The Crystal Structure of Bis(thiourea)copper(I) Chloride

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The crystal structure of bis(thiourea)copper(I) chloride has been determined by three-dimensional single-crystal X-ray diffraction techniques from photographic data taken at ambient temperature. Unit-cell constants are: $a = 35.77 \pm 0.02$, $b = 8.15 \pm 0.01$, $c = 5.81 \pm 0.01$ Å, $\beta = 92.6 \pm 0.1°$. The space group is $P2_1/a$ with eight formula entities per cell. The structure consists of almost trigonal planar Cu^I triangles sharing vertices with adjacent triangles to form a chain, spiralling along the c direction. The triangles are made up in turn of a central Cu^I atom with vertices of sulfur atoms from three different thiourea groups. Each Cu^I atom has associated with it a long Cu–Cl [Cu(1)–Cl(1)] = 3.164 ± 0.006, Cu(2)–Cl(2) = 2.828 ± 0.005 Å] interaction approximately normal to the trigonal plane. Only van der Waals interactions exist between chains. The Cu–Cu distance alternates along the chain from a relatively short distance of 2.981 ± 0.004 Å to a long distance of 4.311 ± 0.004 Å with concomitant Cu–S–Cu bridging angles of 89.5 ± 0.2 and $138.1 \pm 0.2°$. The orientation of the thiourea groups participating in the sharp-angled bridge indicates an electron deficient delocalized three-center bond while that in the broad-angled bridge indicates normal electron pair bonds.

Introduction

Thiourea, here designated as tu, is a chemically interesting ligand in that it has several different possible modes of binding to a metal ion. It may coordinate through the nonbonding electron pairs of the nitrogen atom (Lane, Sen & Quagliano, 1954). This mode, however, has not been conclusively established by single-crystal studies, but only inferred from the infrared spectra. Alternately, thiourea may bind to a metal ion *via* the sulfur atom. For this mode, there are two means by which the sulfur atom may donate electrons: (*a*) electrons from the nonbonding sp^2 lobes or (*b*) electrons from a delocalized π molecular orbital. The C–S and C–N bond lengths of 1.720 (9) Å (here and elsewhere in this paper the error of the least significant digit is in parentheses) and 1.340 (6) Å (Kunchur & Truter, 1958; Truter, 1967) obtained from X-ray data or the 1.746 (9) and 1.350 (4) Å (Elcombe & Taylor, 1968) obtained from neutron diffraction data, as well as the complete planarity of the molecule, including hydrogen atoms, indicate a delocalized π molecular orbital involving all of the non-hydrogen atoms. The C–N bond length could be compared with the value of 1.338 (1) Å found in s-triazine (Lancaster & Stoicheff, 1956), the 1.334 (15) Å found in pyrazine (Wheatley, 1957) and the 1.340 (1) Å found in pyridine (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958), but is considerably shorter than the 1.47 Å expected from the sum of single-bond covalent radii (Pauling, 1960), the 1.474 (5) Å found in methylamine (Nishikawa, 1957) and the 1.472 (8) Å found in trimethylamine (Lide & Mann, 1958). The C–S bond length may be compared with the value of 1.718 Å

found in thiophene (Bak, Christensen, Rastrup-Andersen & Tannenbaum, 1956) which is considerably shorter than the 1.81 Å expected from the sum of single-bond covalent radii (Pauling, 1960), the 1.81 (2) Å found in *cis*-dichlorbis-(4,4′-dichlorodiphenylsulfide)-platinum(II) (Spofford & Amma, 1969) and the 1.819 (5) Å found in methanethiol (Kojima & Nishikawa, 1957). Thus, it is evident from the interatomic distances that thiourea may be described as a conjugated system with delocalized π molecular orbitals containing six electrons (one from S, one from C and two from each N). These molecular orbitals are made up from *p* orbitals from the S, C and N atoms and would give rise to four energy levels as given in Fig. 1 (Gimarc, 1969) in which the a_1 (strongly bonding), b_1 (weakly bonding) and the a_1' (more weakly bonding) orbitals are all filled. π electrons could therefore be donated to a metal ion from the *a* level, and this would probably only slightly (if at all) distort the distances and angles in the thiourea group. Bonding of this sort has been observed in Ag(tu)$_2$Cl (Vizzini & Amma, 1966; Vizzini, Taylor & Amma, 1968), Cu$_4$(tu)$_9$(NO$_3$)$_4$ (Vranka & Amma, 1966), Cu$_2$(tu)$_6$.2BF$_4$ (Taylor & Amma, 1969) and Co(tu)$_4$(NO$_3$)$_2$ and Co(tu)$_4$(NO$_3$)$_2$.H$_2$O (Spofford, Gentile, Boldrini, Carfagno & Amma, 1970).

As part of a continuing investigation of metal ion-thiourea complexes, the crystal structure of Cu(tu)$_2$Cl was undertaken. A preliminary communication has been published (Spofford & Amma, 1968) on this structure and we wish to present the details of the analysis and the structure.

Experimental

Crystals of Cu(tu)$_2$Cl [tu = SC(NH$_2$)$_2$] were prepared by mixing 200 ml of a 0.1M aqueous solution of thiourea with 50 ml of a fresh aqueous suspension of cuprous chloride. The solution was filtered to remove any free

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sulfur and allowed to evaporate. Diffraction-quality single crystals were grown by this means. From Weissenberg and precession photographs the crystals were found to be monoclinic with the systematic extinctions for $h0l$, $h = 2n + 1$; and for $0k0$, $k = 2n + 1$ defining the space group as $P2_1/a$ (*International Tables for X-ray Crystallography*, 1965). The cell constants were determined by back reflection techniques using Cu $K\alpha_1$ ($\lambda = 1.541$ Å), Cu $K\alpha_2$ ($\lambda = 1.544$ Å) and are: $a = 35.77$ (2), $b = 8.15$ (1), $c = 5.81$ (1) Å and $\beta = 92.6$ (1)°. The calculated density with eight formula entities per unit cell was found to be 1.97 g.cm^{-3}, in good agreement with the observed value of 1.94 (2) g.cm^{-3} measured by flotation in a carbon tetrachloride–bromoform mixture.

A single crystal $0.4 \times 0.3 \times 0.8$ mm was mounted about the needle axis (c) on the Weissenberg camera and used to collect 1474 independent hkl pieces of intensity data ($hk0, hk1 \ldots hk4$) by standard equi-inclination multiple-film techniques with Cu $K\alpha$ radiation ($\lambda = 1.542$ Å). The intensities were visually estimated by the use of a calibrated strip. The usual Lorentz–polarization corrections were applied and the intensities reduced to structure factors. Timed $h0l$ and $0kl$ precession photographs were obtained, visually estimated, and used for correlation of the Weissenberg data. The linear absorption coefficient for Cu $K\alpha$ radiation was calculated to be 105 cm^{-1}. No corrections were made for absorption and consequently the systematic error introduced by this effect makes our estimated standard deviations from the least-squares somewhat optimistic. No detailed physical interpretation should be made of the anisotropic atomic temperature factors because of the neglect of absorption corrections as well as the fact that the data are photographic.

Structure determination

With eight Cu(tu)$_2$Cl moieties per unit cell it is most likely that all atoms are in the general position of space group $P2_1/a$, $\pm(x,y,z; \frac{1}{2}+x,\frac{1}{2}-y,z)$. This gives two crystallographically independent Cu(tu)$_2$Cl entities per unit cell. The Cu, S and Cl positions were located from an unsharpened three-dimensional Patterson function (calculated with a program by N. C. Baenziger on the IBM 7040) with the aid of a closely related Patterson function from Ag(tu)$_2$Cl (Vizzini & Amma, 1966; Vizzini, Taylor & Amma, 1968). These atoms were refined by full-matrix least-squares using the program *ORFLS* (Busing, Martin & Levy, 1962) modified by W. A. Spofford, to a conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.43. An electron density map was computed (calculated with a program by N. C. Baenziger on the IBM 7040) and the light atoms located. After several cycles of least-squares with isotropic temperature factors, the R value was reduced to 0.174. At this point, the Cu, S and Cl atoms were allowed to vary anisotropically and the structure was refined by full-matrix least-squares by minimizing the function $\sum w(|F_o| - |F_c|)^2$ with weights as specified by Hughes (1941) ($F_{min} = 2.1$) including real and imaginary anomalous dispersion corrections with scattering factors from a standard source (Cromer & Waber, 1965; Cromer, 1965). The shift in atomic coordinates for the last cycle of refinement was less than 2×10^{-4} ($< 0.1\sigma$) of a cell edge. The final conventional R, weighted $R = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$ and standard error $= [\sum w(|F_o| - |F_c|)^2]^{1/2}/(N_O - N_V)$; $N_O = 1474, N_V = 120$, of an observation at unit weight were found to be 0.102, 0.134 and 1.90 respectively. Final observed and calculated structure factors are listed in Table 1. Final atomic coordinates, temperature factors and errors are enumerated in Table 2. Interatomic distances, angles, dihedral angles and errors calculated by program *ORFFE* (Busing, Martin & Levy, 1964) modified by W. A. Spofford are listed in Table 3. Table 4 contains various least-square planes calculated with a program by W. A. Spofford (1968).

Description of the structure

The structure may be described as made up of almost trigonal planar Cu^I triangles sharing vertices with adjacent triangles to form a chain spiralling along the c direction (Fig. 2). The triangles are made up in turn of a central Cu^I atom with vertices of sulfur atoms from three different thiourea groups (Fig. 3). An important feature of structure is that the Cu–Cu separation alternates between a long and a short distance [4.311 (4)

Orbital Designation	Energy	Symmetry Designation
	$+1.03\beta$	a_1''
	-0.81β	a_1'
	-1.50β	b_1
	-2.23β	a_1

Fig. 1. Energy and symmetry designations for the π molecular orbitals in thiourea.

and 2·981 (4) Å respectively] with an accompanying 'broad' and a 'sharp' Cu–S–Cu bridge angle [138·1 (2) and 82·5 (2)° respectively]. Each Cu atom also has associated with it a 'long' axial Cu–Cl distance [Cu(1)–Cl(1) = 3·164 (6); Cu(2)–Cl(2) = 2·828 (5) Å]. These chlorine atoms may be viewed as more or less ionic, particularly since the analogous Ag–Cl distances in Ag(tu)$_2$Cl are the same or somewhat shorter [Ag(1)–Cl(1) = 2·854 (4); Ag(2)–Cl(2) = 3·035 (5) Å]. A normal tetrahedral Cu–S single bond would be expected to be 2·39 Å (Pauling, 1960). However, it would be expected that Cu–S bonds involving sp^2 Cu orbitals would be shorter than the above and this is borne out by the Cu–S distances in this structure, 2·244–2·309 Å with e.s.d.'s of ±0·005. The e.s.d.'s from the least-squares output are probably optimistic and a more realistic assessment would double these values. One would predict that the S(3) bridging Cu–S distances (2·306, 2·309 Å) should be longer than the Cu(1)–S(4) and Cu(2)–S(1) terminal bonds (2·224, 2·229 Å) since the bridge sulfur atom would have a

double formal charge. The only really surprising feature of the Cu–S distances is the fact that the bridging Cu(1)–S(2) and Cu(2)–S(2) distances are not elongated compared with the terminal Cu–S distances. If they are elongated they are probably not longer by more than 0·03 Å (for discussion of bonding *vide infra*). These M–S distances are also shorter than the 2·503 (6), 2·517 (6), and 2·498 Å Ni–S distances found in Ni(tu)$_6$Br$_2$ (Weininger, O'Connor & Amma, 1969) but longer than the 2·198 (3) Ni–S distances found in Ni[SC$_2$H$_4$N(CH$_3$)$_2$]$_2$ (Girling & Amma, 1967). The C–N distances do not vary by more than two of our optimistic standard deviations and the spread in S–C distances of 1·74 to 1·64 Å is probably within three standard deviations of a more realistic S–C e.s.d. of ±0·04 Å. These C–N and S–C distances are not significantly different from those in free thiourea itself (Kunchur & Truter, 1958; Truter, 1967; Elcombe & Taylor, 1968). Furthermore, the thiourea groups are all planar within experimental error (Table 4).

Table 1(*a*). *Observed and calculated structure factors*

First column is *h* followed by F_{obs} and F_{calc}. $F_{calc} = 10F_{calc}$ absolute.

Table 1(b). *Unobserved reflections with calculated values greater than F_{min}*

First column is h followed by k and F_{calc} on same scale as Table 1(a). $F_{min} = 44$. Number of reflections less than $F_{min} = 591$. Unobserved reflections were not included in the refinement

$$F_{MIN} \le F(CALC) < 2.0 \cdot F_{MIN} \qquad (218)$$

$$2.0 \cdot F_{MIN} \le F(CALC) < 3.0 \cdot F_{MIN} \qquad (48)$$

$$3.0 \cdot F_{MIN} \le F(CALC) \qquad (62)$$

The least-square plane through S(2), S(3), S(4) and Cu(1) is indicated in Table 4 and it is seen that the Cu(1) atom is displaced approximately 0·155 (2) Å from this plane. Further, the S–Cu(1)–S angles are 113·1 (2), 127·7 (2) and 116·8 (2)° [sum = 357·5 (1)°] and consequently the Cu(1), S(2), S(3), S(4) grouping may be described as an approximate trigonal plane. On the other hand, the least-square plane through Cu(2), S(1), S(2), S(3) is a much poorer fit with Cu(2) displaced about 0·230 (2) Å from the plane and a corresponding larger deviation for S(1), S(2) and S(3) compared with the analogous plane for S(2), S(3), S(4) and Cu(1). The S–Cu(2)–S angles are 118·3 (2), 120·3 (2) and 116·0 (2)° [sum = 354·6 (1)°]. Hence, the environment about Cu(2) is more distorted from a trigonal planar configuration. It is interesting to note that the Cu atom with the longest Cu–Cl distance [Cu(1)–Cl(1) = 3·164 (6) Å] is the most nearly planar CuS₃ unit while the Cu atom with the shorter Cu–Cl distance [Cu(2)–Cl(2) = 2·828 (5) Å] is more distorted toward a tetrahedral configuration. Approximately trigonal planar Cu^I has been observed in KCu(CN)₂ (Cromer, 1957). The expected Cu–Cl distance for a 'normal' single bond is 2·34 Å computed from the sum of the covalent radii.

The angle bisector [Cu(1)–Cu(2)]–S(2)–C(2) is 110·2 (7)° and the dihedral angle between planes defined by bisector [Cu(1)–Cu(2)],S(2), C(2) and S(2), C(2), N(3), N(4) is 92 (1)°. Hence the line defined by N(3)–N(4)

Table 2. *Atom positional and thermal parameters**

	x	y	z
Cu(1)	0·10029 (9)	0·1791 (04)	0·2028 (05)
Cu(2)	0·15782 (7)	0·2537 (04)	0·8623 (05)
S(1)	0·2073 (1)	0·1502 (06)	1·0591 (03)
S(2)	0·1184 (1)	0·4189 (05)	0·0505 (07)
S(3)	0·1321 (1)	0·1165 (05)	0·5459 (08)
S(4)	0·0694 (1)	−0·0270 (06)	0·0227 (08)
Cl(1)	0·0228 (1)	0·3200 (06)	0·3551 (08)
Cl(2)	0·1849 (1)	0·4874 (05)	0·5513 (07)
C(1)	0·2398 (5)	0·1179 (24)	0·8737 (37)
N(1)	0·2363 (5)	0·1453 (25)	0·6497 (39)
N(2)	0·2730 (5)	0·0585 (23)	0·9436 (34)
C(2)	0·0856 (4)	0·4712 (19)	−0·1607 (28)
N(3)	0·0493 (4)	0·4808 (17)	−0·1080 (25)
N(4)	0·0955 (4)	0·5032 (21)	−0·3757 (30)
C(3)	0·1486 (5)	−0·0838 (24)	0·5353 (35)
N(5)	0·1671 (4)	−0·1457 (19)	0·7161 (28)
N(6)	0·1413 (4)	−0·1747 (20)	0·3574 (31)
C(4)	0·0405 (5)	−0·1030 (23)	0·2190 (36)
N(7)	0·0483 (5)	−0·0933 (24)	0·4473 (35)
N(8)	0·0110 (4)	−0·1880 (19)	0·1500 (31)

Anisotropic temperature factors of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)] \times 10^4$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	9·8 (3)	67 (5)	157 (11)	−9·7 (9)	−14 (1)	33 (5)
Cu(2)	3·8 (2)	105 (5)	180 (10)	9·1 (7)	−4 (1)	−39 (5)
S(1)	3·8 (3)	114 (8)	93 (16)	8 (1)	1 (2)	1 (8)
S(2)	2·4 (3)	42 (6)	91 (14)	0 (1)	−2 (1)	14 (7)
S(3)	5·7 (4)	15 (7)	168 (17)	3 (1)	−11 (2)	−4 (7)
S(4)	4·6 (3)	101 (8)	66 (15)	−4 (1)	5 (2)	−5 (8)
Cl(1)	6·1 (4)	108 (8)	126 (17)	−4 (1)	5 (2)	1 (8)
Cl(2)	3·3 (3)	60 (7)	94 (14)	0 (1)	5 (1)	1 (7)

Table 2 (cont.)

Isotropic temperature factors for carbon and nitrogen

	B		B		B		B
C(1)	3·0 (7)	C(2)	1·0 (5)	C(3)	2·2 (7)	C(4)	1·9 (7)
N(1)	3·3 (8)	N(3)	1·7 (5)	N(5)	3·3 (5)	N(7)	3·4 (7)
N(2)	2·5 (7)	N(4)	2·1 (6)	N(6)	3·2 (6)	N(8)	2·2 (6)

* Estimated standard deviations of last figure in this and following Tables are in parentheses.

deviates by approximately 8° from being parallel to the Cu(1)–Cu(2) line and the thiourea group of S(2) lies approximately perpendicular to the plane defined by Cu(1)–S(2)–Cu(2). In contrast, the angle bisector [Cu(2)–Cu(1)]–S(3)–C(3) is 165·2 (8)° and the dihedral angle between planes defined by bisector [Cu(2)–Cu(1)], S(3), C(3) and S(3), C(3), N(5), N(6) is 92 (1)°. Consequently the N(5)–N(6) line is also essentially parallel to the Cu(2)–Cu(1) line, but the thiourea group of S(3) lies close to the same plane as that defined by Cu(2)–S(3)–Cu(1). The orientation of the terminal thiourea groups can be seen from the dihedral angles between planes defined by: Cu(1), S(4), C(4) and S(4), C(4), N(7), N(8) [24(1)°] and Cu(2), S(1), C(1) and S(1), C(1), N(1), N(2) [1(1)°] and the angles Cu(1)–S(4)–C(4) [106·2 (7)°] and Cu(2)–S(1)–C(1) [107·2(7)] (Fig. 4).

Discussion

The structure of Cu(tu)$_2$Cl is similar to the structure of Ag(tu)$_2$Cl, but there are several significant and important differences. For example, the Ag–Cl distance analogous to Cu(1)–Cl(1) is 3·035 (5) Å compared with 3·164 (6) Å. Since 3·035 Å can be considered at best only a weak Ag–Cl covalent bond (sum of covalent radii = 2·51 Å) it would be expected that the Cu(1)–Cl(1) distance should be approximately 0·2 Å shorter (sum of covalent radii = 2·34 Å) than the Ag–Cl distance but, in fact, it is 0·1 Å longer. In support of this postulate it is found that the terminal Ag–S distances are 2·487 (4) and 2·433 (5) Å and the terminal Cu–S distances are 2·244 (5) and 2·229 (5) Å, a difference of approximately 0·2 Å. This can only mean that the Cl(1) atom is best
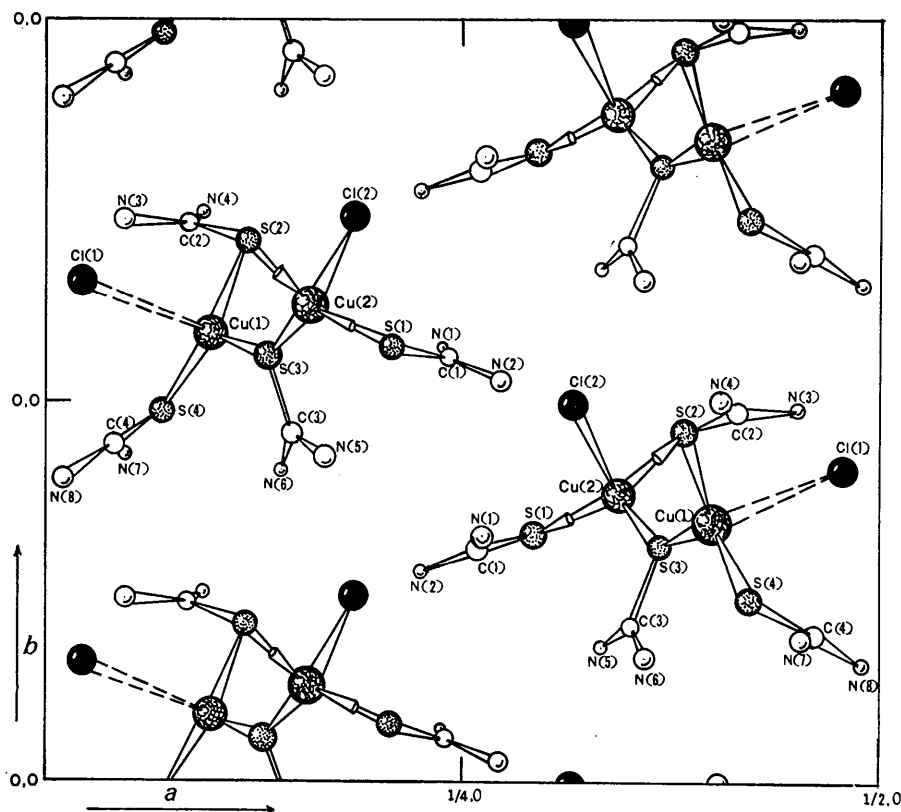

Fig. 2. View of the Cu–S–Cu chain down the c axis, the direction of the spiral. The differences in the orientation of the S(2) and S(3) thiourea groups are to be noted. The cut-off cones denote, for example, Cu(2)–S(1)–S(2) bonds to S(1) and S(2) atoms above those shown.

described as an ionic chlorine atom in Cu(tu)₂Cl. This description is also supported by the fact that the Cu(1) atom is in essentially the same plane as its three sulfur atom neighbors. On the other hand the Cu(2)–Cl(2) distance is 2·828 (5) Å, indicating a greater Cu–Cl directed interaction than Cu(1)–Cl(1). In agreement with

Table 3. *Interatomic distances, angles and estimated standard deviations*

E.s.d.'s of the last figure are given in parentheses.

Bonded distances		Angle	
Cu(1)–S(2)	2·254 (5) Å	S(2)—Cu(1) –S(3)	113·1 (2)^c
Cu(1)–S(3)	2·306 (5)	S(2)—Cu(1) –S(4)	127·7 (2)
Cu(1)–S(4)	2·244 (5)	S(2)—Cu(1) –Cl(1)	93·8 (2)
Cu(2)–S(1)	2·229 (5)	S(3)—Cu(1) –S(4)	116·8 (2)
Cu(2)–S(2)	2·265 (5)	S(3)—Cu(1) –Cl(1)	104·0 (2)
Cu(2)–S(3)	2·309 (5)	S(4)—Cu(1) –Cl(1)	89·0 (2)
S(1)—C(1)	1·640 (22)	S(1)—Cu(2) –S(2)	118·3 (2)
C(1)—N(1)	1·322 (32)	S(1)—Cu(2) –S(3)	120·3 (2)
C(1)—N(2)	1·327 (24)	S(1)—Cu(2) –Cl(2)	107·2 (2)
S(2)—C(2)	1·717 (15)	S(2)—Cu(2) –S(3)	116·0 (2)
C(2)—N(3)	1·349 (20)	S(2)—Cu(2) –Cl(2)	98·4 (2)
C(2)—N(4)	1·337 (25)	S(3)—Cu(2) –Cl(2)	87·3 (2)
S(3)—C(3)	1·739 (20)	Cu(1)–S(2)—Cu(2)	82·5 (2)
C(3)—N(5)	1·318 (24)	Cu(1)–S(3)—Cu(2)	138·1 (2)
C(3)—N(6)	1·288 (26)	Cu(1)–S(2)—C(2)	107·2 (5)
S(4)—C(4)	1·706 (21)	Cu(1)–S(3)—C(3)	109·4 (7)
C(4)—N(7)	1·349 (31)	Cu(1)–S(4)—C(4)	106·2 (7)
C(4)—N(8)	1·289 (23)	Cu(2)–S(1)—C(1)	107·2 (7)
		Cu(2)–S(2)—C(2)	102·9 (6)
		Cu(2)–S(3)—C(3)	111·0 (6)
Nonbonded distances		S(1)—C(1)—N(1)	126 (2)
Cu(1)–Cu(2)	4·311 (4) Å	S(1)—C(1)—N(2)	121 (2)
Cu(2)–Cu(1)	2·981 (4)	N(1)—C(1)—N(2)	114 (2)
Cu(1)–Cl(1)	3·164 (6)	S(2)—C(2)—N(3)	119 (1)
Cu(2)–Cl(2)	2·828 (5)	S(2)—C(2)—N(4)	121 (1)
N(3)—Cl(1)	3·177 (16)	N(3)—C(2)—N(4)	120 (1)
N(1)—Cl(2)	3·376 (21)	S(3)—C(3)—N(5)	119 (2)
N(8)—Cl(1)	3·303 (18)	S(3)—C(3)—N(6)	121 (1)
N(4)—Cl(1)	3·328 (16)	N(5)—C(3)—N(6)	120 (2)
N(4)—Cl(2)	3·248 (16)	S(4)—C(4)—N(7)	121 (1)
N(5)—Cl(2)	3·213 (17)	S(4)—C(4)—N(8)	120 (2)
N(6)—Cl(2)	3·336 (17)	N(7)—C(4)—N(8)	119 (2)
		bisector[Cu(1)–Cu(2)]–S(2)—C(2)	110·2 (7)
		bisector[Cu(2)–Cu(1)]–S(3)—C(3)	165·2 (8)

Dihedral angles between various planes

Plane 1	Plane 2	Angle
Cu(1)–S(2)—Cu(2)	Cu(1)–S(2)–C(2)	101·3 (6)^c
Cu(1)–S(2)—Cu(2)	Cu(2)–S(2)–C(2)	73·9 (6)
Cu(1)–S(3)—Cu(2)	Cu(1)–S(3)–C(3)	164·3 (9)
Cu(1)–S(3)—Cu(2)	Cu(2)–S(3)–C(3)	15·9 (9)
Cu(1)–S(2)—C(2)	Cu(2)–S(2)–C(2)	86·1 (10)
Cu(1)–S(3)—C(3)	Cu(2)–S(3)–C(3)	11·2 (11)
Cu(1)–S(2)—C(2)	S(2)—C(2)–N(3)–N(4)	54·6 (13)
Cu(1)–S(3)—C(3)	S(3)—C(3)–N(5)–N(6)	1·1 (13)
Cu(1)–S(4)—C(4)	S(4)—C(4)–N(7)–N(8)	24·1 (14)
Cu(2)–S(1)—C(1)	S(1)—C(1)–N(1)–N(2)	1·2 (15)
Cu(2)–S(2)—C(2)	S(2)—C(2)–N(3)–N(4)	39·3 (15)
Cu(2)–S(3)—C(3)	S(3)—C(3)–N(5)–N(6)	10·5 (17)
bisector[Cu(1)–Cu(2)]–S(2)–C(2)	S(2)—C(2)–N(3)–N(4)	81·6 (12)
bisector[Cu(2)–Cu(1)]–S(3)–C(3)	S(3)—C(3)–N(5)–N(6)	82·3 (12)

Root-mean-square displacements along principal axes

	Axis 1	Axis 2	Axis 3
Cu(1)	0·128 (5)	0·149 (5)	0·275 (4)
Cu(2)	0·124 (5)	0·156 (5)	0·226 (4)
S(1)	0·126 (10)	0·136 (7)	0·211 (7)
S(2)	0·106 (9)	0·120 (7)	0·140 (8)
S(3)	0·068 (16)	0·141 (7)	0·218 (7)
S(4)	0·101 (13)	0·161 (6)	0·196 (6)
Cl(1)	0·143 (10)	0·178 (7)	0·212 (6)
Cl(2)	0·116 (10)	0·142 (8)	0·154 (5)

this the Cu(2)–S(1)–S(2)–S(3) grouping is more distor-
ted from planarity than the Cu(1)–S(2)–S(3)–S(4) unit.
Hence, it would seem reasonable to say that for a Cu–Cl
distance greater than 3·2 Å there is no directed covalent
interaction while at distances less than 3·0 Å there are
varying amounts of covalent character in the Cu–Cl
bond.

The bridge bonding in Cu(tu)$_2$Cl is of considerable
interest. Since the S(3) thiourea group is bent only 14·8°
(Fig. 5) out of being coplanar with the Cu(2)–S(3)–Cu(1)
plane with a Cu(1)–S(3)–Cu(2) angle of 138·1 (2)°, the
bridge bond can be easily understood as the sulfur atom
contributing two nonbonding sp^2 orbitals and electron
pairs to form two S–donor–Cu–acceptor Cu–S electron
pair bonds. On the other hand, the sharp bridge angle
of 82·5 (2)° for the Cu(1)–S(2)–Cu(2) bridge must be

completely different since the S(2) thiourea group is ap-
proximately 9·8° from being perpendicular to the
Cu(1)–S(2)–Cu(2) plane (Fig. 6). Further, the short
metal–metal distance [2·981 (4) Å] and sharp bridge
angle are reminiscent of methyl carbon electron-defi-
cient bonding found in methyl-bridged polymeric di-
methylberyllium (Snow & Rundle, 1951), dimeric tri-
methylaluminum (Lewis & Rundle, 1953; Vranka &
Amma, 1967), polymeric dimethylmagnesium (Weiss,
1964), dimeric triphenylaluminum (Malone & McDo-
nald, 1967), octamethyldialuminummonomagnesium
(Atwood & Stucky, 1969), lithium tetraethylaluminate
(Gerteis, Dickerson & Brown, 1964) and polymeric di-
ethylmagnesium (Weiss, 1965). In fact, the bonding is
probably very similar. With this geometry, the only or-
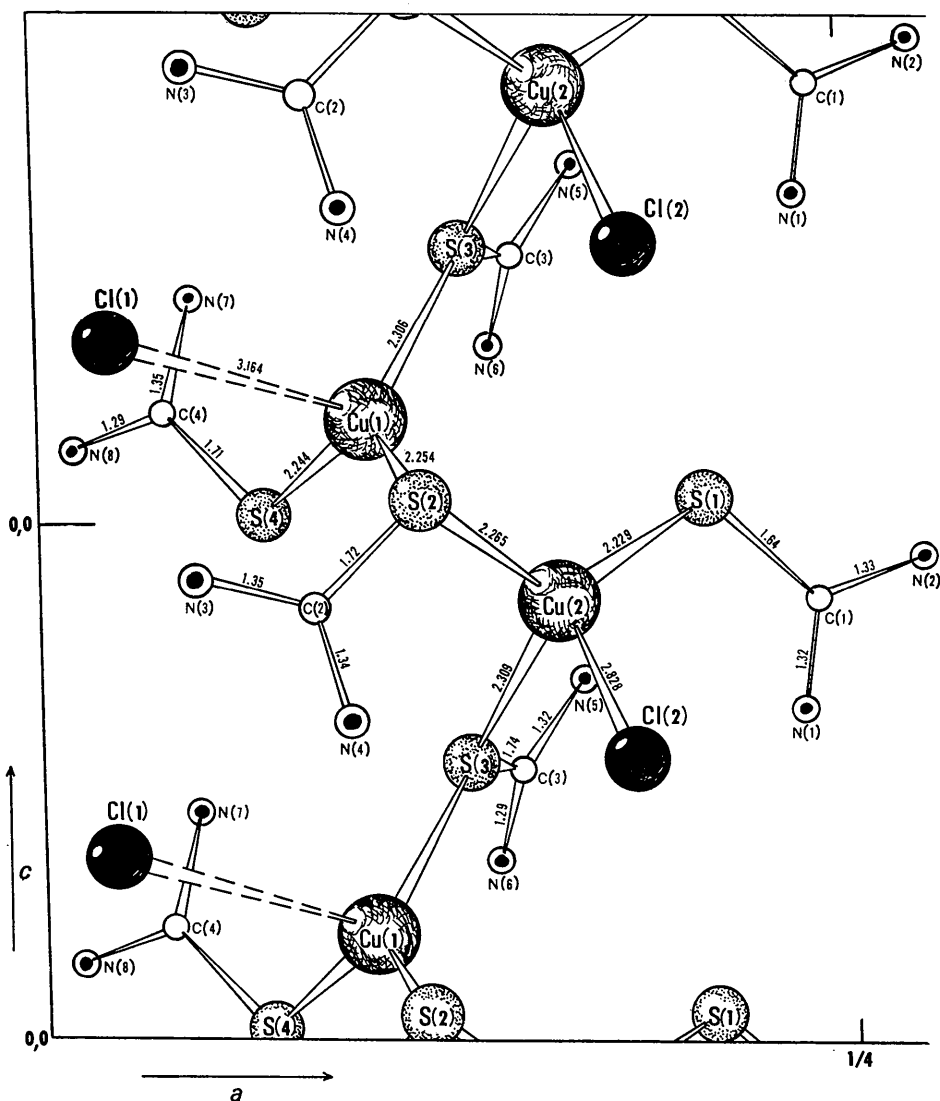bital that the thiourea molecule can contribute to the

Fig.3. Segment of the Cu–S–Cu chain looking down the b axis, showing the bonding distances. Maximum estimated standard
deviations are: for Cu–S, ±0·005; Cu–Cl, ±0·006; S–C, ±0·02; C–N, ±0·03 Å.

bridge bond is the $p\pi$ S–C molecular orbital (MO) with its electron pair. This orbital with two sp^2 hybrid orbitals (as indicated by the stereochemistry about Cu) of the Cu atoms would lead to a delocalized three-center, electron pair electron deficient bridge bond (Fig. 7): $\psi_{ED}=\sigma_1+\sigma_2+\pi$. This might be expected to elongate the S–C bond from that of free thiourea, but if it does, it is too small to be discernible from our data. However, since thiourea is planar including hydrogen atoms and there is evidence for a delocalized π MO involving the non-hydrogen atoms (see above), the electrons in the highest filled π MO, the a_1' level (Fig. 1, approximately nonbonding or weakly bonding), may be donated to the two Cu atoms without strongly affecting the S–C and C–N bond lengths. The strongly bonding a_1 level dominates the S–C and C–N π-interactions. Since it is well accepted that the π^* MO of carbon monoxide and other ligands are important in the stabilization of metal carbonyls and other complexes by behaving as a π^* acceptor for metal electrons, the a_1'' MO of thiourea could fulfill this same function. However, this interaction is energetically expensive and the system has an energetically cheaper option open to it. If one defines an axial system with the x axis in the direction

of the S–C bond, the y axis in the plane of the thiourea molecule and the z axis perpendicular to x and y, then the low-energy empty d_{yz} orbital of sulfur (which does not interact with the π orbitals of the molecule as would d_{xz}) is in a position for overlap with appropriate filled d orbitals of the Cu atoms. The multiple bonding is also supported by the relatively short Cu–S distances observed in this bridge. An alternative description of this bridge bonding might be to view it as if the S–C were behaving as an ethylene type donor. This would mean that an orbital of Cu should be directed toward the midpoint of the S–C bond rather than toward the S itself. Although this description would make the Cu and its three S neighbors even more coplanar by pushing the Cu atom approximately 0.1 Å closer to the plane, it distorts the S–Cu–S angles more from the idealized $120°$. No doubt the maximum in the bonding electron density is displaced somewhat toward the C(2) atom from S(2) and the true bonding is somewhat between the two described.

A similar means of replacing charge on the sulfur atom is probably utilized in the two terminal Cu–S interactions and would account for these bonds being the shortest Cu–S distances observed in this structure.

Table 4. Least-squares planes

(a) Equations of various least-squares planes of the type* $Ax+By+Cz-D=0$

Plane No.	A	B	C	D
1	−0.3348	−0.9309	−0.1462	4.4289
2	−0.1105	−0.9654	−0.2363	3.8324
3	0.8684	0.3163	−0.3819	−3.0741
4	0.5258	−0.8506	−0.0018	−1.4864
5	0.8217	−0.3767	−0.4277	−2.0055
6	0.4976	0.7126	−0.4946	−1.4646

(b) Deviations of atoms from the least-squares planes

Atom	Plane No. 1	2	3	4	Atom	Plane No. 5	Atom	Plane No. 6
S(I)	0.000 (3) Å	0.000 (3) Å	−0.006 (3) Å	0.002 (3) Å	Cu(1)	−0.155 (2) Å	Cu(2)	0.230 (2) Å
C(I)	−0.001 (14)	0.001 (11)	0.021 (12)	−0.009 (13)	S(2)	0.053 (3)	S(1)	−0.080 (3)
N(2I–1)	0.000 (14)	0.000 (10)	−0.007 (10)	0.003 (13)	S(3)	0.046 (3)	S(2)	−0.075 (3)
N(2I)	0.000 (13)	−0.001 (12)	−0.008 (11)	0.003 (11)	S(4)	0.055 (3)	S(3)	−0.075 (3)

I=plane number

* Coordinates x, y, z refer to an internal orthogonal coordinate system (Rollett, 1965). All atoms listed under a particular plane number were used with equal weights in the calculation of the least-squares plane.
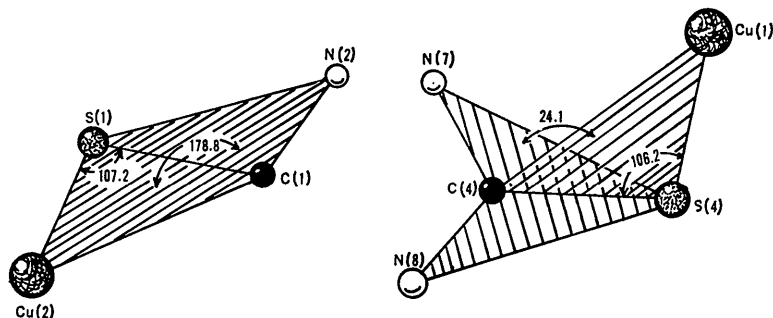

Fig. 4. Relevant angles between planes to specify the orientation of the S(1) and S(4) thiourea groups.

However, the Cu–S(3) bridge distances are the longest Cu–S distances observed and can probably be explained by the fact that in this case the sulfur atom is donating four electrons [two for each Cu–S(3) bond] to the two Cu atoms. This thiourea group is not in a favorable orientation for interaction of the filled d orbitals of Cu with the empty d orbitals of sulfur as is the case for the S(2) bridging thiourea group.

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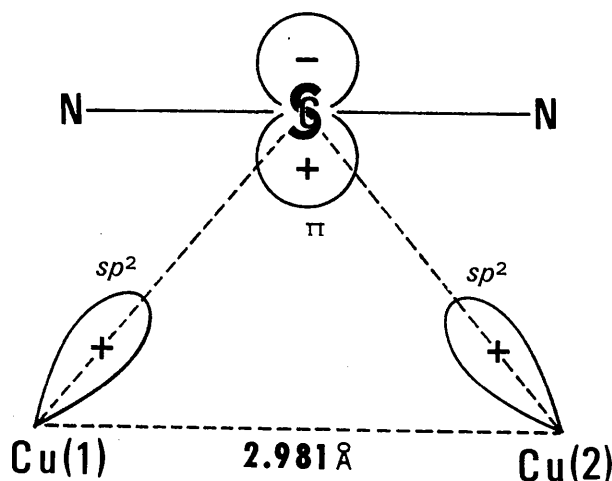Gerteis, R. L., Dickerson, R. E. & Brown, T. L. (1964). *Inorg. Chem.* **3**, 872.

Fig. 7. View of the orbitals perpendicular to the Cu(1)–S(2)–Cu(2) plane used to specify the bonding in the three-center, two-electron bridge bond. Sulfur and carbon atoms are superposed in this idealized projection. The Cu orbitals are sp^2 hybrids as specified by the planarity of the Cu(S)₃ units and the upper orbital is the S–C $p\pi$ MO as specified by the S(2) thiourea group orientation. The three-center MO is then sp^2[Cu(1)] + sp^2[Cu(2)] + tu πMO.
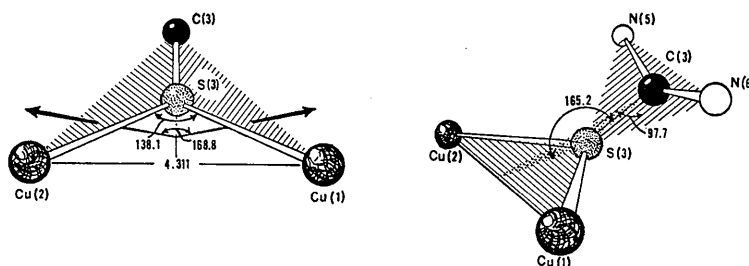

Fig. 5. Two views of the S(3) bridging thiourea group. These distances and angles completely specify the relative orientations of the Cu(1)–S(3)–Cu(2) and S(3)–C(3)–N(5)–N(6) planes.
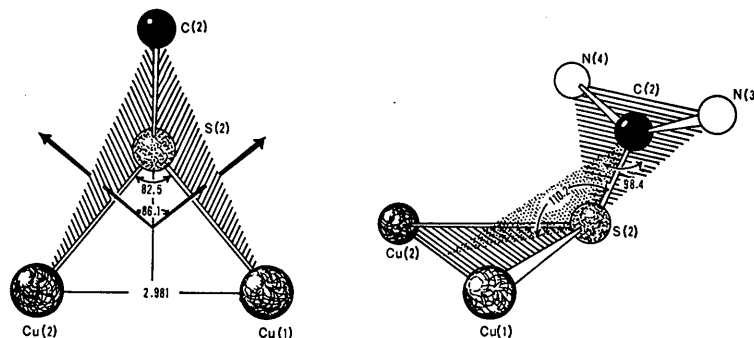

Fig. 6. Two views of the S(2) bridging thiourea group. These distances and angles completely specify the orientation of the planar S(2)–C(2)–N(3)–N(4) grouping relative to the Cu(1)–S(2)–Cu(2) plane.

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Crystal and Molecular Structure of α-Chlorotropane Monohydrate

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The crystals of α-chlorotropane monohydrate, $C_8H_{14}ClN . H_2O$, are monoclinic: space group $P2_1/c$, $a = 14\cdot285$ (1), $b = 6\cdot416$ (2), $c = 25\cdot238$ (2) Å, $\beta = 126\cdot11$ (2)°, $Z = 8$. The piperidine ring is in a very deformed chair form. The CH_3 group is in the equatorial position.

Introduction

The object of the investigation of α-chlorotropane (see Fig. 1) was to establish the attachment of the methyl group to the piperidine ring, the nitrogen atom of which forms no other bonds than two N–C bonds. In related structures the position of the methyl group is probably influenced by either the quaternization of the nitrogen atom or the forming of hydrogen bonds between adjacent molecules (Schenk, MacGillavry, Skolnik & Laan, 1967; Visser, Manassen & de Vries, 1954).

This primary object was not realized because during the investigation it became clear that water of crystallization is present in the ratio of 1:1. The water molecules form hydrogen bonds with the nitrogen atoms of the tropane molecules. Possibly as a result of this the methyl group is found in the equatorial position.

Experimental

α–Chlorotropane was prepared from pseudotropine,

following Archer, Lewis & Zenitz (1958). The liquid compound freezes at approximately 10°C. An attempt to obtain single crystals by putting some liquid into a small glass capillary and cooling in a Weissenberg camera failed. However, in a tightly closed flask placed in a freezing box a number of long thin needles were found after a month. Weissenberg pictures showed the crystals to be monoclinic with the unique axis along the needle axis.

From calibrated Weissenberg diagrams taken at −140°C the cell constants were calculated to be $a = 14\cdot285$ (1), $b = 6\cdot416$ (2), $c = 25\cdot238$ (2) Å, $\beta = 126\cdot11$ (2)° (the standard deviations in parentheses are in units of the last digit). From the systematic absences $h0l$ with $l = 2n + 1$ and $0k0$ with $k = 2n + 1$ it was concluded that the space group is $P2_1/c$. From a density determination by flotation it was concluded that there are 8 molecules in the unit cell (*i.e.* two molecules in the asymmetric unit). Since the crystals are deliquescent this determination was rather inaccurate. Reciprocal planes hkl with k from 0 to 5 were registered with