Crystal Structure of $[Cu_4(tu)_7](SO_4)_2]\cdot H_2O$ and Vibrational Spectroscopic Studies of Some Copper(I) Thiourea Complexes

Raymond C. Bott,[†] Graham A. Bowmaker,*[,‡] Carol A. Davis,[†,§] Gregory A. Hope,*[,†] and Brian E. Jones[‡]

Faculty of Science and Technology, Griffith University, Nathan 4111, Brisbane, Australia,
and Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand

Received July 24, 1997

The complex $[Cu_4(tu)_7](SO_4)_2\cdot H_2O$ was isolated by addition of thiourea to a copper(II) sulfate electrolyte solution consisting of 2 M H_2SO_4 and 0.7 M $CuSO_4$. The crystal structure of this complex was solved by X-ray methods and highlighted a $[Cu_4(tu)_7]^{4+}$ adamantane cluster. A copper(I)−thiourea cluster of this stoichiometry has not been previously reported. The X-ray structure is refined to residual $R = 0.0447$ for 4093 observed reflections. Crystals are orthorhombic, of space group *Pbca*, with $Z = 8$ in a cell of dimensions $a = 10.414(3)$, $b = 17.909(3)$, and $c = 35.818(3)$ Å. The copper atoms lie in a tetrahedral arrangement in which one of the copper atoms is four-coordinate, while the other three display trigonal planar coordination with Cu···Cu distances of 2.899(2)−2.967(2)Å. The copper−thiourea clusters are interlinked by sulfate ions, which strongly interact with the thiourea ligands through hydrogen bonds. The infrared and Raman spectra of the title compound and of the related copper(I) thiourea complexes $[Cu_2(tu)_5](SO_4)\cdot 3H_2O$, $[Cu_2(tu)_6](SO_4)\cdot H_2O$, $[Cu_4(tu)_6](NO_3)_4\cdot 4H_2O$, and $[Cu_4(tu)_9](NO_3)_4\cdot 4H_2O$ were recorded and assigned, and the dependence of ν(CuS) on the coordination environment of the copper was established.

Introduction

Thiourea is widely used in the commercial electroplating and electrowinning of copper from acid sufate electrolytes. The thiourea concentration in the plating solution is generally maintained at less than 3 ppm; the reagent modifies the deposit, in particular, the size of the copper crystallites that form during metal electrodeposition.[1] The mechanism by which thiourea modifies the deposition process has not been clearly established, but it is believed to be related to the formation of copper(I) thiourea species at the cathode surface.[2] It has been assumed, on the basis of polarographic data, that addition of thiourea to acid copper(II) sulfate solutions can generate copper(I) and formamidine disulfide through a redox process.[3] A number of copper(I) thiourea complexes have been prepared and reported in the literature over the last 40 years.[4−14] These include simple monomers, dimers, polymers, and clusters with two-, three-, four-, and higher-coordination about the copper centers. A major impetus for research into copper(I) thiourea complexes has been primarily structural and/or has arisen from investigations into the chemistry of a soft donor ligand with a soft metal acceptor [Cu(I)] or a hard metal acceptor [Cu(II)]. Thiourea[15] and a series of copper(I) thiourea complexes with various counteranions have been crystallographically characterized.[5−13] Prior to this work, four examples of copper(I) thiourea sulfate complexes have been reported.[8,11−13] $[Cu_2(tu)_5](SO_4)\cdot 3H_2O$ displays an alternating chain of trigonal planar and tetrahedral copper(I) centers linked through bridging thiourea molecules.[8] The coordination about each copper(I) center is completed by the remaining monodentate thiourea ligands. The compound $[Cu_2(tu)_6](SO_4)\cdot H_2O$ contains the binuclear $[Cu_2(tu)_6]^{2+}$ complex in which two tetrahedrally coordinated copper(I) atoms are linked by two bridging thiourea molecules. The other four thiourea molecules are terminally bound, two on each copper atom.[12] $[Cu_4(tu)_6](SO_4)_2].2H_2O$ contains tetranuclear $[Cu_4(tu)_6]^{4+}$ cations in which four trigonally coordinated copper(I) atoms are linked together by the six thiourea molecules, each

---

[†] Griffith University.

[‡] University of Auckland.

[§] Present Address: Sunshine Coast University College, Locked Bag 4, Maroochydore, Qld 4558, Australia.

(1) Turner, D. R.; Johnson, G. R. *J. Electrochem. Soc.* **1962**, *109*, 798.

(2) Javet, P.; Hintermann, H. E. *Electrochim. Acta* **1969**, *14*, 527.

(3) Szymaszek, A.; Pajdowski, L.; Biernat, J. *Electrochim. Acta* **1980**, *25*, 985.

(4) Okaya, Y.; Knobler, C. B. *Acta Crystallogr.* **1964**, *17*, 928. Spofford, W. A.; Amma, E. L. *Acta Crystallogr.* **1970**, *B26*, 1474.

(5) Vranka, R. G.; Amma, E. L. *J. Am. Chem. Soc.* **1966**, *88*, 4270. Hanic, F.; Durcanska, E. *Inorg. Chim. Acta* **1969**, *3*, 293. Gash, A. G.; Griffith, E. H.; Spofford, W. A.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1973**, 256. Hunt, G. W.; Terry, N. W.; Amma, E. L. *Cryst. Struct. Commun.* **1974**, *3*, 523.

(6) Taylor, I. F.; Weininger, M. S.; Amma, E. L. *Inorg. Chem.* **1974**, *13*, 2835.

(7) Griffith, E. H.; Hunt, G. W.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1976**, 432.

(8) Ferrari, M. B.; Gasparri, G. F. *Cryst. Struct. Commun.* **1976**, *5*, 935.

(9) Cingi, M. B.; Landfredi, A. M. M.; Tiripicchio, A.; Camellini, M. T. *Acta Crystallogr.* **1977**, *B33*, 3772.

(10) Hunt, G. W.; Terry, N. W.; Amma, E. L. *Acta Crystallogr.* **1979**, *B35*, 1235.

(11) Declercq, J. P.; Kamara, R.; Moreaux, C.; Dereppe, J. M.; Germain, G.; Van Meerssche, M. *Acta Crystallogr.* **1978**, *B34*, 1036.

(12) Van Meerssche, M.; Kamara, R.; Declercq, J. P.; Germain, G. *Bull. Soc. Chim. Belg.* **1982**, *91*, 547.

(13) Van Meerssche, M.; Kamara, R.; Germain, G.; Declercq, J. P. *Bull. Soc. Chim. Belg.* **1982**, *91*, 553.

(14) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1.

(15) Kunchur, N. R.; Truter, M. R. *J. Chem. Soc.* **1958,** 2551.

S0020-1669(97)00910-5 CCC: $15.00

of which connects a pair of copper atoms (the "adamantane" structure).[11,13] $[Cu_8(tu)_{15}](SO_4)_4]\cdot xH_2O$ contains adamantane-like $[Cu_4(tu)_6]^{4+}$ cations that are linked together by additional doubly bridging thiourea molecules which bind to three of the four copper atoms in each cluster.[11]

In-situ SERS (surface-enhanced Raman spectroscopy) studies recently provided evidence for interactions between copper and thiourea at a copper cathode.[16-18] In this paper, we report the isolation and characterization of a new copper(I) thiourea complex isolated from aqueous acid copper(II) sulfate electrolyte and the study of this and a number of other copper(I) thiourea complexes by infrared and Raman spectroscopy. This study was carried out in order to shed more light on the nature of the species involved in the interaction of thiourea with a copper electrode and also to provide a basis for the analysis of the vibrational spectra of copper complexes with other sulfur ligands, many of which are of considerable biological significance.[19]

Experimental Section

Preparation of Compounds. Hexakis(thiourea)dicopper(I) Sulfate Hydrate, $[Cu_2(tu)_6]SO_4\cdot H_2O$. A solution of thiourea (2.5 g, 32.8 mmol) in water (15 mL) was prepared and then cooled in an ice–water bath. To this was slowly added a similarly chilled solution of copper(II) sulfate pentahydrate (2.5 g, 10 mmol) in water (15 mL), with continuous stirring. The reaction mixture was then allowed to stand for a few minutes, at which point a second, chilled solution of thiourea (1.0 g, 13.1 mmol) in water (10 mL) was slowly added while the mixture was vigorously stirred. Upon standing, the solution yielded a crystalline product which was filtered off and recrystallized from a solution of thiourea (0.15 g, 2 mmol) in water (50 mL) which contained a few drops of dilute sulfuric acid (1 mol L^{-1}). Finally, the product was washed with a 5 mL portion of cold water and then a 5 mL portion of 95% ethanol before drying in a desiccator, yielding pale yellow crystals, mp 137–140 °C. Anal. Found: C, 10.23; H, 3.48; N, 23.87. Calc for $C_6H_{26}N_{12}S_7O_5Cu_2$: C, 10.33; H, 3.76; N, 24.09.

Pentakis(thiourea)dicopper(I) Sulfate Trihydrate, $[Cu_2(tu)_5]SO_4\cdot 3H_2O$. This was prepared by the method described above, but with the omission of thiourea in the recrystallization step, yielding white crystals, mp 194–197 °C. Anal. Found: C, 9.03; H, 3.04; N, 21.03. Calc for $C_5H_{26}N_{10}S_6O_7Cu_2$: C, 9.13; H, 3.98; N, 21.29. In view of the relatively poor agreement in the H analysis, the compound was subjected to an X-ray structure analysis, which confirmed that it was identical to the previously reported compound of this composition.[8] This complex was also prepared electrochemically by the dissolution of a copper anode (1 cm × 4 cm) in a 0.5 M thiourea/2 M sulfuric acid solution. The complex formed on the anode as white needle crystals, which dropped to the cell bottom. The crystals were filtered off, washed with distilled water, and allowed to air-dry.

Heptakis(thiourea)tetracopper(I) Disulfate Hydrate, $[Cu_4(tu)_7](SO_4)_2\cdot H_2O$. This compound was formed as an oil by the addition of a thiourea solution (20 mL, 0.66 M) to 75 mL of an electrolyte solution of copper(II) sulfate pentahydrate (45 g L^{-1}) in sulfuric acid (180 g L^{-1}). The electrolyte solution was decanted off and the resulting oil triturated with distilled water to form a white, microcrystalline solid. The crystals were filtered off, washed with distilled water, and recrystallized from hot (*ca.* 70 °C) 2 M sulfuric acid. Large (*ca.* 3 mm) transparent, prismatic crystals with a blue tinge were isolated by vacuum filtration, washed with distilled water, and left to air-dry; mp 217–219 °C. Anal. Found: C, 8.32; H, 3.00; N, 19.52. Calc for $C_7H_{30}N_{14}S_9O_9Cu_4$: C, 8.43; H, 3.03; N, 19.67. An identical complex was isolated by the addition of thiourea to a commercial copper electrorefining tank house electrolyte containing similar concentrations of copper and acid. The oil was separated from the reaction solution, and recrystallized as described above.

Table 1. Crystallographic Data for $[Cu_4(tu)_7](SO_4)_2\cdot H_2O$

empirical formula	$C_7H_{30}N_{14}S_9O_9Cu_4$
fw	997.15
crystal size, mm	0.38 × 0.24 × 0.16
crystal system	orthorhombic
space group	*Pbca*
a, Å	10.414(3)
b, Å	17.909(3)
c, Å	35.818(3)
V, Å^3	6680
Z	8
d_{calc}, g cm^{-3}	1.983
T, °C	20
λ, Å	0.710 73
2θ range, deg	2.28–50
μ, cm^{-1}	31.4
$F(000)$	4016
$R_w(F^2)^a$	0.1257
goodness-of-fit on F^2	1.194
$R(F)^b$ ("obsd" reflns)	0.0446

^{a} $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. ^{b} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$.

Hexakis(thiourea)tetracopper(I) Tetranitrate Tetrahydrate, $[Cu_4(tu)_6](NO_3)_4\cdot 4H_2O$. To a hot solution of thiourea (1.70 g, 22.4 mmol) in deionized water (10 mL) was slowly added a hot solution of $Cu^{II}(NO_3)_2\cdot 3H_2O$ (3.0 g, 12.4 mmol) in deionized water (10 mL). During this addition, the thiourea solution exhibited a greenish color which was by completion strong and persistent. On cooling to room temperature, the solution yielded a flocculent yellow precipitate (sulfur) and a crystalline product. The crystalline product was redissolved by heating the solution, the sulfur was filtered off, and the solution was allowed to cool slowly to room temperature, whereupon a mass of fine, white rodlike needles was obtained. These crystals were filtered off under vacuum and washed with a little chilled water before being dried in a vacuum desiccator. Yield: 1.65 g (52% based on Cu). Mp: 192–195 °C; Anal. Found: C, 7.11; H, 2.00; N, 22.16. Calc for $C_6H_{32}N_{16}S_6O_{16}Cu_4$: C, 6.99; H, 3.13; N, 21.74.

Nonakis(thiourea)tetracopper(I) Tetranitrate Tetrahydrate, $[Cu_4(tu)_9](NO_3)_4\cdot 4H_2O$. This was prepared in a manner similar to that described above for the 4:6 nitrate, but using $Cu^{II}(NO_3)_2\cdot 3H_2O$ (3.0 g, 12.4 mmol) and thiourea (2.4 g, 31.0 mmol). Pale yellow crystals were obtained. Yield: 3.10 g (97% based on Cu). Mp: 118–123 °C. Anal. Found: C, 8.43; H, 2.53; N, 24.56. Calc for $C_9H_{44}N_{22}S_9O_{16}Cu_4$: C, 8.58; H, 3.52; N, 24.47.

X-ray Crystallography. The crystallographic data for the title compound are summarized in Table 1. The data were collected using an Enraf-Nonius CAD-4 diffractometer (graphite-crystal-monochromatized radiation). Of 5870 total reflections collected (h, 0–12; k, 0–21; l, 0–42), 4093 with $I > 2\sigma(I)$ were considered observed and used for structural refinement. Data were corrected for absorption using empirical methods (PSICALC).[20] The structure was solved using the automatic Patterson procedure of SHELXS-86[21] and refined using the least-squares procedure of SHELXL-93.[22] The value of the weighting variable $w = q/[(\sigma^2F_o^2) + (aP)^2 + (bP) + d + (e \sin\theta)]$. However, since only the first two weighting variables were refined in SHELXL-93, the equation reduces to $w = [(\sigma^2F_o^2) + (aP)^2 + (bP)]^{-1}$. $P = [f \times \text{maximum of } (0 \text{ or } F_o^2) + (1 - f)F_c^2]$ where f remained constant at 0.3333. Weighting variables used in the refinement were $a = 4.76 \times 10^{-2}$ and $b = 32.24$. Anisotropic thermal parameters were used for all

---

(16) Loo, B. H. *Chem. Phys. Lett.* **1982,** *89*, 346.

(17) Fleischmann, M.; Hill, I. R.; Sundholm, G. *J. Electoanal. Chem.* **1983**, *157*, 359.

(18) Brown, G. M.; Hope, G. A.; Schweinsberg, D. P.; Fredericks, P. M. *J. Electroanal. Chem.* **1995**, *380*, 161.

(19) Baumgartner, M.; Schmalle, H.; Dubler, E. *Inorg. Chim. Acta* **1993,** *208*, 135.

(20) *MoLEN: An interactive structure solution procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

(21) Sheldrick, G. M. *SHELXS 86: Structure solution package*; University of Göttingen: Göttingen, Germany, 1986.

(22) Sheldrick, G. M. *SHELXL 93: Program for crystal structure determination*; University of Göttingen: Göttingen, Germany, 1992.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Cu_4(tu)_7](SO_4)_2 \cdot H_2O$

Cu(1)−S(1)	2.248(2)	Cu(2)··Cu(3)	2.899(2)
Cu(1)−S(6)	2.281(2)	Cu(3)−S(5)	2.242(2)
Cu(1)−S(4)	2.304(2)	Cu(3)−S(1)	2.278(2)
Cu(1)··Cu(3)	2.932(2)	Cu(3)−S(3)	2.281(2)
Cu(1)··Cu(2)	2.967(1)	Cu(4)−S(4)	2.299(2)
Cu(2)−S(2)	2.252(2)	Cu(4)−S(2)	2.328(2)
Cu(2)−S(6)	2.270(2)	Cu(4)−S(5)	2.340(2)
Cu(2)−S(3)	2.270(2)	Cu(4)−S(41)	2.403(2)
S(1)−Cu(1)−S(6)	125.06(7)	Cu(2)··Cu(3)··Cu(1)	61.16(3)
S(1)−Cu(1)−S(4)	117.66(8)	S(4)−Cu(4)−S(2)	107.40(7)
S(6)−Cu(1)−S(4)	108.30(7)	S(4)−Cu(4)−S(5)	116.82(7)
Cu(3)··Cu(1)··Cu(2)	58.88(3)	S(2)−Cu(4)−S(5)	108.63(7)
S(2)−Cu(2)−S(6)	137.12(7)	Cu(1)−S(1)−Cu(3)	80.76(7)
S(2)−Cu(2)−S(3)	120.60(8)	Cu(2)−S(2)−Cu(4)	89.46(7)
S(6)−Cu(2)−S(3)	101.21(7)	Cu(2)−S(3)−Cu(3)	79.15(7)
Cu(3)··Cu(2)··Cu(1)	59.96(3)	Cu(4)−S(4)−Cu(1)	102.83(7)
S(5)−Cu(3)−S(1)	117.07(7)	Cu(3)−S(5)−Cu(4)	89.20(7)
S(5)−Cu(3)−S(3)	129.33(8)	Cu(2)−S(6)−Cu(1)	81.37(7)
S(1)−Cu(3)−S(3)	112.57(8)		

non-hydrogen atoms. Hydrogen atoms were located in difference-Fourier analyses and included with coordinates refined. Neutral-atom scattering factors and values for f' and f'' terms for anomalous dispersion were taken from ref 23. Interatomic bond distances and angles associated with the metal coordination polyhedra are listed in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and intraligand bond distances and angles.

Spectroscopy. Infrared spectra were recorded at 4 cm^{-1} resolution as KBr disks on a Digilab FTS-60 Fourier transform infrared spectrometer employing an uncooled DTGS detector. Far-infrared spectra were recorded at 4 cm^{-1} resolution at room temperature as pressed polythene disks on a Digilab FTS-60 Fourier transform infrared spectrometer employing an FTS-60V vacuum optical bench with a 6.25 mm Mylar film 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. The 488.0 nm exciting line from a Spectra-Physics Model 2016 argon ion laser was used. Solid state cross-polarization magic-angle-spinning (CP MAS) $^{13}C\{^1H\}$ NMR spectra were obtained at ambient temperature on a Varian Unity-400 spectrometer at 100.58 MHz. Single contact times of 2.5 ms were used with a proton pulse width of 5.2 ms, a proton decoupling field of 60 kHz, and a recycle delay time of 5 s. The samples were packed in silicon nitride rotors and spun at a speed of 5.1 kHz at the magic angle. A total of 14 208 FID's were collected and transformed with an experimental line broadening of 5 Hz. Chemical shift data are referenced to tetramethylsilane.

Results and Discussion

Crystal Structure. The unit cell of the title compound consists of eight $[Cu_4(tu)_7](SO_4)_2 \cdot H_2O$ repeating units. The sulfate ions significantly stabilize the cell through hydrogen bonds primarily with the NH_2 ends of the coordinated thiourea ligands within the $Cu_4(tu)_7$ cages. The water molecule is hydrogen-bonded to one sulfate ion. There is no significant hydrogen bonding involving the water molecule and the $Cu_4(tu)_7$ cages. Each of the discrete cationic cluster cages comprises three (CuS_3) trigonal planar centers and one (CuS_4) distorted tetrahedral copper(I) center.

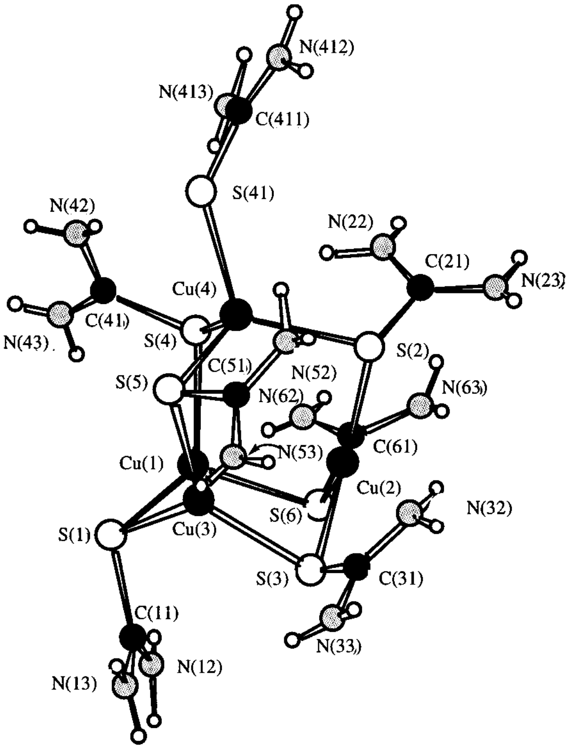

Figure 1. Molecular configuration and numbering scheme for $[Cu_4(tu)_7](SO_4)_2 \cdot H_2O$.

The coordination about the tetrahedral copper center is completed by four thiourea sulfur atoms: S(41) axial; S(2), S(4), and S(5) basal [Cu(4)−S(2) = 2.328(2), Cu(4)−S(4) = 2.299(2), Cu(4)−S(5) = 2.340(2) Å]. In Figure 1, it can be seen that the axial thiourea molecule is the only nonbridging ligand in each cluster [Cu(4)−S(41) = 2.403(2) Å]. Distortion of the tetrahedron is through the closing of the S(41)−Cu(4)−S(5) [95.38(5)°] angle and the opening of the remaining two angles [S(41)−Cu(4)−X, X = S(2) and S(4), 114.84(8) and 113.62(7)°, respectively]. The three basal sulfur atoms bridge to the three trigonal copper centers in each cluster [Cu(1)−S(4) = 2.304(2), Cu(2)−S(2) = 2.252(2), Cu(3)−S(5) = 2.242(2) Å; Cu(4)−S(4)−Cu(1) = 102.83(7), Cu(4)-S(2)-Cu(2) = 89.46(7), Cu(4)-S(5)-Cu(3) = 89.20(7)°].

The coordination about the trigonal copper centers is completed by three thiourea sulfur atoms, two of which bridge the remaining trigonal copper centers to form a pseudo-chair configuration [Cu−S = 2.242(2)−2.304(2) Å; Cu−S−Cu = 101.21(7)−137.12(7)°]. The four-coordinate copper center caps the chair to form an adamantane arrangement (Figure 1), similar to that of other biologically important copper(I) cluster complexes.[7,11,13,19,24] The trigonal copper centers lie in a planar equilateral triangle arrangement and exhibit weak metal−metal interactions [Cu···Cu = 2.899(2), 2.932(2), 2.967(1) Å; Cu−Cu−Cu = 58.88(3), 59.96(3), 61.16(3)°]. This triangle can be considered the base of a tetrahedron with the four-coordinate copper center lying in the axial position. This is typical in most copper(I) thiourea complexes where the copper centers form a tetrahedral arrangement with respect to each other.

The structure of the present complex is the $n = 1$ member of a series of complexes of the type $[Cu_4(\mu_2\text{-tu})_6(tu)_n]^{4+}$ that contain an adamantane-like $[Cu_4(\mu_2\text{-tu})_6]^{4+}$ ion and n terminally bound thiourea ligands. Since each of the four Cu atoms can accommodate a single terminal thiourea ligand, the possible range of n is 0−4. Prior to this work, complexes with $n = 0$

---

(23) Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

(24) Dance, I. G.; Bowmaker, G. A.; Clark, G. R.; Seadon, J. K. *Polyhedron* **1983**, *2*, 1031.

Table 3. Vibrational Data (cm^{-1}) for Thiourea (tu) and Copper(I) Thiourea Sulfate Complexes

thiourea		$[Cu_2(tu)_5](SO_4){\cdot}3H_2O$		$[Cu_2(tu)_6](SO_4){\cdot}H_2O$		$[Cu_4(tu)_7](SO_4)_2{\cdot}H_2O$		
IR	R	IR	R	IR	R	IR	R	assignment
		120, 152, 168 vw		173 vw		171 vw		δ(CuSC), ν(CuS)
		195, 200, 210 vw		206, 225 vw	216vw	205 vw	206 vw	ν(CuS) (4-coord Cu)
		245, 250, 278 vw	249, 281 vw			235−265 vw	236 m	ν(CuS) (3-coord Cu)
410 w		413 vw		414 vw		405 vw		τ(NH)
		442 m	415, 436 m		410 m		419, 447 m	δ(NCN)
480 s, br	476 s	472 s	473, 489 m	473 s	472 m	476 s	478 m	δ(SCN)
628 s		592, 619 m	620 w	613 s	614, 642 w	617 s	613, 634 w	β(SCN)
728 s	732 s	712 m	704, 714 s	718 m	706, 715 s	700 m	720 s	ν(CS)
769 vw		810 vw				863 vw		w(NH)
		991 vw	977 vs	972 vw	971 s	974 vw	977 s	SO_4^{2-}, ν_1 (A_1)
1082 m	1092 m	1105 s	1110 s	1103 s	1093, 1115 s	1075, 1104 s	1108 s	ν(CN), $\rho(NH_2)$
		1194 m		1182 w				
1410 s	1383 w	1391, 1424 s	1399, 1428 m	1389, 1424 s	1392 s	1420 s	1416 s	ν(CN), $\rho(NH_2)$, ν(CS), SO_4^{2-}, ν_3 (T_2)
1472 s		1478 m	1498 w	1481 m	1483 vw	1524 w	1502 vw	ν(CN)
1615 s		1607, 1634 s	1605, 1623 vw	1603, 1634 s	1598, 1639 vw	1629 s	1648 vw	$\delta(NH_2)$ ($\delta(OH_2)$)
3172 s	3196 s	3165 s		3165 s		3125 s		ν(NH) (ν(OH))
3273 s	3316 s	3258 s		3258 s		3182 s	3209 w	ν(NH) (ν(OH))
3375 s		3345 s		3345 s		3299 s	3315 w	ν(NH) (ν(OH))
		3474 m		3476 m			3338	ν(NH) (ν(OH))

and 3 had been reported,[7,13] and the existence of the $n = 4$ member was mentioned previously, although no structure is available.[25] There is clearly a considerable degree of flexibility in the composition of complexes of this type, which can be attributed to the well-known capacity of copper(I) to accommodate three- or four-coordination with sulfur-donor ligands.[26]

The atoms of the thiourea ligands are essentially coplanar, indicating no significant steric strain within the complex. The bridging thiourea molecules of the chair configuration lie either axial to or equatorial with the plane of the ring [axial S(1)−C(11) = 12.2(5)°; equatorial S(3)−C(31) = 73.3(5) and S(6)−C(61) = 61.7(5)°] due to steric considerations. The bond lengths about the thiourea ligands indicate a decrease in the carbon−sulfur double-bond character [($C{=}S$ = 1.64 Å; C−S = 1.82 Å);[15,27] complex mean $\overline{C\cdots S}$ = 1.73(5) Å], consistent with the coordination through the sulfur atoms. Similarly, the carbon−nitrogen bond lengths are too short for single-bond character [C−N = 1.475 Å;[15] complex mean $\overline{C\cdots N}$ = 1.30(9) Å], suggesting the electrons are delocalized over the entire thiourea molecules, forming resonance-stabilized ligands. This is supported by the infrared results reported here and those reported previously.[27] There appears to be no greater influence on the bridging sulfur atoms than on the monodentate sulfur atom, from the crystallographically determined bond lengths and angles.

Solid-State NMR Spectrum. The solid-state ^{13}C CPMAS NMR spectrum of $[Cu_4(tu)_7](SO_4)_2{\cdot}H_2O$ shows a broad signal at about 176 ppm and a narrower signal at 180 ppm. From the relative intensities of these signals, it seems reasonable to assign the broad peak to the six bridging thiourea molecules and the narrow peak to the unique terminally bonded thiourea molecule.

Vibrational Spectra. The bands and assignments for the vibrational spectra of the copper(I) thiourea complexes prepared in this work are listed in Tables 3 and 4. The far-IR and low-wavenumber Raman spectra of $[Cu_2(tu)_5](SO_4){\cdot}3H_2O$ and $[Cu_2(tu)_6](SO_4){\cdot}H_2O$ are shown in Figures 2 and 3. In all of the complexes, the region above 300 cm^{-1} contains bands due to thiourea and the anions (sulfate or nitrate). The thiourea bands are assigned in accordance with previous studies.[27,28] The ν(CS) bands occur at about 710 cm^{-1}, slightly lower than that for the uncomplexed ligand, and there is some evidence of splitting of this band in the Raman spectra, probably as a consequence of the different coordination environments of the ligands (e.g., bridging or terminal). Splitting of this kind is also observed in the δ(NCN) and δ(SCN) bands, which occur in the 400−500 cm^{-1} region.

The region below 300 cm^{-1} contains bands due to the presence of the Cu−S linkages, and this region is particularly important in establishing relationships between the vibrational spectra and the structure of the complexes concerned. The ν(CuS) assignments given in Table 3 are consistent with those given previously for some ethylenethiourea (etu) complexes of copper(I).[29] The complex $[Cu(etu)_3]_2(SO_4)$ contains two crystallographically inequivalent $[Cu(etu)_3]^+$ units with trigonal planar CuS_3 coordination at copper. The sulfate ion lies on a 3-fold axis in proximity to only one of the two cations, and the Cu−S distance in this ion (2.269(2) Å) is appreciably longer than that in the other (2.246(2) Å). Two ν(CuS) bands were observed in the far-IR at 227 and 214 cm^{-1}, and these were assigned to the $[Cu(etu)_3]^+$ ions with the shorter and longer Cu−S bond lengths, respectively. $[Cu(etu)_4](NO_3)$ contains $[Cu(etu)_4]^+$ ions with tetrahedral CuS_4 coordination with a mean Cu−S distance of 2.344 Å and gives a ν(CuS) band at 184 cm^{-1}.[29] These data established the dependence of ν(CuS) on the copper coordination number and also that ν(CuS) shows a regular decrease with increasing d(CuS) of about 500 cm^{-1} Å^{-1}, which is the same as that observed for ν(CuCl) in the spectra of a wide range of copper(I) chloride complexes.[30] The correlation between ν(CuS) and d(CuS) for these ethylenethiourea complexes is shown in Figure 4, and this provides a basis for the assignment of the ν(CuS) bands observed in the present thiourea complexes.

---

(25) Dance, I. G. *J. Am. Chem. Soc.* **1980**, *102*, 3445.
(26) Burdett, J. K.; Eisenstein, O. *Inorg. Chem.* **1992**, *31*, 1758.
(27) El-Etri, M. M.; Scovell, W. M. *Inorg. Chem.* **1990**, *29*, 480.
(28) Yamaguchi, A.; Penland, R. B.; Mizushima, S.; Lane, T. J.; Curran, C.; Quagliano, J. V. *J. Am. Chem. Soc.* **1958**, *80*, 527.
(29) Bowmaker, G. A.; Pakawatchai, C.; Skelton, B. W.; Thavornyutikarn, P.; Wattanakanjana, Y.; White, A. H. *Aust. J. Chem.* **1994**, *47*, 15.
(30) Bowmaker, G. A.; Healy, P. C.; Kildea, J. D.; White, A. H. *Spectrochim. Acta, Part A* **1988**, *44*, 1219.

Table 4. Vibrational Data (cm^{-1}) for Thiourea and Copper(I) Thiourea Nitrate Complexes

$[Cu_4(tu)_6](NO_3)_4{\cdot}4H_2O$		$[Cu_4(tu)_9](NO_3)_4{\cdot}4H_2O$		
IR	R	IR	R	assignment
125, 156, 175, 203 vw		106, 132, 150, 185 vw	154	δ(CuSC), ν(CuS)
		231 vw	220 vs	ν(CuS) (4-coord Cu)
254 vw	242 m		247 vw	ν(CuS) (3-coord Cu)
422 vw				τ(NH)
	420 m		421, 439 m	δ(NCN)
475 s	475 m	473 s	475 vs	δ(SCN)
521 s		540 s		
619 s	626 w		624 w	β(SCN)
696 m	702 s	706 m	698, 710 s	ν(CS)
826 m	825 vw	826 m		w(NH)
982 vw	985 vw			
	1046 s	1047 w	1051 s	NO_3^-, ν_1 (A_1)
1111 s	1115 s	1099 m	1102 s	ν(CN), $\rho(NH_2)$
1383 s	1384, 1429 m	1327, 1385 s	1398, 1428 m	ν(CN), $\rho(NH_2)$, ν(CS), NO_3^-, ν_3 (E′)
1508 w	1530 w	1495 m	1499 vw	ν(CN)
1622 s	1637 w	1614 s	1634 vw	$\delta(NH_2)$ ($\delta(OH_2)$)
3179 s	3220 m	3181 s	3205 m	ν(NH) (ν(OH))
3283 s	3330 m	3285 s	3306 m	ν(NH) (ν(OH))
3360 s	3417 w	3360 s	3381 w	ν(NH) (ν(OH))
		3561 w		

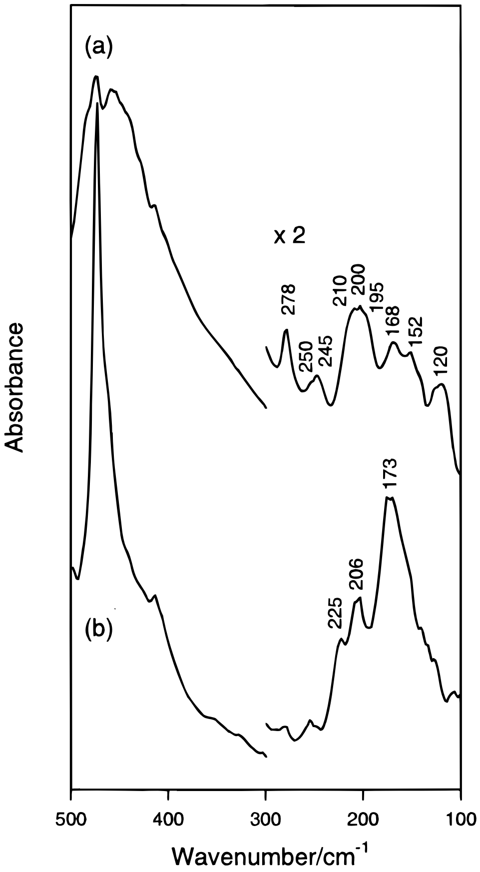

Figure 2. Far-IR spectra of (a) $[Cu_2(tu)_5](SO_4){\cdot}3H_2O$ and (b) $[Cu_2(tu)_6](SO_4){\cdot}H_2O$. The bands assigned as ν(CuS) or δ(CuSC) are labeled with their wavenumbers.

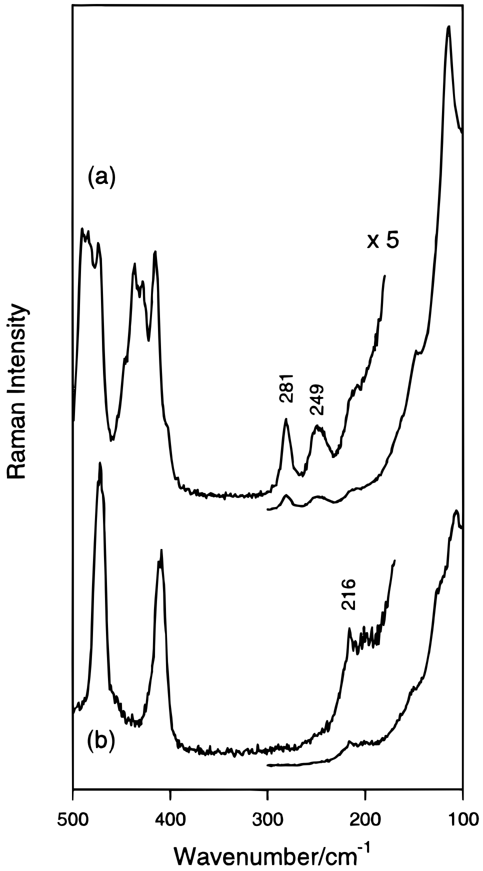

Figure 3. Low-frequency Raman spectra of (a) $[Cu_2(tu)_5](SO_4){\cdot}3H_2O$ and (b) $[Cu_2(tu)_6](SO_4){\cdot}H_2O$. The bands assigned as ν(CuS) are labeled with their wavenumbers.

Bands in the 200−280 cm^{-1} region in the far-IR spectra of $[Cu_2(tu)_5](SO_4){\cdot}3H_2O$ and $[Cu_2(tu)_6](SO_4){\cdot}H_2O$ could thus be assigned as ν(CuS) modes, and the correlation of these with the *d*(CuS) of Cu−S bonds in the structure is shown in Figure 4. The Cu−S bonds involving three-coordinate copper in the structure of $[Cu_2(tu)_5](SO_4){\cdot}3H_2O$ are significantly shorter (2.213(3)−2.277(3) Å) than those for the four-coordinate copper atoms (2.314(3)−2.408(3) Å),[8] so the higher wavenumber ν(CuS) bands are assigned to the three-coordinate copper atoms. Unlike that of the three-coordinate $[Cu(etu)_3]^+$ species, in which all three Cu−S bond lengths are equal due to their 3-fold symmetry, the three-coordinate copper site in $[Cu_2(tu)_5](SO_4){\cdot}3H_2O$ is quite unsymmetrical, so that three separate IR-active ν(CuS) modes occur. The bands labeled ν(CuS) (3-coord Cu) in Table 3 are assigned to these modes. The ν(CuS) bands for the four-coordinate copper in both compounds all occur below 230 cm^{-1} (Table 3), and the correlation between ν(CuS) and *d*(CuS) fits well with that for the three-coordinate Cu sites in

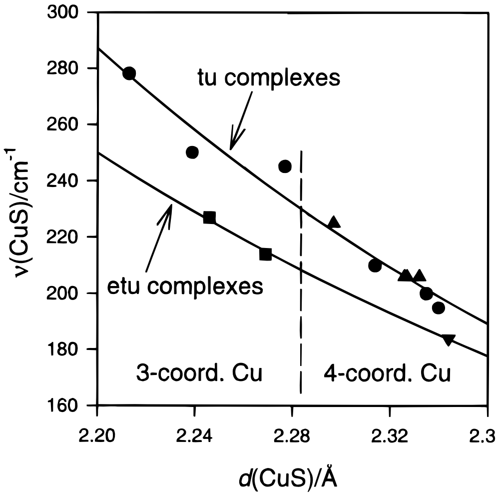

Figure 4. Correlation between the ν(CuS) and the Cu$-$S bond length d(CuS) for $[Cu_2(tu)_5](SO_4)\cdot3H_2O$ (●) and $[Cu_2(tu)_6](SO_4)]\cdot H_2O$ (▲) (tu complexes; this work) and for $[Cu(etu)_3]_2(SO_4)$ (■) and $[Cu(etu)_4](NO_3)$ (▼) (etu complexes; data from ref 29).

$[Cu_2(tu)_5](SO_4)\cdot3H_2O$ (Figure 4). A perfect correlation between these quantities would only be expected if the vibrations of each of the Cu$-$S bonds were completely independent of each other. This is not expected to be the case in the present complex, as the bonds are connected to others by Cu or S atoms. Nevertheless, Figure 4 shows that a reasonable correlation is obtained and that the rate of decrease of ν(CuS) with increasing d(CuS) is very similar to that for the previously studied ethylenethiourea complexes. However, for a given d(CuS), ν(CuS) is about 10% higher for the thiourea relative to the ethylenethiourea complexes, and this can be attributed to the smaller effective mass of thiourea relative to ethylenethiourea. The data for the thiourea complexes in Figure 4 incorporate six of the seven Cu$-$S bonds in $[Cu_2(tu)_5](SO_4)\cdot3H_2O$ and four of the eight Cu$-$S bonds in $[Cu_2(tu)_6](SO_4)\cdot H_2O$. The remaining Cu$-$S bonds are all longer than 2.34 Å, and these are assumed to contribute to the bands observed at about 170 cm^{-1}. However, as this is the region in which the δ(CuSC) modes also occur (Table 3; the corresponding bands in the ethylenethiourea complexes discussed above occur in the 110$-$150 cm^{-1} region[29]), data for these bonds have not been included in the correlation.

The Raman spectra in the low-wavenumber region for these two compounds (Figure 3) show ν(CuS) bands that coincide with some of those observed in the far-IR spectra. Thus, for $[Cu_2(tu)_5](SO_4)\cdot3H_2O$, the bands at 281 and 249 cm^{-1} coincide with the two highest wavenumber ν(CuS) IR bands, which are assigned to the three-coordinate copper environment. For $[Cu_2(tu)_6](SO_4)\cdot H_2O$ only a poorly resolved shoulder is observed at 216 cm^{-1}, which approximately corresponds in position to the two ν(CuS) IR bands at 225 and 206 cm^{-1}.

The ν(CuS) *vs* d(CuS) data shown in Figure 4 for the thiourea complexes $[Cu_2(tu)_5](SO_4)\cdot3H_2O$ and $[Cu_2(tu)_6](SO_4)\cdot H_2O$, and for the previously studied ethylenethiourea complexes,[29] have been fitted to an equation of the form

$$\nu/\mathrm{cm}^{-1} = b(r/\text{Å})^{-m} \qquad (1)$$

with b = 31 180 and 11 450 and m = 5.94 and 4.85 for the thiourea and ethylenethiourea complexes, respectively. Similar correlations were previously observed for Cu$-$X bonds in a range of copper(I) halide complexes with phosphine and amine ligands.[30] For these complexes, b = 13 800, 18 000, and 32 300 and m = 4.9, 5.2, and 5.6 for X = Cl, Br, and I respectively. The behaviors of the thiourea ligands and the halides are thus quite similar in this respect.

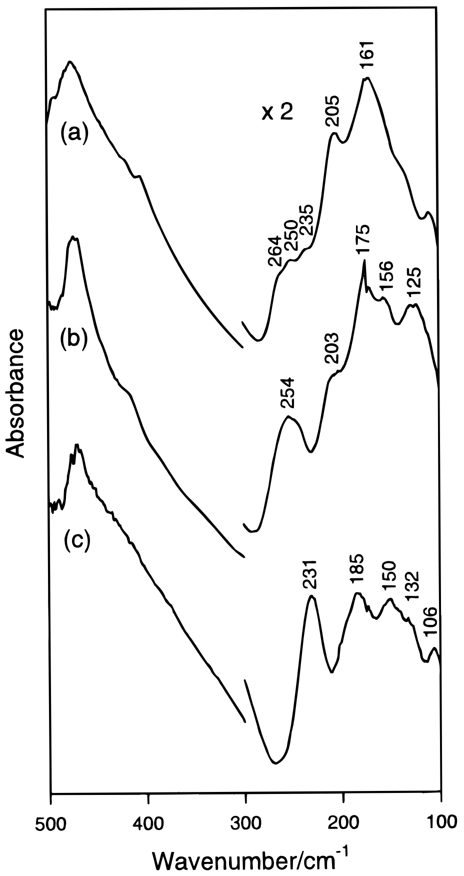

Figure 5. Far-IR spectra of (a) $[Cu_4(tu)_7](SO_4)_2\cdot H_2O$, (b) $[Cu_4(tu)_6](NO_3)_4\cdot4H_2O$, and (c) $[Cu_4(tu)_9](NO_3)_4\cdot4H_2O$. The bands assigned as ν(CuS) or δ(CuSC) are labeled with their wavenumbers.

The low-wavenumber vibrational spectra of $[Cu_4(tu)_7](SO_4)_2\cdot H_2O$ are compared with those of $[Cu_4(tu)_6](NO_3)_{4e}\cdot4H_2O$ and $[Cu_4(tu)_9](NO_3)_4\cdot4H_2O$ in Figures 5 and 6. The structures of the last two compounds are closely related to that determined for the first compound in the present study. They contain $[Cu_4(\mu_2\text{-tu})_6(tu)_n]^{4+}$ ions with an adamantane-like $[Cu_4(\mu_2\text{-tu})_6]^{4+}$ core and n = 0 and 3 terminally bound thiourea ligands, respectively.[7] Thus, all of the copper atoms are three-coordinate in the first of these, while the second contains one three-coordinate and three four-coordinate copper atoms. The assignment of the ν(CuS) modes for all three compounds (Tables 3 and 4) is entirely consistent with the analysis for the other compounds discussed above. Thus, for $[Cu_4(tu)_7](SO_4)_2\cdot H_2O$ (containing predominantly three-coordinate copper) and $[Cu_4(tu)_6](NO_3)_4\cdot4H_2O$ (in which all four copper atoms are three-coordinate), there are bands due to the three-coordinate copper atoms in the range 230$-$260 cm^{-1}. In $[Cu_4(tu)_9](NO_3)_4\cdot4H_2O$, four-coordinate copper predominates. This is reflected in the Raman spectrum (Figure 6), which shows a strong band in the four-coordinate region at 220 cm^{-1} and a weaker band in the three-coordinate region, at 247 cm^{-1}.

The results of the present study can be used to obtain further information about the nature of the species involved in the interaction of thiourea with a copper electrode. Previous studies by SERS have shown a ν(CuS) band at 288,[16] 295,[17] and 283 cm^{-1}.[18] These values are at the high end of the range covered by the data in Figure 4, suggesting the presence of a short and

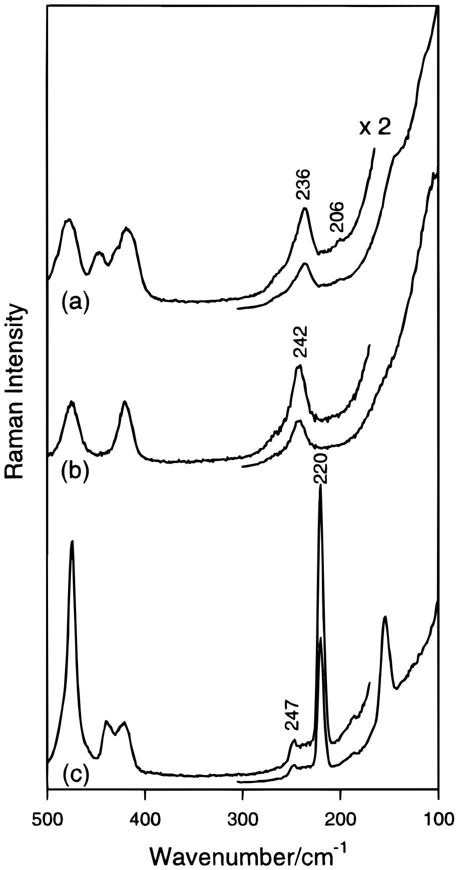

Figure 6. Low-frequency Raman spectra of (a) $[Cu_4(tu)_7](SO_4)_2{\cdot}H_2O$, (b) $[Cu_4(tu)_6](NO_3)_4{\cdot}4H_2O$, and (c) $[Cu_4(tu)_9](NO_3)_4{\cdot}4H_2O$. The bands assigned as ν(CuS) are labeled with their wavenumbers.

therefore strong Cu−S bond on the electrode surface. A similar conclusion was reached for the case of the silver/thiourea system on the basis of the shift in the ν(CuS) band of thiourea.[17] This suggests a relatively low coordination number for the Cu/thiourea system at the metal surface and agrees with the conclusion reached in a previously reported SERS study of the Cu/thiourea and Ag/thiourea systems on the basis of the ratio of the ν(MS) wavenumbers for these two systems.[16]

Conclusion. The previously unknown complex $[Cu_4(tu)_7](SO_4)_2{\cdot}H_2O$ has been prepared and has been shown to possess a $[Cu_4(tu)_7]^{4+}$ cluster. This represents the $n = 1$ member of a series of complexes of the type $[Cu_4(\mu_2\text{-tu})_6(tu)_n]^{4+}$ that contain an adamantane-like $[Cu_4(\mu_2\text{-tu})_6]^{4+}$ ion with six doubly bridging and n terminally bound thiourea ligands. Of the possible range of five such species ($0 \leq n \leq 4$), the three with $n = 0$, 1, and 3 are now known. The existence of this series can be attributed to the well-known capacity of copper(I) to accommodate three- or four-coordination with sulfur-donor ligands. The infrared and Raman spectra of the title compound and of a number of other copper(I)/thiourea complexes show ν(CuS) bands in the range 200−280 cm^{-1}. The ν(CuS) values show a strong dependence on the copper coordination environment, and comparison of the results of the present study with SERS studies of the aqueous copper/thiourea system suggests that the coordination number for the Cu/thiourea species at the metal surface is relatively low, in agreement with the conclusions based on other evidence.

Acknowledgment. The authors acknowledge the assistance of A/Prof. P. C. Healy, Dr. S. Berners-Price, and A/Prof. C. E. F. Rickard. Crystal data collection and preliminary structure solution were undertaken by Mr. K. Byriel of the University of Queensland X-ray facility.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional and thermal parameters, and bond lengths and angles (12 pages). Ordering information is given on any current masthead page.

IC970910Q