman	IR	Raman	IR	Raman
$[Cu(tu)_4]_2SiF_6$	209	204			710	716
$[Cu_4(tu)_{10}]_2(SiF_6)_2$	203, 232	202, 234			706	713
$[Cu_4(tu)_{10}](NO_3)_4 \cdot tu \cdot 3H_2O$	227	219			706−721	693−715
$[Cu(tu)_3]Cl$	202				714	706, 714
$[Cu(tu)_3]Br$	209	210			712	706, 712
$[Cu(tu)_3]I$	198, 217	199, 214			713	707
$[I_4Cu_4(tu)_6] \cdot H_2O$	227	217	139		704	709
$[ClCu(dmtu)_3]$			176	185	728	728
$[BrCu(dmtu)_3]$			154	150	727	727
$[Cu_2(dmtu)_6]I_2$					722	723
$[Cl_2Cu_2(etu)_4]$			235	235	499	501
$[Br_2Cu_2(etu)_4]$			197		497	498
$[ICu(etu)_2]$			168		493	497
$[ICu(etu)_2]_3$			145		497	503

[a] tu = thiourea; dmtu = dimethylthiourea; etu = ethylenethiourea.

10). This is consistent with the observed incorporation of halide in the copper coordination sphere in these compounds. The far-IR spectrum of ionic $[Cu_2(dmtu)_6]I_2$ (Figure 8c) is that of the $[Cu_2(dmtu)_6]^{2+}$ complex. This and the corresponding Raman spectrum show a number of bands below 200 cm^{-1}, but there is insufficient data to allow specific assignments.

The far-IR spectra of $[X_2Cu_2(etu)_4]$ (X = Cl, Br) and $[ICu(etu)_2]$ are shown in Figure 9, and the ν(CuX) assignments are based on the strong downward shift in wavenumber of the bands from X = Cl to I (Table 10). The assignments of ν(CuX) = 235, 197 cm^{-1} (X = Cl, Br; Figure 9 a,b) are in good agreement with the values 234, 197 cm^{-1} predicted on the basis of the mean Cu−Cl and the Cu−Br bond lengths (2.30(3),[7] 2.4987(3) Å).[71] Because of the complex (and different) structures of these dimeric compounds, there is a range of Cu−S bond lengths, so ν(CuS) bands are expected to be complex, and the expected region is masked by the ligand band at about 200 cm^{-1}. The monomeric iodide $[ICu(etu)_2]$ has the simplest structure, with two nearly equal

Cu−S and CuI bond lengths, av 2.235(6), 2.554(21) Å respectively. According to the previously determined correlations these correspond to ν(CuS) = 232, ν(CuI) = 170 cm^{-1},[50,71] but no bands are evident in the spectrum at these positions, although a weak shoulder at 168 cm^{-1} is possibly due to ν(CuI) (Figure 9c). For the cyclic trimer structure $[\mathrm{ICu(etu)_2}]_3$, the Cu−S (bridging and terminal) and Cu−I bond lengths lie in the ranges 2.302(4)−2.430(4) and 2.617(2)−2.638(2), corresponding to ν(CuS) = 201−154, ν(CuI) = 148−141 cm^{-1}. The ν(CuS) wavenumber region is overlapped by the ligand band at about 200 cm^{-1}, but a possible ν(CuI) band occurs as a weak shoulder at 145 cm^{-1} (Figure 9d). The greater complexity of the cyclic trimer relative to the trigonal monomer structure is evident in the broadening and partial splitting of several of the bands in the far-IR spectra (Figures 9c,d).

The ν(CS) assignments in Table 10 are based on those of the uncomplexed ligands and lie at about 700 cm^{-1} for the thiourea and alkyl-substituted thiourea ligands[50,73] and at about 500 cm^{-1} for ethylenethiourea.[74] The ν(CS) wavenumbers for the tu complexes show a downward shift of up to 30 cm^{-1} relative to the uncomplexed ligand, and multiple peaks are observed in some cases. This is most clearly evident in the Raman spectra of $[\mathrm{Cu(tu)_3}]$X (X = Cl, Br) where doublets are observed which are probably due to the presence of two different bonding modes (terminal and bridging) of the thiourea ligand. In the case of $[\mathrm{Cu_4(tu)_{10}}](\mathrm{NO_3})_4\cdot\mathrm{tu}\cdot3\mathrm{H_2O}$, an additional weak band is observed at 746 (IR), 744 (R) cm^{-1}, which is higher than that of solid thiourea (728 (IR), 732 (R) cm^{-1}),[50] and is assigned to the uncoordinated thiourea molecule in this complex. The ν(CS) wavenumbers for the dmtu and etu complexes are less sensitive to coordination and do not show any splitting in the cases where both terminal and bridging thiourea ligands are present, for example, $[\mathrm{X_2Cu_2(etu)_4}]$ (X = Cl, Br).

Conclusion

New methods for the synthesis of bulk samples of copper(I) complexes with thiourea ligands have been developed, and the structures of a number of new complexes have been determined. These results further emphasize the structural diversity of copper(I) thiourea chemistry, and the structure of the new complex $[\mathrm{I_4Cu_4(tu)_6}]\cdot\mathrm{H_2O}$ provides another example of the ubiquity of the adamantanoid $\mathrm{Cu_4S_6}$ unit in copper(I) thiourea chemistry. However, the possibility of forming a cationic derivative of this structure in which the iodide ligands are replaced by four terminal tu ligands is not realized in a newly defined $[\mathrm{Cu_4(tu)_{10}}]^{4+}$ complex, which has a different, although still quite symmetrical, tetranuclear structure involving six bridging and four terminal tu ligands.

Infrared and Raman spectra of several families of copper(I)/thiourea complexes have been recorded, and the metal−ligand vibrational frequencies have assigned in many cases. The results confirm previously observed correlations between the vibrational frequencies and the corresponding bond lengths for complexes of the unsubstituted thiourea ligand. A mechanochemical/IR method was used to synthesize $[\mathrm{I_3Cu_3(etu)_6}]$ from CuI and etu, and to monitor the transition from $[\mathrm{ICu(etu)_2}]$ to $[\mathrm{I_3Cu_3(etu)_6}]$, providing further demonstrations of the utility of this method in synthesis and in the study of polymorphic transitions in metal complexes.[66,67]

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Note Added in Proof: A recent publication (Lobana, T. S.; Sharma, R.; Hundal, G.; Butcher, R. J. *Inorg. Chem.* **2006**, *45*, 9402–9409) describes a new polymorph of CuI/etu (1:1),[40,41] together with a report of the present CuBr/etu (1:2) adduct.

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