Inorganica Chimica Acta, *125* (1986) 37–42

Cu(N,N'-dimethylthiourea)$_2$NO$_3$, a Copper(I) Complex Exhibiting Infinite Chains of Edge-sharing CuS$_4$ Tetrahedra

ERICH DUBLER and WOLFGANG BENSCH

Institute of Inorganic Chemistry, University of Zürich, Winterthurerstr. 190, 8057 Zurich, Switzerland

(Received March 10, 1986)

Abstract

Bis(N,N'-dimethylthiourea)copper(I)nitrate, Cu(SC(NHCH$_3$)$_2$)$_2$NO$_3$, has been synthesized from an aqueous solution of copper(II) nitrate and N,N'-dimethylthiourea. Crystal data are $a = 10.349(3)$, $b = 12.197(2)$, $c = 5.777(3)$ Å, $\alpha = 92.92(3)$, $\beta = 98.84(3)$, $\gamma = 68.03(2)°$, $V = 668.2$ Å^3, space group $P\bar{1}$, $Z = 2$. The crystal structure was solved by Patterson and Fourier methods from diffractometer data and refined to R and R_w of 0.038 and 0.041 including 3213 observed reflections. The compound exhibits a new structure type which has not yet been recognized in copper(I) sulfur complexes. Considerably distorted CuS$_4$ tetrahedra are linked to isolated, infinite chains of the type $[\text{Cu(SR)}_2]_n^{n+}$ by sharing opposite edges. The cationic chains are separated from each other by the nitrate anions, which do not coordinate to the metal atom. Shortest metal-to-metal distances within the chains are 2.865(1) and 2.934(1) Å. The chains are bridged via N–H···O hydrogen bonds involving the nitrate ions. A structural comparison between this compound and the copper(I) thiourea complexes hitherto known is presented.

Introduction

It is well established that copper(I) complexes may be obtained as the result of a redox reaction of copper(II) with thiourea or substituted thioureas. According to Griffith *et al.* [1], copper(II) with thiourea (tu) or substituted thioureas (dmtu, N,N'-dimethylthiourea; detu, N,N'-diethylthiourea; tmtu, N,N'-tetramethylthiourea; etu, N,N'-ethylenethiourea) gives a rose to purple transient intermediate which may further react, yielding a series of polynuclear copper(I) species. A wide variety of stoichiometries and structure types are observed in these complexes with copper-to-sulfur ratios ranging from 1:4 as, for example, in monomeric Cu(tu)$_4$(SiF$_6$)$_{0.5}$ up to 1:1.5 as in tetrameric Cu$_4$(tu)$_6$(NO$_3$)$_4$·H$_2$O.

We have crystallized the title compound Cu(dmtu)$_2$NO$_3$ as the product of an unsuccessful attempt to prepare the copper(II) analogue of Cd(dmtu)$_4$(NO$_3$)$_2$, a complex exhibiting isolated, approximately tetrahedral CdS$_4$ moieties [2]. Cu(dmtu)$_2$NO$_3$ represents one of the rare examples of copper(I) thiourea complexes with a copper-to-sulfur stoichiometry of 1:2. In all previously known complexes of this stoichiometry, there are other ligands in addition to sulfur in the first coordination sphere of copper(I), for example Cl$^-$ in Cu$_2$(etu)$_4$Cl$_2$ [3] and in Cu(tu)$_2$Cl [4].

In view of the biological copper–sulfur coordination, however, model complexes without additional ligands are of interest, since in metalloproteins like copper metallothioneins the metals are thought to be coordinated by cysteine-sulfur atoms only [5]. In copper metallothioneins the copper-to cysteine-sulfur ratios found range from about 1:6.2 to 1:1.2 [6]. A copper-to-sulfur stoichiometry of approximately 1:2 appears to be a common value reported for most mammalian copper thioneins and for the protein from yeast [6]. This is a marked difference from the cadmium-zinc thioneins of animal origin, where usually a metal-to-sulfur ratio of 1:3 is observed [5]. Based on a copper-to-sulfur stoichiometry of 1:2 and on circular dichroism spectral measurements, a polynuclear structure type with copper(I) tetrahedrally coordinated by four cysteine-sulfur atoms has been postulated for copper thioneins [9]. In yeast copper thionein, containing four copper atoms and eight cysteine residues ($M_r \approx 4800$), EXAFS data indicate tetrahedrally coordinated copper atoms with Cu–S distances of 2.22 Å and of 2.36 Å, respectively [7]. To account for the observed copper-to-sulfur ratio of 1:2, a cubane-type Cu$_4$S$_8$ core has been proposed for this thionein [8].

Although the biologically relevant copper–sulfur proteins predominantly contain deprotonated thiolate anions RS$^-$ or thioether groups bound to the metal ion and not thio-amido groups with C=S double bonds, thiourea complexes still may serve as model compounds to mimic the copper–thiolate sites in copper thioneins. This conclusion has been drawn

0020-1693/86/$3.50

from X-ray photoelectron spectroscopy data by Weser *et al.* [10, 11]. The sulfur 2p binding energy in copper(I) thiourea complexes is 162.0 eV, a value identical to that found in thiolate clusters of the type $[Cu_4(SR)_6]^{2-}$ as well as in biogenic copper(I) thioneins.

Experimental

Synthesis

Preparation of the title complex: 1.04 g (10 mmol) *N,N'*-dimethylthiourea and 1.20 g (5 mmol) $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in 150 ml H_2O with gentle heating to about 330 K. After 30 min a yellowish precipitation appeared which was filtered off. The X-ray powder diffraction diagram (Guinier type camera with Cu Kα_1 radiation) of this precipitation is in agreement with the data reported for orthorhombic α-sulfur [12]. From the remaining solution, air-stable transparent needles and plates crystallized within three days by slow evaporation at room temperature. The dimensions of the crystals were up to 5 mm in length and up to 0.5 mm in thickness. *Anal.*: Calc. for $CuC_6H_{16}N_5O_3S_2$ ($M = 333.89$): C, 21.58; H, 4.83; N, 20.98. Found: C, 21,48; H, 4.65; N, 21.23%.

Thermoanalytical measurements (Stanton-Redcroft, Simultaneous Thermal Analysis System STA-780, sample weight 9.0 mg, flowing air atmosphere, heating rate 10°/min) showed that the complex is stable up to about 450 K. Starting at this temperature different overlapping endothermic and exothermic decomposition and reoxidation steps lead to CuO as the final product at about 750 K.

X-ray Crystallography

Triclinic symmetry was established by single crystal Weissenberg photographs and by powder X-ray diffraction data. A single crystal with approximate dimensions $0.50 \times 0.20 \times 0.10$ mm^3 was mounted on an Enraf–Nonius CAD-4 diffractometer with its needle axis parallel to the phi-axis of the instrument. The following lattice parameters were obtained from the least-squares refinement of 25 reflections in the range $10 \leqslant \theta \leqslant 23°$: $a = 10.349(3)$, $b = 12.197(2)$, $c = 5.777(3)$ Å, $\alpha = 92.92(3)$, $\beta = 98.84(3)$, $\gamma = 68.03(2)°$, $V = 668.2$ Å^3, space group $P\bar{1}$. With $Z = 2$ formula units per cell the calculated density (1.659 g cm^{-3}) is in perfect agreement with the value of 1.661 g cm^{-3} determined by the flotation method using $CHCl_3$–CH_2I_2 mixtures at 295 K.

Intensity data were collected up to $2\theta = 70°$ with the ω–2θ scan mode using graphite monochromated Mo Kα radiation (h: 0 to 17, k: −20 to 20, l: −10 to 10). The maximum measuring time per reflection was 60 s. Five standard reflections chosen to lie in different regions of reciprocal space were monitored every 250 reflections and showed no significant variation of their intensities; the loss of intensity during data collection was less than 1%. The intensities were reduced to F_o by applying corrections for Lorentz and polarisation effects. A numerical absorption correction ($\mu = 19.4$ cm^{-1}) did not contribute significantly to the results of the final refinements and therefore was neglected. Of a total of 6283 reflections measured (including standards) 3213 unique observed reflections with $I \geqslant 2\sigma(I)$ remained after averaging equivalent reflections and were used for the structure determination. The structure was solved by Patterson and Fourier techniques and refined with full-matrix least-squares methods including anisotropic temperature coefficients for the non-hydrogen atoms. Anomalous dispersion corrections were applied for all atoms.

All hydrogen atoms could be located on difference Fourier maps and were included in the following way: positional and isotropic thermal parameters of hydrogen atoms attached to nitrogen were refined without constraints, whereas hydrogen atoms of the methyl groups were refined with a common isotropic temperature factor for each individual methyl group. Refinements with fixed X–H distances of 0.96 Å and/or fixed isotropic temperature factors resulted in R values which are not significantly different from the final data.

The refinements (including a correction for isotropic secondary extinction, $g = 3.5 \times 10^{-7}$) converged to values of R and R_w of 0.038 and 0.041, respectively, based on F. The weighting scheme used was $w = k/\sigma^2(F) + 0.0013F^2$; k finally refined to 1.35. The last difference Fourier map showed maximum and minimum peaks of 0.8 and −0.5 e/Å^3. The highest peaks are closely associated with the copper atom, most probably a consequence of uncorrected absorption effects. The calculations were performed with the program system SHELX [13] on an IBM 3033 computer.

Final positional atomic parameters are listed in Table I*.

Description and Discussion of the Structure

The structure of $Cu(dmtu)_2NO_3$ contains copper(I) atoms tetrahedrally coordinated by four thioamido sulfur atoms (Fig. 1) with Cu–S distances ranging from 2.321(1) to 2.456(1) Å and S–Cu–S bonding angles varying from 104.27(6) to 117.56(8)°. These data are indicative of a considerable distortion of the CuS_4 tetrahedra. Interatomic bonding distances and angles are given in Table II.

Linking of the CuS_4 tetrahedra by opposite common edges with two neighboring tetrahedra results

---

*See also 'Supplementary Material'.

TABLE I. Positional and Isotropic Thermal Parameters for $Cu(dmtu)_2NO_3$. U_{eq} values ($Å^2$) were estimated as $(U_{11} + U_{22} + U_{33})/3$

Atom	x/a	y/b	z/c	U_{eq}
Cu	−0.0013(1)	0.0108(1)	0.2538(1)	0.036(1)
S(1)	0.1842(1)	0.0002(1)	0.0620(1)	0.030(1)
S(2)	−0.0663(1)	0.1654(1)	0.5223(1)	0.029(1)
O(1)	0.5968(3)	0.5301(2)	0.3195(6)	0.074(3)
O(2)	0.6579(4)	0.6770(3)	0.3070(5)	0.085(3)
O(3)	0.8132(3)	0.4995(4)	0.3239(7)	0.093(4)
N	0.6914(3)	0.5692(2)	0.3169(4)	0.046(2)
N(11)	0.2616(3)	0.1542(2)	−0.1373(4)	0.044(2)
N(12)	0.1176(3)	0.2295(2)	0.1413(4)	0.040(2)
N(21)	−0.3093(3)	0.3086(2)	0.6539(4)	0.035(2)
N(22)	−0.3263(2)	0.2168(2)	0.3038(4)	0.039(2)
C(1)	0.1869(2)	0.1393(2)	0.0167(4)	0.031(2)
C(2)	−0.2491(2)	0.2361(2)	0.4929(4)	0.028(2)
C(11)	0.3426(4)	0.0636(4)	−0.2864(7)	0.060(4)
C(12)	0.1142(4)	0.3494(3)	0.1252(8)	0.054(3)
C(21)	−0.2353(4)	0.3511(4)	0.8498(6)	0.052(3)
C(22)	−0.4776(3)	0.2762(4)	0.2447(7)	0.051(3)
H(11)	0.254(4)	0.215(3)	−0.159(7)	0.050(10)
H(12)	0.071(4)	0.223(3)	0.237(7)	0.055(11)
H(21)	−0.390(4)	0.338(3)	0.631(6)	0.047(9)
H(22)	−0.277(4)	0.169(3)	0.213(7)	0.048(9)
H(111)	0.277(5)	0.025(4)	−0.399(8)	0.070(7)
H(112)	0.361(5)	0.100(4)	−0.382(8)	0.070(7)
H(113)	0.410(5)	0.005(4)	−0.210(8)	0.070(7)
H(121)	0.224(4)	0.344(3)	0.164(7)	0.063(6)
H(122)	0.060(4)	0.402(4)	0.241(7)	0.063(6)
H(123)	0.076(4)	0.378(4)	−0.021(8)	0.063(6)
H(211)	−0.189(5)	0.397(4)	0.775(9)	0.086(9)
H(212)	−0.163(6)	0.298(5)	0.943(9)	0.086(9)
H(213)	−0.296(5)	0.397(4)	0.962(9)	0.086(9)
H(221)	−0.496(5)	0.364(4)	0.254(7)	0.076(7)
H(222)	−0.501(5)	0.256(4)	0.103(9)	0.076(7)
H(223)	−0.530(5)	0.255(4)	0.369(8)	0.076(7)

in infinite isolated chains of the type $[Cu(SR)_2]_n^{n+}$, running parallel to the *c* axis of the cell (Fig. 2) and separated from each other by the nitrate anions, which do not coordinate to the metal atoms. The periodicity along the chains is 5.777(3) Å, the *c*

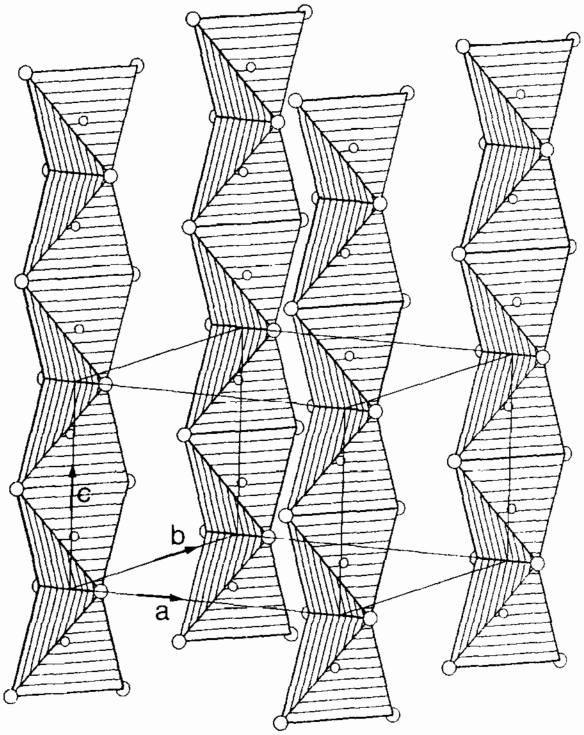

Fig. 2. Alternately stacked CuS_4 tetrahedra in $Cu(dmtu)_2NO_3$ forming infinite chains running along the *c*-axis. Copper atoms occupy the centres of the tetrahedra; sulfur atoms are located at the vertices. The nitrate ions (omitted for clarity) do not coordinate to the metal atom, but bridge the individual chains via hydrogen bonding.

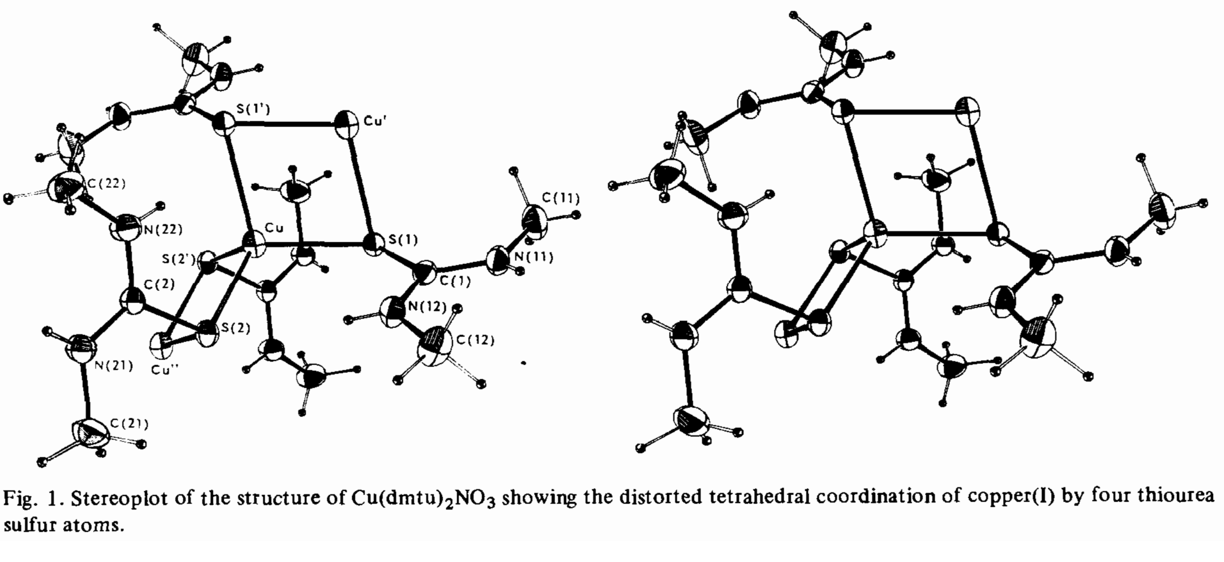

Fig. 1. Stereoplot of the structure of $Cu(dmtu)_2NO_3$ showing the distorted tetrahedral coordination of copper(I) by four thiourea sulfur atoms.

TABLE II. Interatomic Bonding Distances (Å) and Angles (°) in $\mathrm{Cu(dmtu)_2NO_3}$

Distances		Angles	
Cu–Cu′	2.865(1)	Cu–S(1)–Cu′	75.73(6)
Cu–Cu″	2.934(1)	Cu–S(2)–Cu′	74.72(6)
		S(1′)–Cu–S(2′)	115.29(8)
Cu–S(1)	2.321(1)	S(1′)–Cu–S(2)	108.65(8)
Cu–S(1′)	2.456(1)	S(1)–Cu–S(2′)	117.56(8)
Cu–S(2)	2.342(1)	S(1)–Cu–S(2)	105.16(7)
Cu–S(2′)	2.379(1)	S(1)–Cu–S(1′)	104.27(6)
		S(2)–Cu–S(2′)	105.28(6)
S(1)–C(1)	1.741(3)	Cu–S(1)–C(1)	112.04(11)
S(2)–C(2)	1.746(2)	Cu–S(2)–C(2)	111.03(10)
N(11)–C(1)	1.325(4)	Cu′–S(1)–C(1)	102.04(11)
N(11)–C(11)	1.449(5)	Cu′–S(2)–C(2)	108.70(13)
N(12)–C(1)	1.315(3)		
N(12)–C(12)	1.458(4)	O(2)–N–O(1)	118.10(30)
N(21)–C(2)	1.310(3)	O(3)–N–O(1)	119.03(28)
N(21)–C(21)	1.452(5)	O(3)–N–O(2)	122.92(29)
N(22)–C(2)	1.318(4)		
N(22)–C(22)	1.450(4)	C(1)–N(11)–C(11)	125.88(29)
N(11)–H(11)	0.73(4)	C(1)–N(12)–C(12)	125.22(29)
N(12)–H(12)	0.81(5)	C(2)–N(21)–C(21)	124.91(30)
N(21)–H(21)	0.76(4)	C(2)–N(22)–C(22)	125.37(27)
N(22)–H(22)	0.84(4)	N(11)–C(1)–N(12)	119.77(26)
C(11)–H(111)	1.08(5)	S(1)–C(1)–N(12)	119.73(22)
C(11)–H(112)	0.81(5)	S(1)–C(1)–N(11)	120.47(21)
C(11)–H(113)	0.87(4)	N(21)–C(2)–N(22)	120.08(26)
C(12)–H(121)	1.10(5)	S(2)–C(2)–N(22)	118.87(21)
C(12)–H(122)	0.99(4)	S(2)–C(2)–N(21)	121.05(22)
C(12)–H(123)	0.90(4)	C(11)–N(11)–H(11)	117(3)
C(21)–H(211)	1.00(6)	C(1)–N(11)–H(11)	117(3)
C(21)–H(212)	0.91(4)	C(12)–N(12)–H(12)	113(3)
C(21)–H(213)	0.97(5)	C(1)–N(12)–H(12)	122(3)
C(22)–H(221)	1.01(5)	C(21)–N(21)–H(21)	118(3)
C(22)–H(222)	0.87(5)	C(2)–N(21)–H(21)	117(3)
C(22)–H(223)	1.06(6)	C(22)–N(22)–H(22)	122(3)
		C(2)–N(22)–H(22)	112(3)
N–O(1)	1.241(5)		
N–O(2)	1.231(4)	N(11)–H(11)···O(2)	145(4)
N–O(3)	1.224(4)	N(21)–H(21)···O(1)	156(4)
N(11)···O(2)	2.763(3)		
N(21)···O(1)	2.911(3)		

dimension. Similar distances have been found as a unit cell parameter for $\mathrm{KFeS_2}$ (5.39 Å [14]) and for $\mathrm{SiS_2}$ (5.54 Å [15]), both of which have metal–sulfur tetrahedra linked in the same manner as in $\mathrm{Cu(dmtu)_2NO_3}$. Shortest metal-to-metal distances within the chains of $\mathrm{Cu(dmtu)_2NO_3}$ are 2.865(1) and 2.934(1) Å, respectively.

The structure type established for $\mathrm{Cu(dmtu)_2NO_3}$ seems to be unique for copper complexes of thiourea or related compounds. Edge-sharing $\mathrm{CuS_4}$ tetrahedra also occur, for example, in copper(I) sulfides of the type $\mathrm{KCu_4S_3}$ (possibly a mixed valence compound), but there the tetrahedra are connected to form infinite double layers separated by the alkali metal ions [16]. In addition, infinite chains of metal–sulfur tetrahedra sharing opposite edges have been found in $\mathrm{NH_4CuMoS_4}$ [17], but, in contrast to $\mathrm{Cu(dmtu)_2NO_3}$, copper(I) and molybdenum(VI) atoms alternate along the chains in this structure. Finally, with halogen atoms anionic $[\mathrm{CuCl_2}]_n^{n-}$ chains have been recognized in the 'paraquat' salt $\mathrm{pq^{2+}(CuCl_2)_2}$, where $\mathrm{pq^{2+}}$ represents the *N,N′*-dimethyl-4,4′-bipyridylium cation [18].

Different mononuclear and polynuclear structure types of copper(I) complexes of thiourea and substituted thioureas and corresponding metrical details established by X-ray crystallography are summarized in Table III. Parts of the interatomic bond distances and angles listed in this table were calculated based on atomic positional parameters (if available) using

TABLE III. Structural Data of Cu–S Polyhedra in Copper(I) Complexes of Thiourea and Substituted Thioureas. Abbreviations: tu = thiourea, $SC(NH_2)_2$; dmtu = *N,N'*-dimethylthiourea, $SC(NHCH_3)_2$; detu = *N,N'*-diethylthiourea, $SC(NHC_2H_5)_2$; tmtu = *N,N'*-tetramethylthiourea, $SC[N(CH_3)_2]_2$; etu = *N,N'*-ethylenethiourea, (2-imidazolidine-thione), $SC[(NH)_2(CH_2)_2]$

Structure type, formula	Cu:S	Cu–S (Å)	Cu–Cu (Å)	Cu–S–Cu (°)	Reference
Monomeric, trigonal planar or tetrahedral					
$Cu(tu)_3(C_8H_5O_4)$	1:3	2.23–2.25			20
$Cu(tmtu)_3BF_4$	1:3	2.24–2.26			21
$Cu(detu)_3(SO_4)_{0.5}$	1:3	2.24			22
$Cu(etu)_3(SO_4)_{0.5}$	1:3	2.27–2.28			20
$Cu(tu)_4(SiF_6)_{0.5}$	1:4	2.32–2.36			23
$Cu(etu)_4NO_3$	1:4	2.33–2.36			3
Dimeric, edge-sharing tetrahedral (Fig. 3 type a)					
$Cu_2(tu)_6(BF_4)_2$	1:3	2.30–2.43	2.84	72.6	24
$Cu_2(dmtu)_6(BF_4)_2$	1:3	2.30–2.46	2.83	72.3	24
$Cu_2(tu)_6SO_4 \cdot H_2O$	1:3	2.30–2.49	2.83	70.8–73.6	25
$Cu_2(tu)_6(ClO_4)_2$	1:3	2.32–2.46	2.86	72.2	26
Tetrameric (Fig. 3: Adamantan-type b and c)					
$Cu_4(tu)_6(SO_4)_2 \cdot 2H_2O$ (b)	2:3	2.24–2.31 2.23–2.29	2.82–3.36 2.82–3.24	76.9–93.4 77.0–91.2	27
$Cu_4(tu)_6(HSO_4)_2SO_4 \cdot H_2O$ (b)	2:3	2.24–2.30	2.81–3.01	77.2–83.5	27
$Cu_4(tu)_6(NO_3)_4 \cdot 4H_2O$ (b)	2:3	2.19–2.31	2.83–3.09		28
$Cu_4(tu)_9(NO_3)_4 \cdot 4H_2O$ (c)	4:9	2.24–2.42	3.20–3.93		28
$Cu_4(etu)_9(NO_3)_4 \cdot 6H_2O$	4:9	2.24–2.52			29
Polymeric chains (Fig. 3: type d, e and f)					
$Cu(tu)_3Cl$ (d)	1:3	2.28–2.44	4.43	134.1	30
$Cu_2(tu)_5SO_4 \cdot 3H_2O$ (e)	2:5	2.21–2.41	3.64–4.07	103.0–123.7	31
$Cu(dmtu)_2NO_3$ (f)	1:2	2.32–2.46	2.87	74.7–75.7	this work
Polymeric, three-dimensional network					
$Cu_4(tu)_9(NO_3)_4$	4:9		≥2.71	≥69	32
$Cu_4(tu)_{10}(SiF_6)_2 \cdot H_2O$	2:5	2.27–2.46	≥2.82	≥72	33

the program system SDP [19]. Typical structural arrangements of copper(I)–sulfur polyhedra are illustrated in Fig. 3.

From the values given in Table III it is evident that the geometry (including the shortest Cu–Cu distance of 2.87 Å) of the edge-sharing CuS_4 tetrahedra within the chains of $Cu(dmtu)_2NO_3$ matches the data established for isolated dimeric $Cu_2(SR)_6$ units. A significant difference in the Cu–S–Cu' bonding angles is observed, however; these angles are about 2.5° higher (74.7–75.7°) then the corresponding angles in dimeric units (70.8–73.6°). The two crystallographically independent thiourea groups in $Cu(dmtu)_2NO_3$ are planar within experimental error, with maximum deviations of 0.011 Å (molecule 1) and of 0.005 Å (molecule 2) of an individual atom from the best S–C–N–N plane. Somewhat surprisingly the two carbon atoms of the terminal methyl groups of molecule 1 are coplanar with the thiourea group (maximum deviation 0.013 Å), whereas in molecule 2 the interplanar angles S–C–N–N/C–N–C of 21.7 and 5.1°, respectively, substantiate a distinct non-planarity of the dmtu

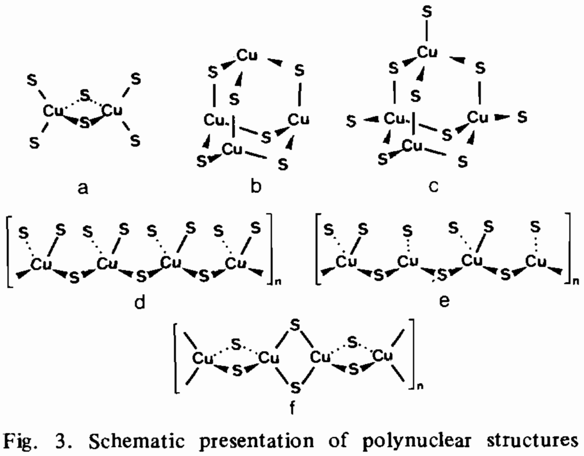

Fig. 3. Schematic presentation of polynuclear structures observed in copper(I) complexes of thiourea and substituted thioureas. (a) Edge-sharing tetrahedral $[Cu_2S_6]$ unit, (b) pseudo-Adamantan-type $[Cu_4S_6]$ cluster, (c) pseudo-Adamantan-type $[Cu_4S_9]$ cluster, (d) infinite chains of corner-sharing tetrahedra, $[CuS_3]_n$, (e) infinite chains of alternating trigonal planar and tetrahedral metal atoms, $[Cu_2S_5]_n$, (f) infinite chains of edge-sharing tetrahedra, $[CuS_2]_n$. For details see Table III.

group. The individual distances and angles within the dmtu ligand otherwise do not differ significantly from those expected.

The nitrate ion is perfectly planar and ordered. This seems to be a consequence of the fact that the nitrate ion is fixed by two medium-strong hydrogen bonds of the type $N–H\cdots O_{nitrate}$ with $N\cdots O$ distances of 2.76 and 2.91 Å. Bridging of the individual chains of edge-sharing CuS_4 tetrahedra occurs via these hydrogen bonds only.

$Cu(dmtu)_2NO_3$ represents an easily accessible and air-stable copper(I) model complex exhibiting infinite chains of isolated edge-sharing CuS_4 tetrahedra. A detailed comparison of its spectroscopical properties with corresponding data of biogenic copper(I) sulfur proteins could prove (or disprove) the occurrence of this structural element (or parts of it) in biological systems.

Supplementary Material

Supplemenatry material including tables of observed and calculated structure factors and of anisotropic thermal parameters may be obtained on request from one of the authors (E.D.).

Acknowledgements

We thank Ch. Behringer and R. Hany for the preparation of the crystals. Financial support from the Schweizerischer Nationalfonds zur Unterstützung der wissenschaftlichen Forschung (project No. 2.023–0.83) is gratefully acknowledged.

References

1 E. A. H. Griffith, W. A. Spofford, III and E. L. Amma, *Inorg. Chem., 17,* 1913 (1978).

2 P. F. Rodesiler, N. G. Charles, E. A. H. Griffith and E. L. Amma, *Acta Crystallogr., Sect. C, 39,* 1350 (1983).

3 L. P. Battaglia, A. B. Corradi, M. Nardelli and M. E. V. Tani, *J. Chem. Soc., Dalton Trans.,* 143 (1976).

4 W. A. Spofford, III and E. L. Amma, *Acta Crystallogr., Sect. B, 26,* 1474 (1970).

5 J. H. R. Kägi and M. Nordberg (eds.), 'Metallothionein, Proc. 1st Int. Meeting on Metallothionein and other Low Molecular Weigth Metal-binding Proteins', Birkhäuser, Basle, 1979.

6 K. Lerch, in H. Sigel (ed.), 'Metal Ions in Biological Systems', Vol. 13, Marcel Dekker, New York/Basle, 1981, p. 299.

7 J. Bordas, M. H. J. Koch, H.-J. Hartmann and U. Weser, *Inorg. Chim. Acta, 78,* 111 (1983).

8 M. Linss, M. G. Weller and U. Weser, *Inorg. Chim. Acta, 80,* 201 (1983).

9 H. Rupp and U. Weser, *Biochim. Biophys. Acta, 533,* 209 (1978).

10 U. Weser, H. J. Hartmann, A. Fretzdorff and G. J. Strobel, *Biochim. Biophys. Acta, 493,* 465 (1977).

11 U. Weser, *2nd Int. Meeting, Metallothionein and other Low Molecular Metal-binding Proteins,* Zürich, 1985, Abstr. p. 37.

12 *JCPDS, Powder Diffraction File, Card No. 8–247,* Swarthmore, Pa, U.S.A.

13 G. M. Sheldrick, 'SHELX76', program for crystal structure determination, Univ. Cambridge, 1976.

14 W. Bronger, *Z. Anorg. Allg. Chem., 359,* 225 (1968).

15 W. Büssem, H. Fischer and E. Gruner, *Naturwissenschaften, 23,* 740 (1935).

16 W. Bronger, *Angew. Chem., 93,* 12 (1981).

17 W. P. Binnie, M. J. Redman and W. Mallio, *Inorg. Chem., 9,* 1449 (1970).

18 C. K. Prout and P. Murray-Rust, *J. Chem. Soc., A,* 1520 (1969).

19 B. A. Frenz, 'Structure Determination Packages', Enraf-Nonius, Delft, 1982.

20 M. B. Cingi, A. M. M. Lanfredi, A. Tiripicchio and M. T. Camellini, *Acta Crystallogr., Sect. B, 33,* 3772 (1977).

21 M. S. Weininger, G. W. Hunt and E. L. Amma, *J. Chem. Soc., Chem. Commun.,* 1140 (1972).

22 R. Kamara, J. P. Declercq, G. Germain and M. Van Meerssche, *Bull. Soc. Chim. Belg., 91,* 339 (1982).

23 G. W. Hunt, N. W. Terry, III and E. L. Amma, *Acta Crystallogr., Sect. B, 35,* 1235 (1979).

24 I. F. Taylor, Jr., M. S. Weiniger and E. L. Amma, *Inorg. Chem., 13,* 2835 (1974).

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

26 F. Hanic and E. Durcanska, *Inorg. Chim. Acta, 3,* 293 (1969).

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

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

29 A. L. Crumbliss, L. J. Gestaut, R. C. Rickard and A. T. McPhail, *J. Chem. Soc., Chem. Commun.,* 545 (1974).

30 Y. Okaya and C. B. Knobler, *Acta Crystallogr., Sect. B, 17,* 928 (1964).

31 M. B. Ferrari and G. F. Gasparri, *Cryst. Struct. Commun.,* 935 (1976).

32 R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc., 88,* 4270 (1966).

33 A. G. Gash, E. H. Griffith, W. A. Spofford, III and E. L. Amma, *J. Chem. Soc., Chem. Commun.,* 256 (1973).