# A Six-membered $Cu_3S_3$ Ring in Decakis(thiourea)tetracopper(I) Hexafluorosilicate Monohydrate: *X*-Ray Crystallographic Structure Determination

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*Summary* The crystal structure of $Cu_4[SC(NH_2)_2]_{10}(SiF_6)_2,H_2O$ has been determined and found to consist of six-membered rings of alternating Cu and S atoms connected by sulphur bridges to form chains, which are in turn interconnected *via* a $Cu_2S_2$ four-membered ring to form a three-dimensional polymer.

COPPER(I) is capable of a wide variety of stoicheiometry and stereochemistry, and linear, trigonal planar,[1] tetrahedral, and square-planar[2] examples are known. Clusters containing two, three, four, and eight copper(I) atoms have been reported.[3] We report here on the structure of a new cluster, decakis(thiourea)tetracopper(I) hexafluorosilicate monohydrate, $Cu_4[SC(NH_2)_2]_{10}(SiF_6)_2,H_2O$, $\{Cu_4(tu)_{10}(SiF_6)_2,H_2O\}$ which was prepared by treating a 0·1 M-aqueous thiourea solution with a 0·1 M-aqueous $Cu(H_2O)_6(SiF_6)$ solution in a ratio of 1:3. The excess of sulphur was removed and diffraction quality crystals were formed in the solution. *Crystal data:* monoclinic, $P2_1/c$; $a = 18{\cdot}316(3)$, $b = 14{\cdot}557(3)$, $c = 21{\cdot}064(5)$ Å, $\beta = 127{\cdot}31(1)°$, $U = 4467$ Å$^3$, $Z = 4$, $Cu_4(tu)_{10}(SiF_6)_2,H_2O$, $D_m = 1{\cdot}93$, $D_c = 1{\cdot}96$ g cm$^{-3}$, $\mu = 24{\cdot}9$ cm$^{-1}$; $\lambda = 0{\cdot}71068$ Å; maximum variation in transmission coefficient[4] was 0·83—0·68; crystal size 0·59 mm × 0·082 mm × 0·069 mm (mounted about long direction); 3554 non-zero independent *hkl* counter measured intensities.† The structure was solved by direct methods using Fame, *etc.*,[5] for initial phases and Fourier methods thereafter. The structure was refined with

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† Data collected with card-controller Picker full-circle diffractometer using Mo-$K_\alpha$ radiation, $\lambda = 0{\cdot}71068$ Å.

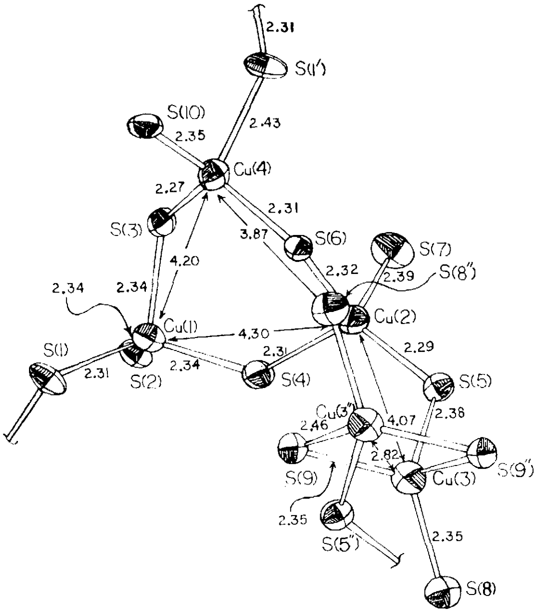

**FIGURE.** *The structure of* $Cu_4[SC(NH)_2]_{10}(SiF_6)_2,H_2O$ *showing only the* Cu *and* S *atoms and indicating only distances involving these atoms. E.s.d.'s* Cu–Cu ± 0·005, Cu–S ± 0·007 Å. *The six-membered ring is* Cu(1), S(3), Cu(4), S(6), Cu(2), *and* S(4) *The chain is built up by the bridging of the rings through* S(1) *and* S(1′), etc., via *a screw axis that runs through* S(1) *and* S(1′). *The chains are bound together to form the polymer by bridging sulphur atoms* via *four-membered rings*, e.g., Cu(3), S(9), Cu(3′), *and* S(9″) *with a centre of symmetry at the mid-point. The double-primed atoms are related to the unprimed atoms (lower right hand corner) by a centre of symmetry.*

full-matrix least-squares including anomalous dispersion corrections for Cu, S, and Si and including anisotropic temperature factors to a final $R$ of 0·049.

The structure may be described as a three-dimensional polymer (Figure) made up of six-membered rings ($Cu_3S_3$) which are sulphur-bridged to form chains. The chains in turn are interconnected by Cu–S–Cu bonds forming four-membered $Cu_2S_2$ rings between the chains.

The six-membered rings are in the boat form. The orientation of the thiourea groups in which the sulphur forms the bridging atom in the ring and between rings to form the chain is such that each sulphur contributes two electron pairs from $sp^2$ non-bonding orbitals to form the Cu–S–Cu bonds.

For the four-membered rings, the Cu–S distances are significantly different from one another (2·35 and 2·46 Å). The Cu–Cu distance at 2·82 Å is much shorter than in the other Cu–S–Cu bridges in this structure, and the Cu–S–Cu angle is much smaller than the others, at 72°. In contrast to the other types of Cu–S–Cu bridges in this structure, the orientation of the thiourea groups is such that the short Cu–S bond is made up from an $sp^2$ orbital and electron pair, whereas the long Cu–S bond is made up of a S–C $p_\pi$ orbital and electron pair.

The environment of all the Cu atoms in the structure may be described as a very distorted tetrahedron in which the S–Cu–S angles vary from 95—120°. The $SiF_6^{2-}$ ions and water molecules seem to do no more than participate in hydrogen bonding in the structure.

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[2] T. Ogura, R. D. Mounts, and Q. Fernando, *J. Amer. Chem. Soc.*, 1973, **95**, 949.

[3] J. K. Stalick and D. W. Meek, *J. Amer. Chem. Soc.*, in the press; L. E. McCandlish, E. C. Brissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *ibid.*, 1968, **90**, 7357 and references therein.

[4] Absorption corrections made with local variations on program GONO-9 originally written by W. C. Hamilton, Brookhaven National Laboratory, New York.

[5] Programs Fame, Magic, Link, and Sympl written by R. Dewar, A. Stone, and E. B. Fleischer with local modifications; For computer programs used, source of scattering factors and other details, see R. L. Girling and E. L. Amma, *Inorg. Chem.*, 1971, **10**, 335.