

# X-ray diffraction study of copper(I) thiourea complexes formed in sulfate-containing acid solutions

O. E. Piro,<sup>a</sup> R. C. V. Piatti,<sup>b</sup> A. E. Bolzán,<sup>b</sup> R. C. Salvezza<sup>b</sup> and A. J. Arvia<sup>b\*</sup>

<sup>a</sup>Universidad Nacional de La Plata and Instituto IFLP (CONICET), Departamento de Física, Facultad de Ciencias Exactas, Casilla de Correo 67, 1900 La Plata, Argentina, and <sup>b</sup>INIFTA (UNLP-CONICET-CICBsAs), Sucursal 4, Casilla de Correo 16, 1900 La Plata, Argentina

Correspondence e-mail:  
ajarvia@inifta.unlp.edu.ar

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The formation of three different copper(I) thiourea complexes in sulfate-containing acid solutions was observed. The ratio between Cu<sup>I</sup> and thiourea (tu) in these complexes depends on the amount of thiourea and copper sulfate in the solution. The crystal and molecular structure of a new complex, [Cu<sub>2</sub>(tu)<sub>6</sub>](SO<sub>4</sub>)·H<sub>2</sub>O, was determined, and the formation and structures of [Cu<sub>2</sub>(tu)<sub>5</sub>](SO<sub>4</sub>)·3H<sub>2</sub>O and [Cu<sub>4</sub>(tu)<sub>7</sub>](SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O were confirmed. The compound [Cu<sub>2</sub>(tu)<sub>6</sub>](SO<sub>4</sub>)·H<sub>2</sub>O crystallizes in the  $P\bar{1}$  space group, with  $a = 11.079$  (2),  $b = 11.262$  (1),  $c = 12.195$  (2) Å,  $\alpha = 64.84$  (1),  $\beta = 76.12$  (1),  $\gamma = 66.06$  (1)°, and  $Z = 2$ . The Cu-thiourea complex is arranged as a Cu<sup>I</sup> tetranuclear ion, [Cu<sub>4</sub>(tu)<sub>12</sub>]<sup>4+</sup>, sited on a crystallographic inversion center. All copper ions are in a tetrahedral coordination with thiourea ligands and located at alternate sites on an eight-membered, crown-like ring.

## 1. Introduction

At low concentrations (< 1 mM), thiourea is a well known additive for copper electroplating acting as a levelling agent (Ke *et al.*, 1959). It is also employed as an inhibitor for copper corrosion in aqueous aggressive environments (Alodan & Smyrl, 1998). However, despite its practical use, the physical and chemical mechanism of thiourea in both anodic and cathodic process at copper electrodes is still far from proven. Electrochemical (Ratajczak *et al.*, 1976; Szymaszek *et al.*, 1977) and spectroscopic (Brown *et al.*, 1995) data have shown the complexity level of aqueous solutions of metal ions in the presence of thiourea. Recently it has been found that weak copper–thiourea interactions occur at low concentrations of thiourea, whereas strong effects are observed at high concentration (> 1 mM; Alodan & Smyrl, 1998; Bolzán *et al.*, 2000). A brief review of the literature (Cotton & Wilkinson, 1980) reveals that Cu<sup>I</sup> compounds with soft donor ligands give rise to an array of stoichiometries and geometric configurations, including polynuclear species. Thiourea in aqueous solution is able to reduce Cu<sup>II</sup> ions to Cu<sup>I</sup>, which further reacts yielding complex ions containing a variable number of Cu<sup>I</sup> and thiourea units along with the participation of water molecules.

The chemistry of thiourea in copper-ion-containing solutions is rather complex due to the formation of a number of Cu<sup>I</sup> complex species with different molecular structures (Vranka & Amma, 1966; Hanic & Durcanská, 1969; Spofford & Amma, 1970; Weininger *et al.*, 1972; Gash *et al.*, 1973; Taylor *et al.*, 1974; Griffith *et al.*, 1976; Ferrari & Gasparri, 1976; Griffith *et al.*, 1978). In acid solution complex species are positively charged and the molecular structure of crystallized complex salts depends on the nature of the counter ions. Several crystal and molecular structures of these copper

**Table 1**

Experimental details.

Crystal data	
Chemical formula	[Cu <sub>2</sub> (CH <sub>4</sub> N <sub>2</sub> S) <sub>6</sub> ](SO <sub>4</sub> )·H <sub>2</sub> O
Chemical formula weight	697.89
Cell setting	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.079 (2)
<i>b</i> (Å)	11.262 (1)
<i>c</i> (Å)	12.195 (2)
$\alpha$ (°)	64.843 (10)
$\beta$ (°)	76.119 (10)
$\gamma$ (°)	66.059 (10)
<i>V</i> (Å <sup>3</sup> )	1254.6 (3)
<i>Z</i>	2
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.847
Radiation type	Mo <i>K</i> $\alpha$
Wavelength (Å)	0.71073
No. of reflections for cell parameters	23
$\theta$ range (°)	13.5–21.7
$\mu$ (mm <sup>-1</sup> )	2.322
Temperature (K)	293 (2)
Crystal form	Prism
Crystal size (mm)	0.40 × 0.24 × 0.16
Crystal color	Colorless
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Data collection method	$\omega$ -2 $\theta$ scans
Absorption correction	Numerical (Busing & Levy, 1957)
<i>T<sub>min</sub></i>	0.570
<i>T<sub>max</sub></i>	0.734
No. of measured reflections	6343
No. of independent reflections	5781
No. of observed reflections	5184
Criterion for observed reflections	<i>I</i> > 2 $\sigma$ ( <i>I</i> )
<i>R<sub>int</sub></i>	0.022
$\theta_{max}$ (°)	27.97
Range of <i>h</i> , <i>k</i> , <i>l</i>	-13 → <i>h</i> → 14 -13 → <i>k</i> → 14 0 → <i>l</i> → 16
No. of standard reflections	1
Frequency of standard reflections	Every 30 min
Intensity decay (%)	1.4
Refinement	
Refinement on	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.0255
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.0646
<i>S</i>	1.094
No. of reflections used in refinement	5781
No. of parameters used	393
H-atom treatment	Isotropic
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 0.7410P]$ , where $P = (F_o^2 + 2F_c^2)/3'$
( $\Delta/\sigma$ ) <sub>max</sub>	-0.005
$\Delta\rho_{max}$ (e Å <sup>-3</sup> )	0.511
$\Delta\rho_{min}$ (e Å <sup>-3</sup> )	-0.718
Extinction method	None
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs	
Data collection	CAD-4 (Enraf–Nonius, 1989)
Cell refinement	CAD-4 (Enraf–Nonius, 1989)
Data reduction	SDP (B. A. Frenz, 1983); SHELX76 (Sheldrick, 1976)
Structure solution	SHELXS86 (Sheldrick, 1990)
Structure refinement	SHELXL93 (Sheldrick, 1993)
Preparation of material for publication	SHELXL93 (Sheldrick, 1993)

complex salts have been reported mainly related to ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> as counter ions (Vranka & Amma, 1966; Hanic & Durcanská, 1969; Spofford & Amma, 1970; Weininger *et al.*, 1972; Gash *et al.*, 1973; Taylor *et al.*, 1974; Griffith *et al.*, 1976; Ferrari & Gasparri, 1976; Griffith *et al.*, 1978). For a sulfate-containing solution, the structure of [Cu<sub>4</sub>(tu)<sub>6</sub>](SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (Declercq *et al.*, 1978; Van Meerssche *et al.*, 1982*b*), [Cu<sub>4</sub>(tu)<sub>7</sub>](SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (Bott *et al.*, 1998), [Cu<sub>8</sub>(tu)<sub>15</sub>](SO<sub>4</sub>)<sub>4</sub>·*x*H<sub>2</sub>O (Declercq *et al.*, 1978), [Cu<sub>2</sub>(tu)<sub>5</sub>](SO<sub>4</sub>)·3H<sub>2</sub>O (Ferrari & Gasparri, 1976) and binuclear [Cu<sub>2</sub>(tu)<sub>6</sub>](SO<sub>4</sub>)·H<sub>2</sub>O (Van Meerssche *et al.*, 1982*a*) complexes have been described.

Recent electrochemical and surface analysis data (Bolzán *et al.*, 2000; Haseeb *et al.*, 2000) of copper surfaces in contact with aqueous dilute thiourea acid solutions have shown the formation of passive layers with different characteristics depending on the applied electric potential and thiourea concentration in the solution. The electrodisolution of copper in these solutions yields soluble and insoluble Cu<sup>I</sup> species, their ratio depending on the rate of copper ion formation and thiourea concentration at the metal|solution interface. Thus, the strongest inhibitor effect of thiourea for copper electrodisolution appears to be related to the formation of a complex copper thiourea film on the metal surface. In the copper electrodisolution potential range, at lower potentials the copper–thiourea interaction favors thiourea deprotonation, so that deprotonated thiourea mainly reacts yielding copper(I) thiourea complexes rather than formamidine disulfide (Suarez & Olson, 1992), which does not produce complexes with copper ions (Ferrari & Gasparri, 1976). Therefore, the knowledge of the chemistry of copper thiourea complexes is of utmost importance to understand the mechanism of a number of processes in which copper ions, thiourea and sulfuric acid species are involved, including the corrosion and passivation of copper in thiourea-containing environments.

This work describes the chemical preparation, and crystal and molecular structure of three different copper(I) thiourea complexes from acidic copper sulfate and thiourea aqueous solutions at room temperature. Two of these complexes have been reported in the literature (Ferrari & Gasparri, 1976; Bott *et al.*, 1998) and their structures have been confirmed in this work. Depending on the thiourea/copper sulfate concentration ratio, different complexes can be isolated by crystallization. We report here the crystal and molecular structure of a new tetranuclear copper(I) thiourea complex.

## 2. Experimental

### 2.1. Preparative

Copper(I) thiourea complexes were prepared by mixing in a 50 cm<sup>3</sup> glass reactor, with stirring, different amounts of *x* mM (0.2 ≤ *x* ≤ 2) of copper sulfate and *y* mM (0.6 ≤ *y* ≤ 20) of thiourea aqueous 0.5 M sulfuric acid at room temperature. Base solutions (0.1 M CuSO<sub>4</sub> and 1 M CS(NH<sub>2</sub>)<sub>2</sub>) were prepared from analytical reagent-grade chemicals and MilliQ\*

**Table 2**

Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ).

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U^C$  tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Cu1	0.36373 (2)	0.09604 (3)	0.25273 (2)	0.02625 (7)
Cu2	0.61892 (2)	0.21689 (3)	0.40109 (2)	0.02576 (7)
S1	0.43116 (4)	0.20730 (5)	0.34944 (4)	0.01967 (9)
C1	0.3067 (2)	0.2259 (2)	0.4656 (2)	0.0198 (3)
N11	0.3264 (2)	0.1354 (2)	0.5770 (2)	0.0253 (3)
N12	0.1935 (2)	0.3305 (2)	0.4428 (2)	0.0372 (5)
S2	0.38331 (5)	-0.13383 (5)	0.38708 (4)	0.02166 (10)
C2	0.2514 (2)	-0.1741 (2)	0.3785 (2)	0.0229 (4)
N21	0.1358 (2)	-0.0767 (3)	0.3506 (3)	0.0530 (7)
N22	0.2664 (2)	-0.3033 (2)	0.4010 (2)	0.0318 (4)
S3	0.56537 (5)	0.46395 (5)	0.32683 (5)	0.02554 (11)
C3	0.6995 (2)	0.5131 (2)	0.3072 (2)	0.0267 (4)
N31	0.8220 (2)	0.4318 (3)	0.2874 (2)	0.0395 (5)
N32	0.6806 (2)	0.6345 (3)	0.3086 (3)	0.0464 (6)
S4	0.15999 (5)	0.25658 (6)	0.19267 (5)	0.02974 (12)
C4	0.1302 (2)	0.2588 (2)	0.0600 (2)	0.0243 (4)
N41	0.2148 (2)	0.1754 (2)	0.0050 (2)	0.0367 (5)
N42	0.0176 (2)	0.3486 (2)	0.0107 (2)	0.0336 (4)
S5	0.81648 (5)	0.10555 (5)	0.31497 (4)	0.02552 (11)
C5	0.8032 (2)	0.1776 (2)	0.1611 (2)	0.0253 (4)
N51	0.8813 (2)	0.1086 (2)	0.0918 (2)	0.0360 (5)
N52	0.7167 (2)	0.3037 (2)	0.1105 (2)	0.0371 (5)
S6	0.54034 (6)	0.04699 (6)	0.11653 (5)	0.03014 (12)
C6	0.5426 (2)	0.1959 (2)	-0.0033 (2)	0.0276 (4)
N61	0.6394 (3)	0.1920 (3)	-0.0919 (2)	0.0458 (6)
N62	0.4501 (2)	0.3185 (2)	-0.0135 (2)	0.0431 (5)
S	0.00488 (4)	0.71477 (5)	0.25222 (4)	0.01961 (9)
O1	0.02456 (15)	0.6791 (2)	0.37890 (13)	0.0317 (3)
O2	0.0715 (2)	0.8136 (2)	0.17049 (14)	0.0335 (3)
O3	0.0593 (2)	0.5864 (2)	0.2242 (2)	0.0393 (4)
O4	-0.13794 (14)	0.7783 (2)	0.23400 (14)	0.0297 (3)
Ow	0.3260 (2)	0.5319 (2)	0.1455 (2)	0.0470 (5)

water. The extent of the reaction could be followed spectrophotometrically by the decrease of the hexaquaacopper(II) ion absorption band at 790 nm (Jaffé & Orchin, 1965). Depending on the amount of mM of thiourea and copper(II) species, different solid copper(I) thiourea complexes were isolated by direct crystallization. Thus, for  $x = 2$  and  $y < 4.5$ , the solution remained transparent (stage I); when  $x = 2$  and  $y = 4.5$ , the solution became opaque due to flocculation of a polymer-like jelly compound (stage II). This precipitate was sticky and very difficult to dissolve, except by adding an excess of thiourea (stage III), *i.e.* when  $x = 2$  and  $y \gg 5$ .

The recrystallization of products from stages I, II and III yielded crystals of different sizes. Well defined crystals of products resulting from stages I and III of average size smaller than 1 mm were obtained for X-ray diffractometry. The precipitate from stage III was dried to obtain useful samples for single-crystal X-ray diffraction measurements.

The  $[\text{Cu}_2(\text{tu})_6](\text{SO}_4) \cdot \text{H}_2\text{O}$  complex was obtained at stage III by increasing the amount of thiourea in the copper solution, *i.e.* from 4.5 to 20 mM and over 20 mM. Under this excess of thiourea in the solution, the crystallization process gave good single crystals with the minimum formula  $[\text{Cu}_2(\text{tu})_6](\text{SO}_4) \cdot \text{H}_2\text{O}$ . Amounts of thiourea between 6 and 12 mM produced very small crystals which were inadequate for X-ray analysis.

**Table 3**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

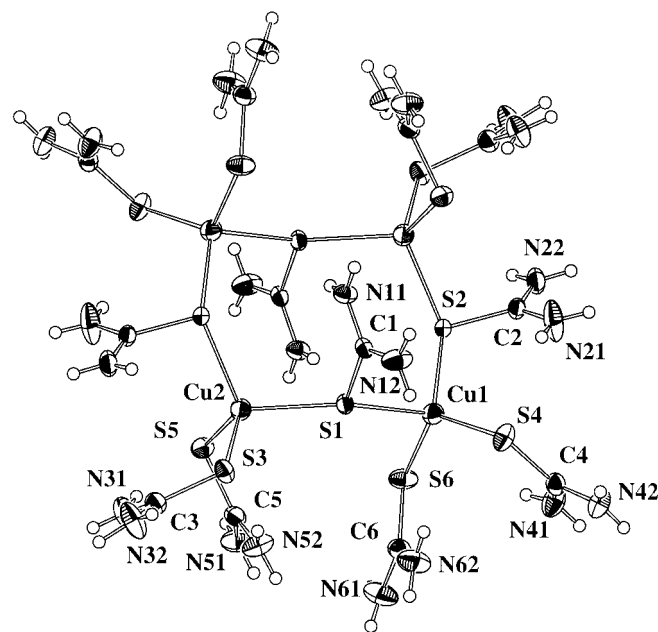
Cu1—S6	2.2882 (7)	Cu2—S5	2.2924 (7)
Cu1—S4	2.2925 (7)	Cu2—S2 <sup>i</sup>	2.3414 (7)
Cu1—S2	2.3542 (6)	Cu2—S1	2.3674 (6)
Cu1—S1	2.4409 (6)	Cu2—S3	2.3853 (6)
S6—Cu1—S4	122.34 (3)	S5—Cu2—S1	114.10 (2)
S6—Cu1—S2	99.03 (2)	S2 <sup>i</sup> —Cu2—S1	109.36 (2)
S4—Cu1—S2	120.02 (3)	S5—Cu2—S3	113.14 (2)
S6—Cu1—S1	103.12 (2)	S2 <sup>i</sup> —Cu2—S3	107.47 (2)
S4—Cu1—S1	101.74 (2)	S1—Cu2—S3	100.00 (2)
S2—Cu1—S1	109.25 (2)	Cu2—S1—Cu1	142.98 (2)
S5—Cu2—S2 <sup>i</sup>	111.98 (2)	Cu2 <sup>i</sup> —S2—Cu1	125.78 (2)

Symmetry codes: (i)  $1 - x, -y, 1 - z$ .

Another copper(I) thiourea complex was found when the amount of  $\text{CuSO}_4$  in the glass reactor was set to 0.2 mM and thiourea was added slowly to reach 1.2 mM in the glass reactor. The samples resulting from the crystallization process were extremely thin plates, which diffracted rather poorly in comparison to those obtained for  $[\text{Cu}_2(\text{tu})_6](\text{SO}_4) \cdot \text{H}_2\text{O}$ . The X-ray diffraction data of these crystals showed the formation of a compound with the formula  $[\text{Cu}_2(\text{tu})_5](\text{SO}_4) \cdot 3\text{H}_2\text{O}$ , which has a polymeric structure and is coincident with that reported elsewhere (Ferrari & Gasparri, 1976).

A third copper(I) thiourea compound was obtained from stage II by drying the sticky precipitate obtained by the slow addition of 4.5 mM of tu to the glass reactor containing 2 mM of  $\text{CuSO}_4$ . Single crystal diffraction data showed that it corresponded to the  $[\text{Cu}_4(\text{tu})_7](\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  complex, whose structure has already been reported (Bott *et al.*, 1998).

The  $[\text{Cu}_2(\text{tu})_6](\text{SO}_4) \cdot \text{H}_2\text{O}$  complex was also obtained electrochemically by dissolving a copper anode (wire of 2 cm in

**Figure 1**

ORTEP (Johnson, 1965) plot of a  $\text{Cu}_4[\text{SC}(\text{NH}_2)_2]_{12}$  tetramer showing the labeling of the non-H atoms and their displacement ellipsoids at 50% probability. Single lines denote Cu—S bonds.

length and 0.1 cm diameter) in aqueous 1 M thiourea + 0.5 M sulfuric acid.

## 2.2. Diffraction data and structure solution and refinement

Crystal data, data collection procedure, structure determination methods and refinement results for  $[\text{Cu}_2(\text{tu})_6](\text{SO}_4)\cdot\text{H}_2\text{O}$  are summarized in Table 1. All H atoms were located in a difference Fourier map and refined isotropically.

## 3. Crystallographic structural results and discussion

Atomic fractional coordinates and equivalent isotropic displacement parameters for  $[\text{Cu}_2(\text{tu})_6](\text{SO}_4)\cdot\text{H}_2\text{O}$  are given in Table 2. Selected intramolecular bond distances and angles are in Table 3. Fig. 1 is an ORTEP (Johnson, 1965) drawing of part of the asymmetric unit content.

The two crystallographically different  $\text{Cu}^{\text{I}}$  ions are in a quasi-tetrahedral environment of thiourea ligands with Cu—S distances ranging from 2.2882 (7) to 2.4409 (6) Å and S—Cu—S angles in the range 99.03 (2)–122.34 (3)°. An inversion symmetry operation on the independent  $\text{Cu}_2(\text{tu})_6$  molecular group generates the other half fragment of a centrosymmetric  $[\text{Cu}_4(\text{tu})_{12}]^{4+}$  complex. The tetranuclear  $\text{Cu}^{\text{I}}$  complex has the shape of an eight-membered elliptical ring with a crown-like conformation (see Fig. 1). The ring maximum and minimum transversal Cu—Cu distances are 6.518 (3) and 5.832 (4) Å. The crystal is further stabilized by a net of N—H...O hydrogen bonds involving thiourea ligands and sulfate oxygen atoms [the strongest with  $d(\text{H}\cdots\text{O}) = 1.93$  Å] and by weak intra- and intermolecular thiourea N—H...S interactions [the strongest with  $d(\text{H}\cdots\text{S}) = 2.73$  Å]. The water molecule acts as a hydrogen-bond donor in relatively strong Ow—H...S [ $d(\text{H}1\text{w}\cdots\text{S}1) = 2.65$  Å] and Ow—H...O [ $d(\text{H}2\text{w}\cdots\text{O}3) = 1.96$  Å] interactions and also as an acceptor of a relatively weak N—H...Ow bond [ $d(\text{H}52-\text{Ow}) = 2.08$  Å]. The detail of these hydrogen bonds is provided as supplementary material (Table 7).<sup>1</sup>

It should be noted that the structure of another substance with the same chemical formula has been reported (Van Meerssche *et al.*, 1982b). This compound crystallizes in the orthorhombic *Pbca* space group with binuclear  $[\text{Cu}_2(\text{tu})_6]^{2+}$  complexes arranged in the lattice as distinct dimeric units. The two Cu atoms in the dimer are also in a tetrahedral environment, but now linked by two bridging thiourea molecules. The tetrahedral coordination around each Cu atom is completed by two, terminally bound, thiourea ligand groups.

## 4. Conclusions

The interaction of thiourea with copper(II) ions in aqueous  $\text{CuSO}_4$  solutions produces the reduction of  $\text{Cu}^{\text{II}}$  ions to  $\text{Cu}^{\text{I}}$  with the formation of at least three types of complexes which we have structurally characterized by single-crystal X-ray

diffraction methods. These compounds are, in increasing order of the  $\text{Cu}^{\text{I}}/\text{tu}$  atomic ratio in the solid,  $[\text{Cu}_2(\text{tu})_6](\text{SO}_4)\cdot\text{H}_2\text{O}$ , polymeric  $[\text{Cu}_2(\text{tu})_5](\text{SO}_4)\cdot 3\text{H}_2\text{O}$  and  $[\text{Cu}_4(\text{tu})_7](\text{SO}_4)_2\cdot\text{H}_2\text{O}$ . The structure and composition of these complexes depend on the  $\text{Cu}^{\text{II}}/\text{tu}$  concentration ratio in the mother solutions. This phenomena could explain the anodic behavior of copper in thiourea-containing solutions through the formation of soluble complexes when the  $\text{Cu}^{\text{II}}/\text{tu}$  ratio is lower or higher than a certain critical value. In such cases, a soluble product is formed favoring the dissolution of copper. On the other hand, in the  $[\text{Cu}^{\text{II}}]/[\text{tu}]$  concentration ratio range related to the critical region  $1/3 \leq [\text{Cu}^{\text{II}}]/[\text{tu}] \leq 4/7$ , the reaction product is insoluble, being the one which is probably related to the passivation of the electrode surface.

The crystal structure of  $[\text{Cu}_2(\text{tu})_6](\text{SO}_4)\cdot\text{H}_2\text{O}$  contains a  $[\text{Cu}_4(\text{tu})_{12}]^{4+}$  complex where all four  $\text{Cu}^{\text{I}}$  ions are in a tetrahedral coordination with thiourea ligands. This centrosymmetric  $\text{Cu}^{\text{I}}$  tetranuclear cation has the form of an eight-membered, crown-like ring, a conformation observed for the first time in these systems.

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<sup>1</sup>Supplementary data for this paper are available from the IUCr electronic archives (Reference: CA0005). Services for accessing these data are described at the back of the journal.

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