Preparation and *X*-Ray Crystal Structure of a Novel Tetranuclear Copper(I) Ethylenethiourea Cluster Complex, μ_4-Ethylenethiourea-*cyclo*-tetrakis-μ-(ethylenethiourea)tetrakis[ethylenethioureacopper(I)] Nitrate Hexahydrate

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Summary The structure, geometry, and bonding in $[Cu_4(C_3H_6N_2S)_9(NO_3)_4],6H_2O$ have been established by *X*-ray analysis which reveals discrete $Cu_4(C_3H_6N_2S)_9{}^{4+}$ cations containing an alternating Cu–S eight-membered ring with a unique ethylenethiourea ligand in an axial position bridging four copper atoms.

IT is now well established that copper(I) complexes with sulphur atom donors are capable of exhibiting different structural forms for compounds having the same stoicheiometry, and consequently prediction of the co-ordination geometry from the copper: ligand ratio is unreliable.[1] We here report the preparation and structure of a novel diamagnetic complex of this class, $[Cu_4(ettu)_9(NO_3)_4],6H_2O$ (ettu = ethylenethiourea), which contains a discrete copper cluster involving one-, two-, and four-co-ordinated ettu ligands.

A solution of $Cu(NO_3)_2,3H_2O$, (31 mmol) in water (20 ml) was added dropwise to a hot stirred solution of ettu (88 mmol). The resulting solution was filtered while hot and the crystals which deposited slowly were filtered, washed with anhydrous ether, and air dried. Slow recrystallization from aqueous solution under nitrogen yielded colourless, air-stable crystals of composition $[Cu_4(ettu)_9(NO_3)_4],6H_2O$; m.p. 81—82 °C.

Colourless monoclinic crystals of the complex belong to space group $C2/c$ (C_{2h}^6), $a = 31{\cdot}48(1)$, $b = 9{\cdot}49(1)$, $c =$

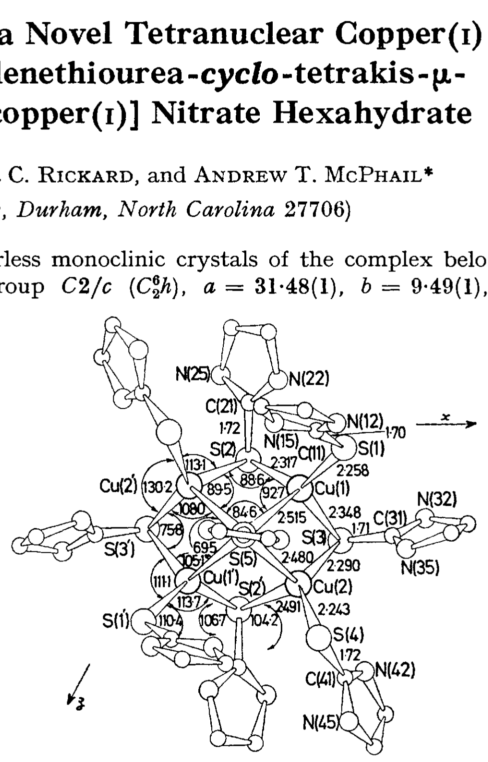

FIGURE. The $Cu_4(ettu)_9{}^{4+}$ cluster viewed along the C_2 axis. E.s.d.'s for distances are, Cu–S ± 0·002, C–S ± 0·007 Å, and for angles S–Cu–S ± 0·06°, Cu–S–C ± 0·2°. Torsion angles around the C-S bonds are N(22)–C(21)–S(2)–Cu(2′) = 102°, N(22)–C(21)–S(2)–Cu(1) = 9°, N(15)–C(11)–S(1)–Cu(1) = − 31°, N(35)–C(31)–S(3)–Cu(1) = 70°, N(35)–C(31)–S(3)–Cu(2) = − 9°, N(42)–C(41)–S(4)–Cu(2) = 24°.

23·16(1) Å, $\beta = 119{\cdot}75(10)^\circ$, $U = 6004$ Å^3, $D_m = 1{\cdot}68$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}692$ g cm^{-3}. The structure was solved by the heavy-atom approach using 3225 independent observed reflexions visually estimated from Weissenberg photographs (Cu-K_α radiation, $\lambda = 1{\cdot}542$ Å) and refined by full-matrix least-squares calculations (anisotropic Cu, S, O, N, C; fixed H contributions) to $R = 0{\cdot}050$ over 3727 reflexions with $I > 2\sigma(I)$ from diffractometer measurements to $\theta = 30^\circ$ using Mo-K_α ($\lambda = 0{\cdot}7107$ Å) radiation.

The structure of the copper cluster cation viewed along the crystallographic C_2 axis is shown in the Figure. In the ettu ligands the individual C–S distances at 1·701—1·716 Å do not differ significantly from the mean, 1·711 Å, which is close to that reported[2] for unco-ordinated ettu, 1·708 Å, and similar to the corresponding distances in other thiourea complexes[3–5].

The copper atoms have common tetrahedral co-ordination with significant differences among the Cu–S distances which range from 2·243 to 2·515(2) Å, and three different types of bonding situations may be identified in the complex. At the monodentate ettu ligands the sulphur atoms are co-ordinated through donation of a non-bonding sp^2-electron pair into a vacant sp^3 copper orbital. The bridging ettu ligands are co-ordinated through donation of an sp^2-electron pair as well as through the sulphur $p\pi$ orbital to form an eight-membered ring with alternating Cu–S distances; the latter mode of co-ordination has been found in other metal–thiourea complexes[4,6] Of particular interest is the unique ettu ligand sulphur atom which shares two sp^2 non-bonded electron pairs with four vacant copper sp^3 orbitals thus forming a pair of electron deficient three centre bonds of a type first encountered for Cu$^{\text{I}}$ in polymeric $Cu_4(\text{thiourea})_9(NO_3)_4$ which has the same stoicheiometry as the present complex but an entirely different geometry.[7] Supporting evidence for the existence of these bonds comes not only from the ligand orientation but also from the shorter Cu(1)–Cu(2) separation, 2·849(1) Å, relative to the Cu(1)–Cu(2′) distance, 3·362(1) Å. The present complex appears to be the first known to contain two pairs of these bonds involving a common ligand sulphur donor atom.

Nitrate ions and water molecules of solvation participate in an extensive hydrogen-bonding network which involves the ettu nitrogen atoms.

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[1] M. S. Weininger, G. W. Hunt, and E. L. Amma, *J.C.S. Chem. Comm.*, 1972, 1140, and references therein.

[2] P. J. Wheatley, *Acta Cryst.*, 1953, **6**, 369.

[3] G. D. Andreetti, L. Cavalca, and A. Musatti, *Acta Cryst.* (*B*), 1968, **24**, 683.

[4] W. A. Spofford, tert., P. Boldrini, E. L. Amma, P. Carfagno, and P. S. Gentile, *Chem. Comm.*, 1970, 40.

[5] M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J. Chem. Soc.* (*A*), 1971, 3195.

[6] P. D. Brotherton and A. H. White, *J.C.S. Dalton*, 1973, 2696.

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