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Syntheses and structures of $[Ag(etu)_3]_2SO_4$ and $[Cu(etu)_3]_3$ (etu = ethylenethiourea): a new μ_3 -S coordination mode for etu

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Syntheses and structures of $[\text{Ag}(\text{etu})_3]_2\text{SO}_4$ and $\{[\text{Cu}(\text{etu})\text{I}]_3\}_n$ (etu = ethylenethiourea): a new $\mu_3\text{-S}$ coordination mode for etu

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$[\text{Ag}(\text{etu})_3]_2\text{SO}_4$ (**1**) and $\{[\text{Cu}(\text{etu})\text{I}]_3\}_n$ (**2**) (etu = ethylenethiourea) have been synthesized by reaction of etu with Ag_2SO_4 or CuI and their crystal structures determined. In **1** both crystallographically independent Ag^+ ions are trigonally coordinated by three monodentate etu ligands. Complex **2** is composed of a one-dimensional polymer assembled by cyclic $[\text{Cu}(\text{etu})\text{I}]_3$ trimers. In the $\{[\text{Cu}(\text{etu})\text{I}]_3\}_n$ polymer, the chair-type $\text{Cu}_4\text{S}_2\text{I}_2$ core is formed by $\mu_3\text{-S}$ bridging etu ligands and this represents a new coordination mode for etu. The Cu^+ ions have a distorted tetrahedral coordination geometry.

Keywords: Silver(I); Copper(I); Ethylenethiourea; Crystal structure; Coordination mode

1. Introduction

Ethylenethiourea (etu), and its *N*-mono or *N,N'*-dialkyl substituted derivatives, which contain chemically reactive thioamide groups, have invited considerable interest in their coordination behaviour [1, 2]. A series of silver(I) and copper(I) complexes with etu and its *N*-alkyl derivatives has been reported. The ligands display terminal monodentate thione-*S*, $\mu_2\text{-S}$ and $\mu_4\text{-S}$ bridging coordination modes, with the former being dominant; mononuclear complexes with trigonal [3–10], and tetrahedral [11] geometries at the metal are known. Both terminal thione-*S* and $\mu_2\text{-S}$ bridging coordination modes are observed in binuclear complexes such as $[\text{Cu}_2(\text{etu})_4\text{Cl}_2]$ [11], and $[\text{Cu}_2(\text{etu})_6](\text{ClO}_4)_2$ [12]. In the tetranuclear complex $[\text{Cu}_4(\text{etu})_9](\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ [13], a $\mu_4\text{-S}$ bridging ligand is found in the planar Cu_4 aggregate. However, the $\mu_3\text{-S}$ bridging mode has not been reported to date. With etu and its derivatives, copper(I) halides form either mononuclear [4–7] or binuclear complexes [11]. However, no polymeric copper(I) halide complex with etu has been reported as far as we know. Here, we report the synthesis and crystal structures of $[\text{Ag}(\text{etu})_3]_2\text{SO}_4$ (**1**) and $\{[\text{Cu}(\text{etu})\text{I}]_3\}_n$ (**2**). In the novel polynuclear $\{[\text{Cu}(\text{etu})\text{I}]_3\}_n$ complex, the $\mu_3\text{-S}$ coordination mode has been observed for the first time for etu.

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2. Experimental

2.1. Materials and measurements

All reagents were commercially available and used without further purification. FTIR spectra (KBr pellets) were recorded on a Nicolet Magna-IR 550 spectrophotometer. C,H,N analyses were obtained with a MOD 1106 system.

2.2. Syntheses

2.2.1. [Ag(etu)₃]₂SO₄ (1). A DMF solution (5 cm³) containing Ag₂SO₄ (0.312 g, 1 mmol) was added to a stirred solution of DMF (30 cm³) containing etu (0.306 g, 3 mmol). After stirring for 30 mins, the colourless solution was filtered and the filtrate left to stand at room temperature. Colourless blocky crystals of **1** were deposited after two weeks. Yield: 65%. Anal. Calcd for C₁₈H₃₆N₁₂O₄S₇Ag₂ (%): C, 23.38; H, 3.92; N, 18.18. Found: C, 23.25; H, 3.85; N, 17.91. IR (cm⁻¹): 3340s, 3260s, 2886m, 2604w, 1624w, 1525s, 1501s, 1462s, 1385m, 1370w, 1316m, 1281s, 1204s, 1115s, 1038m, 999m, 968m, 914m, 615m, 590m, 498m.

2.2.2. [{Cu(etu)I}₃] (2). A solution of CuI (0.190 g, 1 mmol) in DMF (5 cm³ L) was added to a stirred solution of DMF (30 cm³) containing etu (0.102 g, 1 mmol). After stirring for 30 mins, the resulting solution was left to stand at room temperature. Colourless blocky crystals of **2** were deposited after about one month. Yield: 85%. Anal. Calcd for C₉H₁₈N₆I₃S₃Cu₃ (%): C, 12.31; H, 2.07; N, 9.57. Found: C, 12.22; H, 2.11; N, 9.34. IR (cm⁻¹): 3330s, 3283s, 3260s, 2886m, 2573w, 1528vs, 1474m, 1385m, 1369w, 1319s, 1288s, 1200s, 1088s, 1038m, 988m, 968m, 911m, 702w, 525m, 490m.

2.3. Crystallography

Intensities were collected at 193(2) K on a Rigaku Mercury CCD diffractometer using the ω scan method with graphite-monochromated Mo-K α radiation ($\lambda = 0.071073$ nm) using a crystal of size $0.12 \times 0.11 \times 0.10$ mm³ for **1** and of $0.20 \times 0.19 \times 0.10$ mm³ for **2**. Absorption corrections were applied for all data using multi-phi scans. The structures were solved with direct methods using SHELXS-97 [14] and structure refinements were carried out against F^2 with SHELXL-97 [15]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters using a riding model. Technical details of data acquisition and selected refinement results are summarized in table 1.

3. Results and discussion

[Ag(etu)₃]₂SO₄ (**1**) crystallizes in the trigonal space group $R3c$ with six formula units in the unit cell. Fractional atomic coordinates and equivalent isotropic displacement

Table 1. Crystal data and structure refinement details for the complexes.

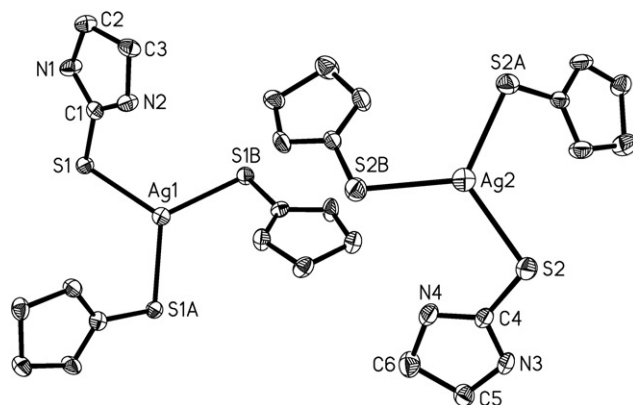
CCDC No.	607148	259627
Chemical formula	C ₁₈ H ₃₆ N ₁₂ O ₄ S ₇ Ag ₂	C ₉ H ₁₈ N ₆ I ₃ S ₃ Cu ₃
Formula weight	924.75	877.79
<i>T</i> (K)	193(2)	193(2)
λ (Mo-K α) (Å)	0.71073	0.71073
Space group	<i>R</i> 3 <i>c</i>	<i>P</i> 1̄
<i>a</i> (Å)	12.983(3)	7.9179(6)
<i>b</i> (Å)	12.983(3)	12.1698(10)
<i>c</i> (Å)	34.894(7)	12.6444(6)
α (°)		69.023(5)
β (°)		73.269(5)
γ (°)		87.855(7)
Volume (Å ³)	5093.6(17)	1086.56(13)
<i>Z</i>	6	2
<i>D</i> _C (g cm ⁻³)	1.809	2.683
Absorption coefficient (mm ⁻¹)	1.630	7.465
<i>F</i> (000)	2796	816
θ range for data collection (°)	3.14 $\leq \theta \leq$ 27.47	3.04 $\leq \theta \leq$ 25.35
Index ranges	-16 $\leq h \leq$ 15, -16 $\leq k \leq$ 16, -45 $\leq l \leq$ 38	-9 $\leq h \leq$ 9, -14 $\leq k \leq$ 14, -15 $\leq l \leq$ 15
Reflections collected	17892	10809
Independent reflections	2495 (<i>R</i> _{int} = 0.0563)	3970 (<i>R</i> _{int} = 0.0278)
Data/restraints/parameters	2495/1/132	3970/0/218
Goodness of fit on <i>F</i> ²	1.264	1.029
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0446, <i>wR</i> ₂ = 0.0588	<i>R</i> ₁ = 0.0231, <i>wR</i> ₂ = 0.0485
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0521, <i>wR</i> ₂ = 0.0599	<i>R</i> ₁ = 0.0283, <i>wR</i> ₂ = 0.0507
Largest diff. peak and hole (e Å ⁻³)	0.396 and -0.841	0.732 and -0.866

parameters for **1** are listed in table 2. The structure contains two crystallographically independent [Ag(etu)₃]⁺ cations. Both silver(I) ions are trigonally coordinated by three etu ligands (figure 1). In [Ag(1)(etu)₃]⁺ and [Ag(2)(etu)₃]⁺ the three Ag–S bonds are chemically equivalent. Ag–S bond lengths are 2.5060(13) for Ag(1)–S(1) and 2.4671(13) Å for Ag(2)–S(2), and are consistent with those in [Ag(Hmimt)₃]₂NO₃ (Hmimt = 1-methyl-2(3H)-imidazolinethione) (2.476(2)–2.510(2) Å) [10].

Although the oxygen atoms of the sulfate have no influence on coordination, they have significant influence on the crystal packing of [Ag(etu)₃]⁺ cations in **1**. Extensive hydrogen bonds are observed between SO₄²⁻ ions and –NH groups of etu, and four oxygen atoms of sulfate are involved in N–H...O hydrogen bonds. In the crystal structure, six [Ag(etu)₃]⁺ units (three [Ag(1)(etu)₃]⁺ and three [Ag(2)(etu)₃]⁺ units) assemble to form a planar hexagon around an SO₄²⁻ ion (figure 2). The central sulfate ion is in contact with the six [Ag(etu)₃]⁺ units through its O(2), O(2a) and O(2b) atoms by six N–H...O hydrogen bonds (2.855(5) Å for N(1)–H(1)...O(2) in [Ag(1)(etu)₃]⁺; 2.795(5) Å for N(3)–H(3)...O(2) in [Ag(2)(etu)₃]⁺) (table 3). The hexagons extend in the same manner with SO₄²⁻ ions forming a layered structure parallel to (001). In the layer, each [Ag(etu)₃]⁺ unit interacts with three SO₄²⁻ ions via three hydrogen bonds. The fourth oxygen atom of the sulfate ion forms a hydrogen bond [N(2)–H(2)...O(1)] between the layers, leading to a three-dimensional network. Changes to ligand dimensions on coordination involve a lengthening of the C–S distance from 1.694(4) [16] to 1.714(5) Å and a shortening of the N–C(=S) distance from 1.394(3) [16] to

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for **1**.

	x/a	y/b	z/c	$U(\text{eq})$
Ag(1)	0.6667	0.3333	0.514751(15)	0.02479(16)
Ag(2)	0.3333	0.6667	0.684170(16)	0.02983(18)
S(1)	0.64390(10)	0.13005(10)	0.51228(4)	0.0232(2)
S(2)	0.43338(12)	0.88565(10)	0.68136(3)	0.0290(3)
S(3)	0.6667	0.3333	0.63718(5)	0.0150(4)
O(1)	0.6667	0.3333	0.59507(14)	0.0292(13)
O(2)	0.5687(3)	0.2196(3)	0.65111(10)	0.0250(8)
N(1)	0.4593(4)	-0.0694(3)	0.54047(11)	0.0278(9)
N(2)	0.4784(4)	0.0907(4)	0.56612(12)	0.0258(10)
N(3)	0.6142(4)	1.0341(3)	0.63692(14)	0.0303(10)
N(4)	0.6003(4)	0.8614(4)	0.64085(13)	0.0297(10)
C(1)	0.5228(4)	0.0486(4)	0.54062(11)	0.0211(9)
C(2)	0.3628(4)	-0.1156(4)	0.56841(14)	0.0264(11)
C(3)	0.3719(4)	-0.0017(4)	0.58515(15)	0.0269(11)
C(4)	0.5546(4)	0.9274(4)	0.65230(14)	0.0207(10)
C(5)	0.7127(4)	1.0490(4)	0.61298(15)	0.0279(11)
C(6)	0.7094(5)	0.9308(5)	0.61838(16)	0.0345(13)

Figure 1. Structures of the two crystallographically independent $[\text{Ag}(\text{etu})_3]^+$ cations in the crystal structure of $[\text{Ag}(\text{etu})_3]_2\text{SO}_4$ with the atom labelling (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

1.322(5) \AA (table 3). Fractional atomic coordinates and equivalent isotropic displacement parameters are listed in table 4.

$[\{\text{Cu}(\text{etu})\text{I}\}_3]$ (**2**) crystallizes in the triclinic space group $P\bar{1}$ with $Z=2$ cell. The asymmetric unit is a cyclic $[\text{Cu}(\text{etu})\text{I}]_3$ trimer (figure 3), in which three Cu(I) ions are linked by three sulfur atoms from three etu ligands into an alternating six-membered Cu_3S_3 ring; each Cu(I) ion is also coordinated by a iodine atom pointing out of the ring. Cyclic $[\text{Cu}(\text{etu})\text{I}]_3$ trimers assemble into $\text{Cu}_4\text{S}_2\text{I}_2$ and $\text{Cu}_2\text{S}_4\text{I}_2$ cores (figure 4) which are alternately connected through Cu–S bonds forming neutral polymeric chains parallel to b (figure 5). The novel chair-type core $\text{Cu}_4\text{S}_2\text{I}_2$ is constructed by two cyclic $[\text{Cu}(\text{etu})\text{I}]_3$ trimers through bridges involving S(1) and I(1) atoms to complete the tetrahedral coordination geometry of the metal (figure 4). In the $\text{Cu}_4\text{S}_2\text{I}_2$ core, the central rhomboidal Cu_2S_2 unit is formed via a bridging S(1) atom with the imidazolidine ring

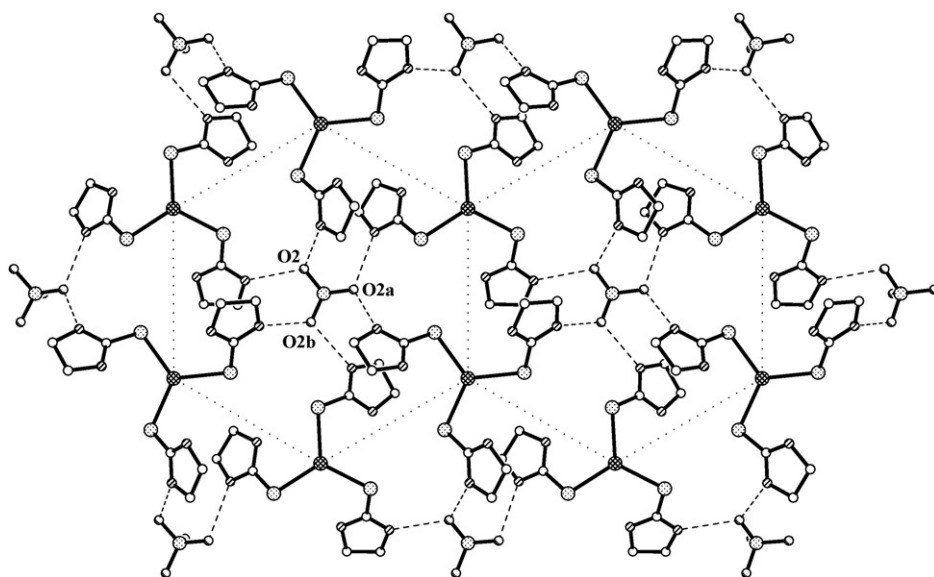


Figure 2. View of packing of $[\text{Ag}(\text{etu})_3]_2\text{SO}_4$ showing hydrogen bond interactions viewed along c . Hydrogen atoms are omitted for clarity.

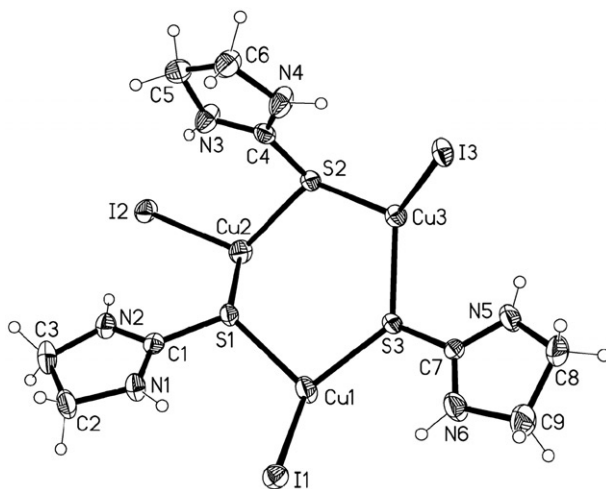
Table 3. Selected bond and hydrogen bond distances (\AA) and angles ($^\circ$) for **1**.

Ag(1)–S(1)	2.5060(13)	Ag(2)–S(2)	2.4671(13)
S(1)–C(1)	1.705(5)	S(2)–C(4)	1.717(5)
N(1)–C(1)	1.328(6)	N(1)–C(2)	1.458(6)
N(2)–C(1)	1.318(6)	N(2)–C(3)	1.460(6)
N(3)–C(4)	1.316(6)	N(3)–C(5)	1.457(6)
N(4)–C(4)	1.325(6)	N(4)–C(6)	1.468(6)
S(1)–Ag(1)–S(1) ^a	119.883(5)	S(2)–Ag(2)–S(2) ^b	119.844(4)
Ag(1)–S(1)–C(1)	102.70(17)	Ag(2)–S(2)–C(4)	105.01(15)
D–H...A	d(H...A)	d(D...A)	$\angle(\text{D–H}\cdots\text{A})$
N(3)–H(3)...O(2) ^c	1.92	2.795(5)	175.6
N(2)–H(2)...O(1)	2.26	3.036(4)	147.1
N(1)–H(1)...O(2) ^d	2.01	2.855(5)	159.4

adopting a *trans* position. Three crystallographically independent etu ligands show the μ -S bridging mode, but in two different ways. Ligand 1 acts as a μ_3 -S bridge with S(1) coordinating to Cu(1), Cu(1a) and Cu(2) within the $\text{Cu}_4\text{S}_2\text{I}_2$ core, whereas ligands 2 and 3 act as μ_2 -S bridging ligands. The μ_3 -S bridge observed in **2** represents a new coordination mode for etu. Cu–Cu distances range from 2.7517(9) to 2.9579(8) \AA (table 5) and are comparable to those observed in $[\text{Cu}_4(\text{etu})_9](\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ (2.849(1) \AA) [13] and $[\{\text{Cu}(\text{tzdt})\}_4]$ (tzdt = 1, 3-thiazolidine-2-thione) (2.692(4)–2.882(5) \AA) [17]. The copper(I) ions have distorted tetrahedral geometry (figure 4). Cu(1) has an S_3I donor set with bond angles at the metal ranging from 98.34(4) to 124.57(3) $^\circ$, and both Cu(2) and Cu(3) have an S_2I_2 donor set with bond angles at the metal ranging from 97.38(4) to 119.94(3) $^\circ$ (table 5). Cu–S distances (2.2833(10)–2.3865(11) \AA)

Table 4. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for **2**.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq)
Cu(1)	0.44719(7)	0.48482(4)	-0.08876(4)	0.02940(13)
Cu(2)	0.34095(7)	0.29888(4)	0.26798(4)	0.02821(13)
Cu(3)	0.43645(7)	0.11836(4)	0.04797(4)	0.02489(12)
I(1)	0.32774(3)	0.64076(2)	-0.24626(2)	0.02530(8)
I(2)	0.16245(4)	0.30564(2)	0.47514(2)	0.03043(8)
I(3)	0.26437(3)	0.00047(2)	-0.03293(2)	0.02496(8)
S(1)	0.25380(13)	0.42165(8)	0.10428(8)	0.0210(2)
S(2)	0.31992(13)	0.11812(8)	0.23720(8)	0.0229(2)
S(3)	0.52904(14)	0.30450(8)	-0.09405(8)	0.0248(2)
N(1)	0.0710(4)	0.6142(3)	0.0463(3)	0.0250(7)
N(2)	0.0553(4)	0.5433(3)	0.2325(3)	0.0261(8)
N(3)	-0.0149(4)	0.1033(3)	0.3757(3)	0.0336(9)
N(4)	0.0053(5)	0.0306(3)	0.2408(3)	0.0391(9)
N(5)	0.6165(5)	0.2084(3)	-0.2618(3)	0.0426(10)
N(6)	0.5790(5)	0.3938(3)	-0.3291(3)	0.0336(9)
C(1)	0.1221(5)	0.5318(3)	0.1283(3)	0.0202(8)
C(2)	-0.0385(6)	0.6959(4)	0.0917(4)	0.0332(10)
C(3)	-0.0556(6)	0.6428(4)	0.2239(4)	0.0385(11)
C(4)	0.0948(5)	0.0842(3)	0.2845(3)	0.0229(9)
C(5)	-0.1941(5)	0.0561(4)	0.4037(3)	0.0288(9)
C(6)	-0.1835(6)	0.0181(4)	0.2989(4)	0.0344(10)
C(7)	0.5753(5)	0.3019(3)	-0.2334(3)	0.0203(8)
C(8)	0.6332(6)	0.2316(4)	-0.3872(4)	0.0374(11)
C(9)	0.6391(7)	0.3660(4)	-0.4371(4)	0.0384(11)

Figure 3. Structure of the asymmetric trimeric unit $[\text{Cu}(\text{etu})\text{Br}]_3$ in **2** with the atom labelling (50% probability ellipsoids).

agree with those observed in other tetrahedrally coordinated Cu(I)-etu complexes (2.284(1)–2.362(1) \AA) [11, 12]. The Cu–I_t (terminal) distance (2.5897(6) \AA), which is comparable to that in the trigonally coordinated complex $[\text{Cu}(\text{petu})_2]\text{I}$ (petu = *N*-propylethylenethiourea) [5], is shorter than Cu–I_b (bridging) bonds (2.6230(5)–

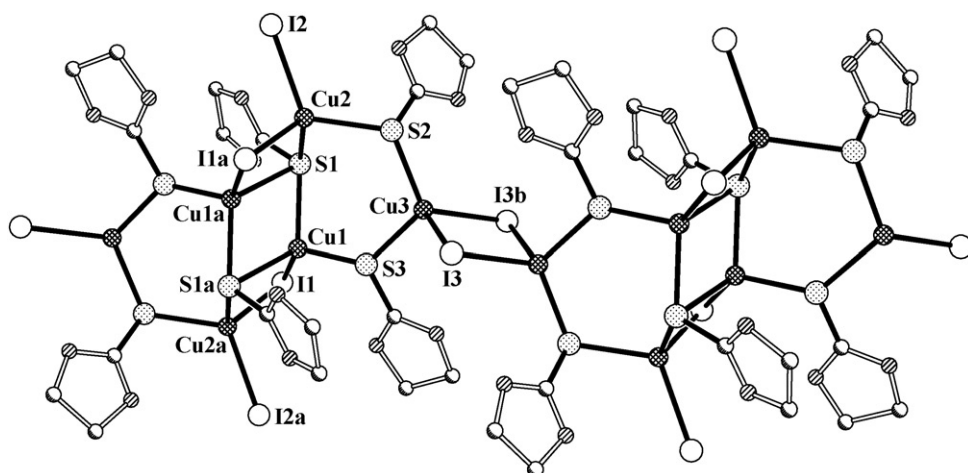


Figure 4. View of $\{[\text{Cu}(\text{etu})\text{I}]_3\}_n$ assembled from $[\text{Cu}(\text{etu})\text{I}]_3$ trimers. Hydrogen atoms are omitted for clarity.

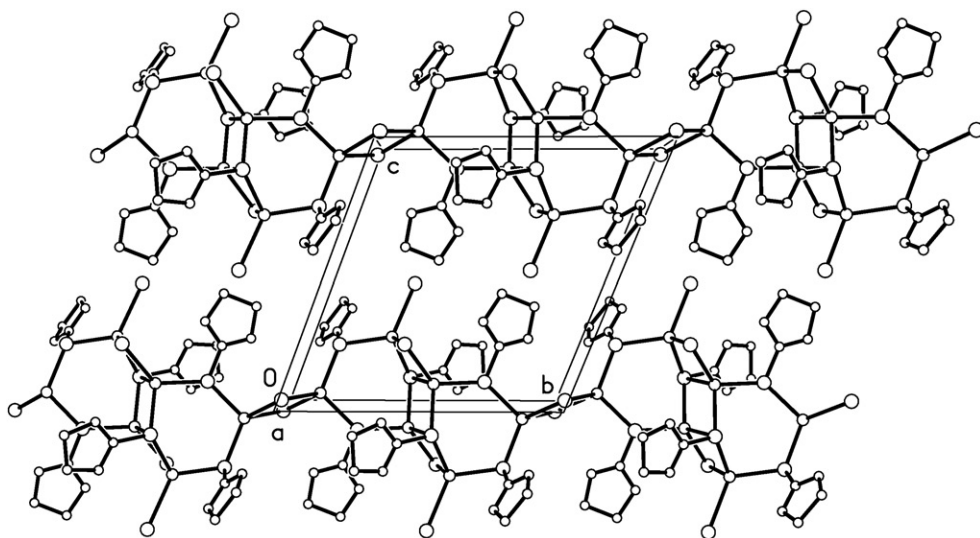


Figure 5. Crystal packing of **2** showing $\{[\text{Cu}(\text{etu})\text{I}]_3\}_n$ polymeric chains viewed along *a*. Hydrogen atoms are omitted for clarity.

2.7240(6) Å). The bridging angles Cu–I(1)–Cu and Cu–I(3)–Cu are 68.556(19) and 81.943(17)° (table 5), respectively. Compound **2** is the first example of a polynuclear copper(I) halide complex with etu.

In IR spectra of **1**, bands at 3260 (s), 1525 (s) cm^{-1} and 498 cm^{-1} can be assigned to $\nu(\text{NH})$, $\nu(\text{CN})$ and $\nu(\text{CS})$, respectively. These three bands in free etu ligand are observed at 3240, 1520 and 507 cm^{-1} [18], respectively. Thus positive shifts of $\nu(\text{NH})$ and $\nu(\text{CN})$, and a negative shift of $\nu(\text{CS})$ occur when etu coordinates to silver(I). The magnitude of the shifts of **2** is similar to those of **1**. These shifts are consistent with the fact that

Table 5. Selected bond distances (Å) and angles (°) for **2**.

Cu(1)⋯Cu(1a)	2.7517(9)	Cu(1)⋯Cu(2a)	2.9579(8)
Cu(1)–S(1)	2.3423(11)	Cu(1)–S(1a)	2.5910(11)
Cu(1)–S(3)	2.2833(10)	Cu(2)–S(1)	2.3503(10)
Cu(2)–S(2)	2.3865(11)	Cu(3)–S(2)	2.3023(10)
Cu(3)–S(3)	2.3124(11)	Cu(1)–I(1)	2.5897(6)
Cu(2)–I(2)	2.6230(5)	Cu(2)–I(1a)	2.6612(6)
Cu(3)–I(3)	2.6384(5)	Cu(3)–I(3b)	2.7240(6)
S(1)–C(1)	1.727(4)	S(2)–C(4)	1.724(4)
S(3)–C(7)	1.706(4)	N(1)–C(1)	1.308(5)
N(2)–C(1)	1.326(5)	N(3)–C(4)	1.319(5)
N(4)–C(4)	1.322(5)	N(5)–C(7)	1.313(5)
N(6)–C(7)	1.315(5)		
Cu(1a)⋯Cu(1)⋯Cu(2a)	91.77(3)	S(1)–Cu(1)–S(1a)	112.41(3)
S(1)–Cu(1)–S(3)	98.34(4)	S(3)–Cu(1)–S(1a)	100.44(4)
S(1)–Cu(1)–I(1)	114.69(3)	S(3)–Cu(1)–I(1)	124.57(3)
I(1)–Cu(1)–S(1a)	105.64(3)	S(1)–Cu(2)–S(2)	97.38(4)
S(2)–Cu(2)–I(1a)	111.55(3)	S(1)–Cu(2)–I(1a)	110.75(3)
S(2)–Cu(2)–I(2)	117.50(3)	S(1)–Cu(2)–I(2)	116.42(3)
I(2)–Cu(2)–I(1a)	103.475(18)	S(2)–Cu(3)–S(3)	113.63(4)
S(2)–Cu(3)–I(3)	119.94(3)	S(2)–Cu(3)–I(3b)	109.98(3)
S(3)–Cu(3)–I(3)	108.99(3)	S(3)–Cu(3)–I(3b)	104.02(3)
I(3)–Cu(3)–I(3b)	98.057(17)	Cu(1)–S(1)–Cu(2)	121.88(4)
Cu(1)–S(1)–Cu(1a)	67.59(3)	Cu(2)–S(1)–Cu(1a)	73.36(3)
Cu(2)–S(2)–Cu(3)	118.13(4)	Cu(1)–S(3)–Cu(3)	129.71(4)
Cu(1)–I(1)–Cu(2a)	68.556(19)	Cu(3)–I(3)–Cu(3b)	81.943(17)

Symmetry codes are a: $-x+1, -y+1, -z$; b: $-x+1, -y, -z$.

the C–S distance increases and the N–C(=S) distance decreases when etu coordinates to silver(I) and copper(I) ions by its thione sulfur atom.

Supplementary material

Crystallographic data for the structures have been deposited at the Cambridge Crystallographic Data Centre as supplementary data CCDC 607148 and 259627. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033, or E-mail: deposit@ccdc.cam.ac.uk.

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