Adducts of 1,3,5-Trithian with Copper(I) Chloride: the Crystal Structure of $2(C_3H_6S_3),3CuCl$

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THE cyclic trithioether 1,3,5-trithian forms many crystalline adducts with silver(I) and mercury(II) salts,[1] five of which have recently been shown to be polymeric by *X*-ray diffraction analysis.[2] We report the preparation of two adducts of this ligand with copper(I) chloride and the crystal structure of one of them.

From the reaction of copper(I) chloride with 1,3,5-trithian in ethanolic hydrochloric acid, two adducts are obtained with stoicheiometric ratios $2(C_3H_6S_3),3CuCl$ and $(C_3H_6S_3),3CuCl$, depending upon the experimental procedure. Both are stable crystalline materials which decompose on heating at about 160° and 240°, respectively. They are not soluble in any common solvent except hydrochloric acid.

A crystal-structure analysis of the adduct $2(C_3H_6S_3),3CuCl$, based on some 1500 independent reflections, recorded photographically, has shown it to be a polymer.

Crystals of $2(C_3H_6S_3),3CuCl$ are orthorhombic, with $a = 6{\cdot}7628 \pm 0{\cdot}0006$, $b = 7{\cdot}3588 \pm 0{\cdot}0005$, $c = 31{\cdot}954 \pm 0{\cdot}002$ Å; $U = 1590{\cdot}2$ Å^3; $D_m = 2{\cdot}5 \pm 0{\cdot}3$ g.cm.$^{-3}$ (by flotation); $Z = 4$, $D_c = 2{\cdot}395$ g.cm.$^{-3}$; $F(000) = 1113{\cdot}6$. Space group: $P2_12_12_1$ (No. 19) from systematic absences. Cu-K_α radiation, $\mu = 162{\cdot}2$ cm.$^{-1}$. The crystal data were derived by least-squares methods from calibrated zero-layer Weissenberg photographs, using only reflections from Cu-$K_{\alpha1}$ radiation (λ taken as $1{\cdot}540562$ Å). The limits of errors given are generous estimates of maximum errors.

The structure was solved in the *h0l* projection by means of a direct-phase determining procedure based on the iterative application of Sayre's equation,[3] a method similar to the symbolic addition procedure of Karle and Karle.[4] Approximate values for the *y* co-ordinates were obtained by a computer-programmed systematic trial.

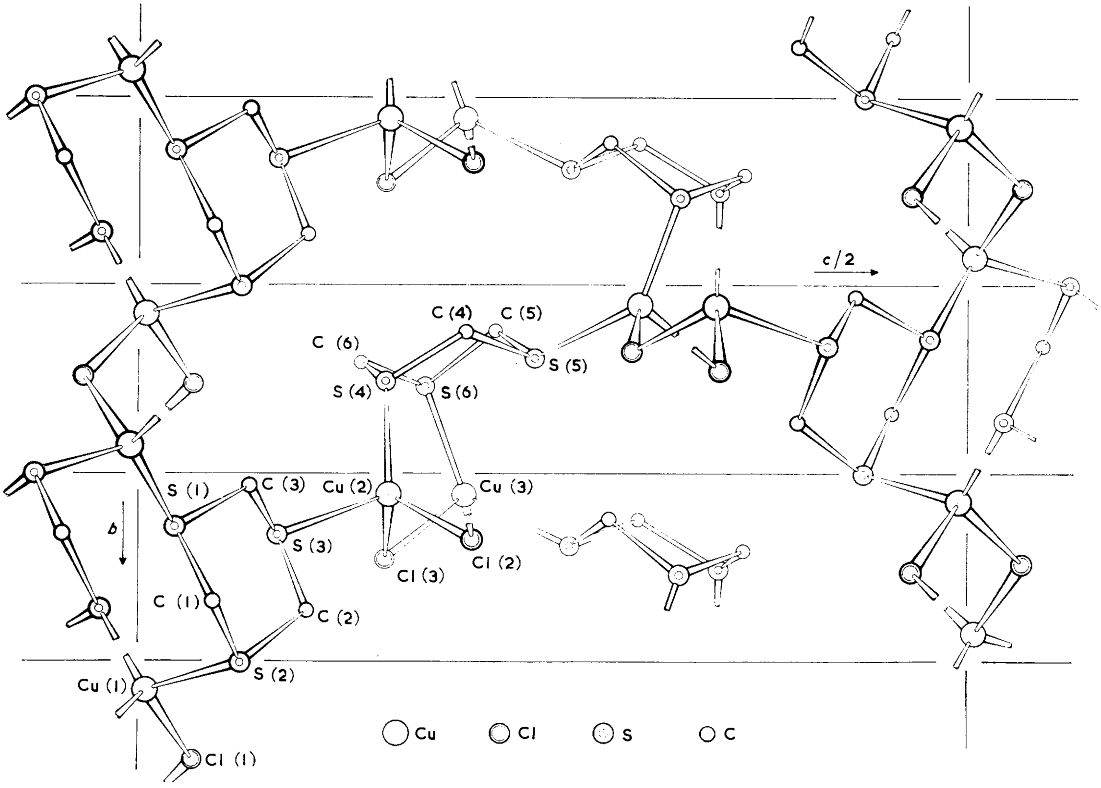

FIGURE. $2(C_3H_6S_3),3CuCl$: *projection of the structure along* [100].

The three-dimensional refinement was carried out by anisotropic block-diagonal least-squares techniques to an *R* value of 0·099. Further refinement is in progress.

The projection of the structure along the [100] direction is shown in the Figure. The copper and chlorine atoms form chains of two different types, propagating through the crystal in the *a* direction; the repeating unit of each chain consists of two copper and two chlorine atoms in the conformational sequence GGGG in one case, and GTG*T in the other. Both types are found in the two crystal structures of cuprous chloride itself; the first along [100] in the zinc blende structure of the low-temperature form,[5] the second along [112] in the same structure. The second also occurs along $[10\bar{1}0]$ in the wurtzite structure of the high-temperature form[6] and has been found also as an independent unit in catena-μ-chloro-(cyclo-octatetraene)copper(I).[7] All chains are bound together in a three-dimensional network by the terdentate ligand molecules, as shown in the Figure.

Two crystallographically independent ligand molecules occur in the crystal, both in the chair conformation (which is typical of the free ligand[8]) and connected to three separate metal atoms. They differ, however, in (i) their type of bonding, one being linked to three chains of two different types, the other one to two chains of the same type, and (ii) the orientation of the metal–sulphur contacts with respect to the ring, which is *eae* for the first molecule and *aea* for the second one.

Each of the three crystallographically independent copper atoms is bound tetrahedrally to two chlorine and two sulphur atoms. The copper–chlorine and copper–sulphur bond lengths vary from 2·30 to 2·43 Å and from 2·25 to 2·41 Å respectively, in good agreement with literature values for similar structures.[9]

(*Received, July 30th*, 1968; *Com.* 1036.)

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[1] D. A. Hukin, B.Sc. Thesis, Oxford, 1963; J. A. W. Dalziel and T. G. Hewitt, *J. Chem. Soc.* (*A*), 1966, 233.

[2] W. R. Costello, A. T. McPhail, and G. A. Sim, *J. Chem. Soc.* (*A*), 1966, 1190; R. S. Ashworth, C. K. Prout, A. Domenicano, and A. Vaciago, *ibid.* 1968, 93; A. Domenicano, L. Scaramuzza, A. Vaciago, R. S. Ashworth, and C. K. Prout, *ibid.*, 1968, 866.

[3] D. Sayre, *Acta Cryst.*, 1952, **5**, 60.

[4] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[5] R. W. G. Wyckoff and E. Posnjak, *J. Amer. Chem. Soc.*, 1922, **44**, 30.

[6] M. R. Lorenz and J. S. Prener, *Acta Cryst.*, 1956, **9**, 538.

[7] N. C. Baenziger, G. F. Richards, and J. R. Doyle, *Inorg. Chem.*, 1964, **3**, 1529.

[8] N. F. Moerman and E. H. Wiebenga, *Z. Krist.*, 1937, **97**, 323; O. Hassel and H. Viervoll, *Acta Chem. Scand.*, 1947, **1**, 149.

[9] C. I. Brändén, *Acta Chem. Scand.*, 1967, **21**, 1000, and references therein.