

Short Communications

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Refinement of the crystal structure of tris(thiourea)copper(I) chloride. By Y. OKAYA* and C. B. KNOBLER,† *IBM Thomas J. Watson Research Center, Yorktown Heights, New York, U.S.A.*

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The crystal structure of tris(thiourea)copper(I) chloride was determined several years ago (Knobler, Okaya & Pepinsky, 1959, hereafter called KOP(I)); although the work revealed the presence of infinite chains consisting of $\text{Cu}(\text{thiourea})_4$ tetrahedra, the refinement was left incomplete because of the lack of adequate computing facilities. Inequality in the C–N bonds of the thiourea ligands remained unexplained and it was felt that the bond distances had to be refined. The present communication deals with a further attempt in refining the structure using a full-matrix least-squares program on an IBM 7094 computer. The crystal belongs to the tetragonal system with $a=13.41$, $c=13.79$ Å, with space group $P4_12_12$.

Comparison between the observed and calculated structure factors in the previous article indicated that the intensities were affected by the secondary extinction. Therefore, F_o 's are corrected for the effect by using the formula:

$$F_o^{\text{corr}} = F_o^{\text{obs}} \exp \{g \cdot L P F \cdot F_{\text{calc}}^2\},$$

where $g=0.4 \times 10^{-4}$. The reported isotropic temperature factors were then converted into anisotropic temperature factors and used together with the listed atomic coordinates as the starting parameters.

At no time was the contribution of hydrogen atoms included. Weights, w , were assigned to the reflections according to the scheme

$$(i) |F_{\text{obs}}| > 150 \quad w = 10.0/|F_{\text{obs}}|$$

$$(ii) 150 \geq |F_{\text{obs}}| \geq 20.0 \quad w = 20.0/|F_{\text{obs}}|$$

$$\text{and} \quad (iii) 20.0 \geq |F_{\text{obs}}| \quad w = 0.0025 \cdot |F_{\text{obs}}|^2.$$

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† Present address: 300 South Michigan Avenue, Pasadena, California.

The atomic coordinates and their standard deviations after seven cycles of refinement are given in Table 1(a); a list of anisotropic temperature factors is given in Table 1(b). The anisotropic temperature factors were decoded into the three principal axes of their vibration ellipsoids; these data are studied in connection with the equations of the thiourea ligands. The final value of R was 0.096 including unobserved reflections. Tables of observed and calculated structure factors are available from one of the authors (Y. O.) on request.

Discussion

Bond distances and angles have been calculated from the atomic coordinates in Table 1(a); the equations of the least-squares planes for the thiourea ligands have also been calculated. The intramolecular distances and bond angles are shown in Figs. 1 and 2 respectively; deviations of atoms from the ligand planes are shown in Table 2.

As explained previously (KOP(I)), the crystal structure is ionic, consisting of chloride ions and infinite chains of cationic $[\text{Cu}(\text{thiourea})_3]^+$; the infinite chain is formed by linear arrangement of $\text{Cu}(\text{thiourea})_4$ tetrahedra by shared corners. As shown in Figs. 1 and 2, the bond distances and angles in the tetrahedron have become more normal than the previous values; the inequality of C–N bonds, especially those of ligand (III), has been removed and the values are closer to those in free thiourea (Kuncher & Truter, 1958). It is observed that ligand (I), which acts as a bridge between two Cu atoms, possesses two equal C–N distances, whereas the other two ligands still exhibit unequal C–N bonds; however, these results must be given a conservative estimate in view of the standard deviations involved in these bonds. The C–S distances have also been shortened to give values closer to the C–S distance in free thiourea, and the

Table 1(a). *Final atomic coordinates (in fractions of cell edges) and their standard deviations, σ (in 10^{-3} Å)*

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Cu	0.9713	2	0.3558	2	0.0847	2
S _I	0.8901	2	0.4931	2	0.0005	2
C _I	0.9246	11	0.6065	11	0.0493	10
N _I	0.8924	14	0.6898	10	0.0117	11
N _{I'}	0.9789	12	0.6110	10	0.1280	10
S _{II}	0.1179	3	0.3145	3	0.0116	3
C _{II}	0.2634	14	0.0843	14	0.0994	11
N _{II}	0.2290	15	0.9977	16	0.1210	12
N _{II'}	0.2417	18	0.6585	17	0.0815	12
S _{III}	0.8447	3	0.2354	3	0.0749	3
C _{III}	0.8942	12	0.1235	10	0.1087	10
N _{III}	0.9948	11	0.1081	11	0.1107	13
N _{III'}	0.6626	12	0.5460	12	0.1165	13
Cl ⁻	0.5157	2	0.3559	2	0.0931	2

Table 1(b). List of thermal parameters in the expression $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$
The standard deviations are less than 2×10^{-4}

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.0056	0.0055	0.0045	0.0003	0.0016	-0.0011
S _I	0.0038	0.0034	0.0028	0.0005	-0.0003	0.0000
C _I	0.0041	0.0053	0.0027	0.0003	0.0010	-0.0022
N _I	0.0111	0.0038	0.0055	0.0000	-0.0060	0.0019
N _I '	0.0086	0.0054	0.0047	0.0014	-0.0108	-0.0018
S _{II}	0.0042	0.0062	0.0046	0.0021	0.0021	0.0022
C _{II}	0.0070	0.0070	0.0035	0.0093	-0.0051	-0.0030
N _{II}	0.0097	0.0095	0.0041	0.0038	0.0012	0.0013
N _{II} '	0.0141	0.0108	0.0058	-0.0105	-0.0086	0.0096
S _{III}	0.0038	0.0046	0.0045	-0.0004	-0.0010	-0.0020
C _{III}	0.0053	0.0033	0.0039	-0.0006	-0.0005	-0.0003
N _{III}	0.0043	0.0062	0.0083	0.0022	-0.0036	0.0015
N _{III} '	0.0060	0.0052	0.0017	0.0019	0.0044	0.0021
Cl ⁻	0.0128	0.0039	0.0049	0.0017	-0.0040	-0.0009

Table 2

(a) Planarity of the ligands. The least-squares planes, $AX + BY + CZ = D$ †, and shifts (A) of atoms from the planes. Cu(A) and Cu(B) are away from S_I by 3.43₄ and 2.37₉ Å respectively. See Fig. 1.

Ligand I		Ligand II		Ligand III	
$A = 0.8171$, $B = 0.0239$		$A = 0.2655$, $B = -0.9048$		$A = 0.0229$, $B = 0.3021$	
$C = -0.5760$, $D = 9.9132$		$C = 0.3330$, $D = 0.2150$		$C = 0.9530$, $D = 2.1993$	
Atoms	Shifts	Atoms	Shifts	Atoms	Shifts
S _I	-0.006	S _{II}	0.002	S _{III}	-0.001
C _I	0.020	C _{II}	-0.007	C _{III}	0.004
N _I	-0.007	N _{II}	0.003	N _{III}	-0.002
N _I '	-0.007	N _{II} '	0.002	N _{III} '	-0.002
*Cu(A)	0.171	*Cu	-0.685	*Cu	0.655
*Cu(B)	0.945				

(b) Configuration around S_I

$$A = 0.9347, B = 0.1315, C = -0.3303, D = 13.3230$$

Atoms	Cu(A)	Cu(B)	S _I	C _I	N _I *	N _I '*
Shifts	0.093	0.098	-0.298	0.099	0.025	0.442

* These atoms were not included in the evaluation of the equations.

† X, Y, Z , and D are measured in Å.

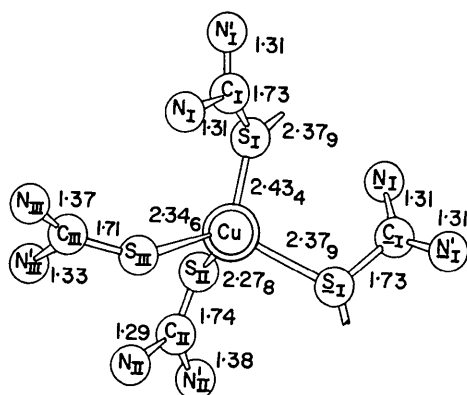


Fig. 1. Tris(thiourea)copper(I) ion: Bond distances. The standard deviations are of the order of 0.005 Å for Cu-S, 0.02 Å for S-C and 0.03 Å for distances between lighter atoms.

Cu-S-C angles also become closer to the usual angle. Recently, Lopez-Castro & Truter (1963) made a table of C-S and C-N distances in various thiourea complexes; our previous values for the C-S bonds (1.80 ~ 1.83 Å)

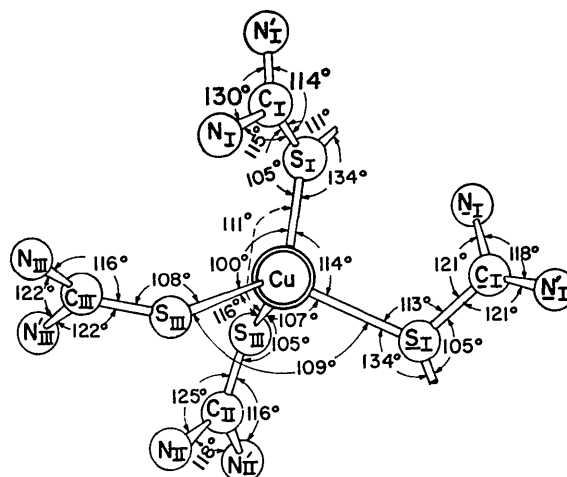


Fig. 2. Tris(thiourea)copper(I) ion: Bond angles. The deviations of these values are about 0.4° for angles around Cu and 3° for other angles. The previous values in ligand (I) are also shown (top of this figure) for comparison.

are considerably longer than those in free thiourea and

were interpreted as examples of increases in C-S bond lengths. However, the present result has brought down the C-S distances to values almost equal to the free molecule value. The Cu-S-C angles fall within 105° and 111°; that around S_{II}, which was 99°, has changed to a more reasonable value of 105°.

The ligands are all planar within experimental error and analyses of the anisotropic temperature factors reveal that the nitrogen atoms have the directions of the largest thermal vibration nearly perpendicular to the planes of the ligands. The central copper atom is about 0.7 Å away from the planes of ligands (II) and (III). (See Table 2.) Each NH₂ group is associated with one short NH-Cl contact; the N-Cl distances are between 3.24 and 3.44 Å and surround the chloride ion in a rather unusual way (*cf.* Fig. 5(a) and (b) of KOP(I)); the possible hydrogen-bond formation has been explained in the previous report. It should also be noted here that all

N-N distances are longer than 3.4 Å and no N-H...N hydrogen bond is expected in the structure; in this structure, not all of the available hydrogens are involved in hydrogen-bond formation. As reported previously (KOP(I)), several N-S separations shorter than 3.4 Å are also found in the structure; according to a recent review paper by Wallwork (1962), these separations might be interpreted as N-H...S hydrogen bonds.

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Crystallographic data for LiBr.2(CH₃)₃.COH.H₂O, a lithium bromide-tertiary butyl alcohol complex. By DAVID J. HAAS, *Department of Biophysics, State University of New York at Buffalo, Roswell Park Graduate Division, Buffalo, N. Y., U. S. A.*

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Spectral studies (Bufalini & Stern, 1961) of mixtures of alcohols and electrolytes suggest that, in many cases, strong interactions occur between the hydroxyl group of the alcohol and the ions in solution. Occasionally, the interactions are sufficiently strong to precipitate crystalline complexes.

A crystalline complex of lithium chloride or lithium bromide with tertiary butyl alcohol (TBA) is obtained by one of two methods: (1) by floating pure TBA on top of a saturated salt solution, whereupon crystals form at the interface; (2) by mixing the two liquids together, heating, and allowing them to cool to room temperature. By the second method, single crystals form in the less dense alcohol layer; large well-shaped crystals with distinct cleavage directions for LiBr and thin flexible platelets for LiCl. These crystals are stable in pure TBA, but decompose when placed in air, the saturated salt solution, water, benzene, dioxane, or hydrocarbons. It was possible, however, to determine the densities of the crystals by the flotation method in a mixture of TBA and carbon tetrachloride. These are: LiBr-TBA, 1.04 g.cm⁻³; LiCl-TBA, 0.98 g.cm⁻³.

The composition of the LiBr-TBA complex was obtained from a titration of the bromide ion and by heating the crystals and determining the percentage of alcohol in the distillate. The titration indicated that the crystals contain approximately 30% LiBr by weight, while the alcohol determination established the formula as LiBr.2(CH₃)₃COH.H₂O.

Only the LiBr complex was examined by X-rays, for the crystals are more stable than those of the LiCl complex which give a very poor diffraction pattern.

Using a GE XRD 5 with Single Crystal Orienter and Cu K α radiation, we found that the LiBr complex crystallizes in the orthorhombic system with a C-centered cell. The lattice constants and conditions for reflections are:

$$\begin{aligned} a &= 19.31 \text{ \AA} \mp 0.01 \text{ \AA} & hkl & h+k=2n \\ b &= 32.23 \text{ \AA} \mp 0.01 \text{ \AA} & hk0 & h=2n, k=2n \\ c &= 15.88 \text{ \AA} \mp 0.01 \text{ \AA} \end{aligned}$$

The space group, as determined from these conditions, is either *C2ma* or *Cmma*. From the formula, unit-cell size, and density, one finds that there are 24 formula weights in the unit cell (calculated density, 1.03 g.cm⁻³). If the space group is *C2ma*, there can be three formula units in the asymmetric unit provided that none are in special positions, whereas *Cmma* requires at least some of these atoms to be in special positions. No further work is intended on either of these compounds.

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