Crystal and Molecular Structure of Tris(ethylenethiourea)copper(I) Sulphate and Tris(tetramethylthiourea)copper(I) Tetrafluoroborate [Examples of Trigonal Planar Copper(I) Stereochemistry]

By M. S. WEININGER, G. W. HUNT, and E. L. AMMA*

(*Department of Chemistry, University of South Carolina, Columbia, South Carolina* 29208)

Summary The crystal structures of tris(ethylenethiourea)-copper(I) sulphate and tris(tetramethylthiourea)copper(I) tetrafluoroborate have been determined and both shown to contain $Cu^{(I)}$ and three sulphur atoms in a planar arrangement.

THE stereochemistry of copper(I) is important not only because of its chemical interest, but also because of its relevance to oxidation–reduction in copper-containing enzymes.[1] With soft ligands, *e.g.*, sulphur, compounds with the same stoicheiometry may have different stereochemistry. Tris(thiourea)copper(I) tetrafluoroborate, $[Cu(tu)_3]BF_4$,[2] and tris-(*NN'*-dimethylthiourea)copper(I) tetrafluoroborate, $[Cu(s\text{-}dmtu)_3]BF_4$,[3] are sulphur-bridged dimers with tetrahedral Cu^I; while tris(ethylenethiourea)-copper(I) sulphate and tris(tetramethylthiourea)copper(I) tetrafluoroborate are trigonal planar Cu^I monomers. Hence, the stereochemistry of Cu^I with "soft" atom donors is very flexible. We report here the crystal and molecular structure of the last two complexes.

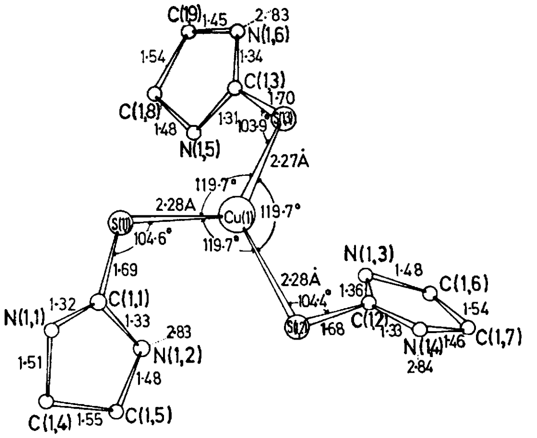

FIGURE 1. *The structure of the* $Cu(etu)_3^+$ *ion showing the arrangement of ligands.* N–H · · · O *hydrogen bonds are from* N(1,2), N(1,4), *and* N(1,6) *to oxygen atoms of a sulphate group. There are two independent ions per cell, but they are essentially identical and only one is shown. E.s.d.s of bond lengths* Cu–S ± 0·004, S–C ±0·012, C–N *and* C–C, ±0·02 Å *or less. E.s.ds of angles:* S–Cu–S ±0·1, Cu–S–C ± 0·2°.

Tris(ethylenethiourea)copper(I) sulphate, $[Cu(etu)_3]_2SO_4$, was prepared by mixing at room temperature equal volumes of aqueous 0·0025M-$CuSO_4$ and 0·01M-ethylenethiourea. The solution was filtered and colourless, diffraction-quality crystals formed from this solution. *Crystal data:* monoclinic, *Ic*; a = 18·916(1), b = 12·772(1), c = 13·974(1) Å, β = 96·99(1)°; Z = 4; D_m = 1·66, D_c = 1·66 g cm^{-3}; μ = 17·8 cm^{-1} with Mo-K_α radiation.

Diffraction data were collected on a Picker card-programmed automated diffractometer out to 2θ = 60°; 2918 non-zero reflections were used in structure solution and refinement. Absorption corrections were made and the maximum and minimum transmission coefficients were found to be 0·624 and 0·562, respectively.[4] Structure was solved by standard heavy-atom methods and refined by full-matrix least-squares including anisotropic temperature factors and anomalous dispersion corrections for Cu and S to a final R of 0·047.[5] The structure consists of isolated monomeric $Cu(etu)_3^+$ units with planar CuS_3 and some N–H · · · O hydrogen bonding (Figure 1).

The isolated $Cu(etu)_3^+$ ions are propellor-shaped with a left-hand screw, but maintain a trigonal planar CuS_3 unit. The twisting and tilting (see Figure 1 and caption) are largely due to N–H · · · O hydrogen bonding between the sulphate groups and one nitrogen of each ethylenethiourea group. These N · · · O distances vary from 2·76 to 2·84 Å with an N–H · · · O angle of *ca.* 160°. Such distances indicate significant hydrogen bonding.

Tris(tetramethylthiourea)copper(I) tetrafluoroborate, $[Cu(tmtu)_3]BF_4$, was prepared as above except from $Cu(BF_4)_2$ and tetramethylthiourea. *Crystal data:* $P2_1/c$; a = 15·987-(8), b = 12·596(5), c = 13·495(6) Å, β = 102·88(1)°; Z = 4; D_m = 1·36, D_c = 1·34 g cm^{-3}; μ = 11·05 cm^{-1} with Mo-K_α.

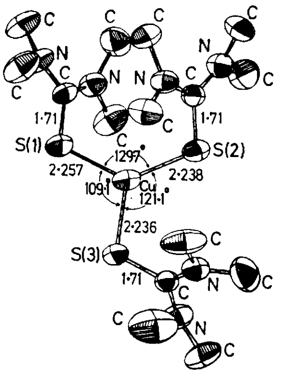

FIGURE 2. *An ORTEP drawing of the molecular structure of the* $Cu(tmtu)_3^+$ *ion. E.s.d.s of bond lengths are* Cu–S ± 0·002, S–C 0·004 Å. *E.s.d.s of angles* S–Cu–S ± 0·05, Cu–S–C ± 0·2°.

The maximum and minimum transmission factors were found to be 0·754 and 0·628, respectively. Data were collected as for $[Cu(etu)_3]_2SO_4$ and the structure was solved and refined as above, but H atom contributions were included for a final R of 0·049 with 3360 reflections. The structure consists of monomeric $Cu(tmtu)_3^+$ units with planar CuS_3 fragments (Figure 2).

$Cu(tmtu)_3^+$ is considerably distorted from trigonal configuration. This distortion arises, no doubt, from steric interactions between adjacent tetramethylthiourea groups as can be seen in the S–Cu–S angles. In both structures the S–C, C–N, and C–C distances and corresponding angles are those expected.

With the same stoicheiometries as the present two structures, $[Cu(tu)_3]BF_4$, $[Cu(s\text{-dmtu})_3]BF_4$,[3] and tris(*NN*-dimethylthiourea)copper(I) tetrafluoroborate, $[Cu(u\text{-dmtu})_3]BF_4$,[6] are all sulphur-bridged dimers with tetrahedral Cu^I.

On the other hand, $Cu(tu)_2Cl$ contains trigonal planar CuS_3[7,8] in a chain structure and $Cu(s\text{-dmtu})_3Cl$[5] contains a distorted tetrahedral CuS_3Cl unit, whereas $Cu_4(tu)_{10}(NO_3)_4$[9] contains fused eight- and four-membered alternating Cu–S rings. In addition, $[Cu_4(tu)_{10}](SiF_6)_2,H_2O$ contains an alternating Cu–S six-membered ring with tetrahedral Cu and a CuS_3 unit with trigonal pyramidal Cu^I.

Therefore, when soft ligands are involved, it is particularly difficult to make predictions concerning the stereochemistry of Cu^I based on the stoicheiometry.

We thank the N.I.H. for partial support.

(*Received*, 1*st August* 1972; *Com.* 1349.)

---

[1] J. Peisach, P. Aisen, and W. E. Blumberg, 'The Biochemistry of Copper,' Academic Press, New York, 1966.

[2] I. F. Taylor, jun., and E. L. Amma, 158th National Amer. Chem. Soc. Meeting, Sept., 1969, New York, paper INOR 208 (to be published in *Inorg. Chem.*).

[3] M. S. Weininger and E. L. Amma, to be published.

[4] Absorption corrections made with GONO 9, originally written by W. C. Hamilton, Brookhaven National Laboratory, with local modifications.

[5] For computer programs, source of scattering factors, *etc.*, see R. L. Girling and E. L. Amma, *Inorg. Chem.*, 1971, **10**, 335.

[6] G. W. Hunt and E. L. Amma, to be published.

[7] W. A. Spofford, tert., and E. L. Amma, *Acta Cryst.*, 1970, **B26**, 1474.

[8] (a) This is not meant to imply that trigonal planar Cu^I has not been previously observed. For example, see P. G. Eller and P. W. R. Corfield, *Chem. Comm.*, 1971, 105; (b) A. H. Lewin, R. J. Michl, P. Ganis, and U. Lepore, *J. C. S. Chem. Comm.*, 1972, 661.

[9] R. G. Vranka and E. L. Amma, *J. Amer. Chem. Soc.*, 1966, **88**, 4270.

[10] E. A. H. Griffith, W. A. Spofford, tert., A. G. Gash, and E. L. Amma, to be published.