Adamantane-like Cage Units in the Crystal Structure of a Polymeric Adduct of 1,3,5-Trithian with Copper(I) Chloride

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Summary Crystals of $(C_3H_6S_3),3CuCl$ are shown by *X*-ray diffraction analysis to contain a two-dimensional network of cage units with an adamantane-like structure.

IN a previous Communication[1] we reported the preparation of two adducts of 1,3,5-trithian with copper(I) chloride, namely $2(C_3H_6S_3),3CuCl$ and $(C_3H_6S_3),3CuCl$, and the crystal structure of the first. Since then we have succeeded in obtaining single crystals of $(C_3H_6S_3),3CuCl$ suitable for *X*-ray diffraction work, and the present Communication briefly describes the novel polymeric structure of this compound.

Crystals of $(C_3H_6S_3),3CuCl$ are monoclinic, space group $P2_1/n$, with $a = 6{\cdot}529$, $b = 15{\cdot}179$, $c = 9{\cdot}962$ Å, $\beta = 90°18'$; $U = 987{\cdot}3$ Å^3; $Z = 4$, $D_c = 2{\cdot}928$ gcm^{-3}; $F(000) = 821{\cdot}9$. Cu-K_α radiation, $\mu = 202{\cdot}5$ cm^{-1}. Owing to the extremely small dimensions of the crystals obtained we were unable to perform density measurements. We assumed $Z = 4$ by molecular volume considerations.

The structure was solved by a fully automated iterative application of Sayre's equation,[2] and refined by block-diagonal least-squares techniques with anisotropic thermal parameters to $R = 0{\cdot}094$. The intensities of 1034 independent non-zero reflections from photographic records were used in the refinement. Approximate absorption corrections were applied, assuming that specimens were cylindrical.

The most conspicuous feature in the structure is the existence of a network of adamantane-like cage units, each

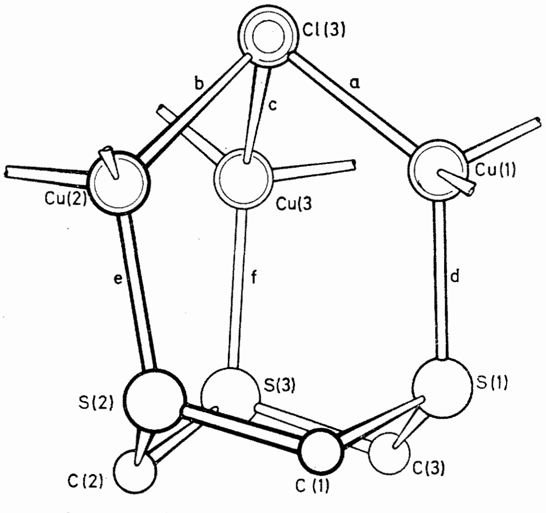

FIGURE. *A perspective view of the adamantane-like cage unit. Some relevant bond distances and angles are*: a = 2·332, b = 2·343, c = 2·366, d = 2·269, e = 2·275, f = 2·254 Å (*all* ±0·006 Å); ab = 90·8, ac = 87·6, bc = 81·2, ad = 122·8, be = 123·5, cf = 127·6° (*all* ±0·2°). *The* Cu–Cu *separations are all longer than* 3·0 Å.

composed of a 1,3,5-trithian molecule, three copper, and one chlorine atoms (see Figure). The tridentate ligand molecule forms three axial donor bonds, which had not previously been observed with this ligand. A somewhat similar cage unit, involving three (bivalent) copper atoms and one sulphate ion as ligand, has recently been found in μ_3-hydroxo-μ_3-sulphato-tri-μ-(pyridine-2-aldehydeoximato)-tricopper(II).[3]

The cage units are connected through chlorine bridges in a two-dimensional network, forming a corrugated layer parallel to (010). Adjacent layers are held together only by Van der Waals forces.

The unusually narrow range of the copper–sulphur bond distances [2·254—2·275 Å, as compared to 2·25—2·41 Å in $2(C_3H_6S_3),3CuCl$] and their fairly short values† are indicative of a strong, covalent interaction, with probable back-donation from the filled 3*d* orbitals of the metal to the empty 3*d* orbitals of the sulphur atoms.

The co-ordination geometry of the three independent copper atoms in the crystal-chemical unit is approximately tetrahedral, as it is in $2(C_3H_6S_3),3CuCl$. Large distortions in the bond angles are produced, however, by the requirement of fitting the larger Cu_3Cl moiety on the smaller triple "bite" of the ligand. This forces the sulphur–copper–Cl(3) angles to spread out to about 125°, whilst the angles at the apical chlorine atom, Cl(3), are drastically reduced to values even smaller than 90°. The resulting cage is, however, stabilized by the strong sulphur–copper interactions, as well as entropy factors.

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† Literature values for the copper(I)–sulphur bond distances in a number of similar structures vary from 2·23 to 2·47 Å.[4]

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