Synthesis and Single Crystal *X*-Ray Structure of a Di-copper(I) Hexathia Macrocyclic Complex $[Cu_2(L)(NCMe)_2](ClO_4)_2$ (L = 1,4,7,10,13,16-hexathiacyclo-octadecane)

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1,4,7,10,13,16-hexathiacyclo-octadecane (L) (hexathia-18-crown-6) can bind two copper(I) ions to yield the binuclear complex $[Cu_2(L)(NCMe)_2]^{2+}$; each copper(I) ion is bound in a distorted tetrahedron to three sulphur donor atoms of the hexadentate macrocycle and to one acetonitrile molecule, and the metal–metal separation is 4.25 Å.

In the blue copper proteins plastocyanin and azurin, the copper ion present at the active site has been reported to have a distorted tetrahedral geometry with two nitrogen and two sulphur ligands.[1—3] These donor atoms are in three close neighbours in the chain (cys-84, his-87, and met-92) together with the remote his-37. Since both the nature of the co-ordinating ligands and the stereochemical constraints imposed by them upon the metal centre control the rate of electron transfer within these systems,[4] mono- and bi-nuclear copper-(I) and -(II) complexes that mimic these stereochemical (mixed N and S donors) and electrochemical requirements are promising synthetic targets for modelling the reactivity of these and related proteins.[5] Furthermore, the paucity of homoleptic sulphur macrocyclic complexes has led us to investigate the general binding of polythiocrown ethers to transition metal centres.

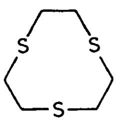
During the preparation of the trithia macrocycle 1,4,7-trithiacyclononane (**1**) by condensation of bis-(2-mercaptoethyl) sulphide and 1,2-dichloroethane,[6] we also isolated the corresponding 2+2 condensation product 1,4,7,10,13,16-hexathiacyclo-octadecane (**2**)[7,8] the sulphur analogue of the polyether 18-crown-6. The binding of (**2**) to cobalt(II) and nickel(II) has been reported,[8] and the octahedral stereochemistry of these mononuclear products confirmed by crystallographic studies.[9] Binuclear co-ordination of polythia macrocycles is rare,[10] and we report here the synthesis and crystal structure of a binuclear copper(I) complex incorporating the hexadentate ligand (**2**).

Addition of a two-fold molar excess of $[Cu(NCMe)_4](ClO_4)$ to a solution of (**2**) in dichloromethane–acetonitrile followed by warming at 35 °C for 0.5 h under N_2 gave a pale yellow solution. Removal of solvent *in vacuo* and recrystallisation of the solid residue from acetonitrile yielded pale brown crystals of $[Cu_2(\mathbf{2})(NCMe)_2](ClO_4)_2$ (**3**), in 75% yield.

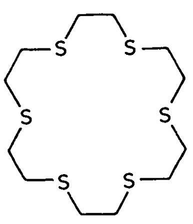
Crystal data: $C_{16}H_{30}Cu_2N_{26}{}^{+}2ClO_4{}^{-}$, $M = 768.7$, triclinic, space group $P\bar{1}$, $a = 9.184(6)$, $b = 9.317(3)$, $c = 9.598(7)$ Å, $\alpha = 81.18(4)$, $\beta = 73.07(6)$, $\gamma = 67.93(3)°$; $U = 727.2$ Å^3, $D_c = 1.76$ g cm^{-3}, $Z = 1$, 2539 data measured to $\theta = 25°$, refinement based on 1926 data with $I > 3\sigma(I)$. At convergence, $R = 0.044$, $R_w = 0.056$ for 128 parameters. The structure was solved using the DIRDIF system;[11] unrealistic bond distances and thermal parameters for the methylene carbon atoms revealed a two-fold disorder which was successfully modelled and refined, the site occupancies for the two forms being 0.55 and 0.45. Hydrogen atoms were included in fixed calculated positions. The perchlorate ion is disordered about a molecular three-fold axis. Two alternative positions were refined anisotropically and then fixed when the electron density was satisfactory modelled, and, at convergence, the difference electron map showed no features >0.6 e Å^{-3}.†

The cation of (**3**) is shown in Figure 1. Its crystallises with imposed C_i ($\bar{1}$) symmetry and consists of two identically bound copper(I) ions, each co-ordinated to three sulphur atoms of the macrocycle, Cu–S(1) = 2.32, Cu–S(4) = 2.34, Cu–S(7) = 2.33 Å, and one acetonitrile molecule, Cu–N(1) = 1.94 Å, to give a distorted tetrahedral S_3N donor set. The proximity of S(7′) to Cu (3.32 Å) distorts the co-ordination towards a trigonal bipyramidal configuration. The sulphur atoms of the macrocycle adopt a chair-like conformation with three sulphur donors to Cu forming a plane 0.98 Å from the plane of the sulphur atoms bound to Cu′; each copper atom lies 1.08 Å above the plane of its co-ordinated S_3 set, ∠N(1)–Cu–S(1) 120.6, N(1)–Cu–S(4) 122.9, N(1)–Cu–S(7) 110.9, S(1)–Cu–S(4) 92.1, S(4)–Cu–S(7) 91.6, S(1)–Cu–S(7) 114.7°. There is no apparent Cu–Cu′ interaction, with a metal-metal separation of 4.25 Å. An interesting intramolecular contact between S(7) and S(7′) (3.64 Å) is observed despite the fact that these atoms are separated by nine bonds in the macrocyclic ring.

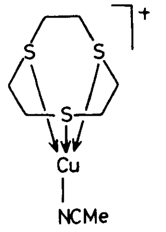
Complex (**3**) is stable to aerial oxidation in acetonitrile and nitromethane at room temperature reflecting the net π-acceptor properties of the S_3N donor set and its ability to stabilise



(**1**)



(**2**)



(**4**)

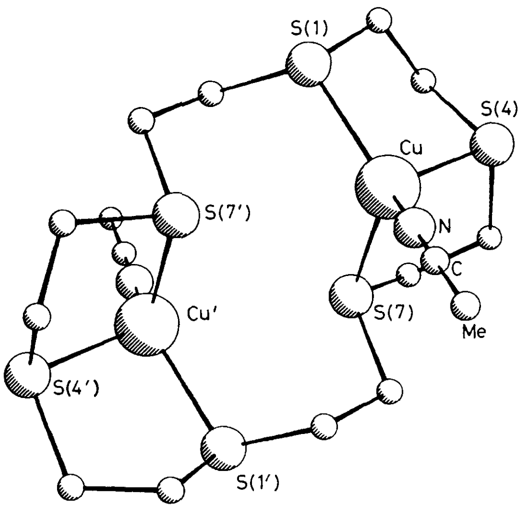


Figure 1. The molecular structure of the cation of (**3**), $[Cu_2(\mathbf{2})(NCMe)_2](ClO_4)_2$, and atom numbering scheme used. Hydrogen atoms have been omitted for clarity.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

the low-valent copper(I) state. Addition of $HClO_4$ leads to oxidation of (**3**); this process can presumably occur *via* protonation of co-ordinated acetonitrile, and may be of relevance to the acid-mediated oxidation and dissociation of nitrogen donor ligands from copper(I) at the active site of plastocyanin.[12] Complex (**3**) is oxidised by O_2 in dimethylformamide (dmf), while addition of NCS^- to (**3**) affords the terminally bound dithiocyanate species $[Cu_2(\mathbf{2})(NCS)_2]$.[13]

The co-ordination of (**2**) to each copper(I) ion is reminiscent of the facial co-ordination observed[6] in the octahedral complex $[Cu(\mathbf{1})_2]^{2+}$ and suggests that mononuclear species in which copper(I) is bound to (**1**), *e.g.* complexes of type (**4**), could be prepared. Substitution reactions of co-ordinated MeCN in (**3**) and (**4**) by N-, P-, and S-donor ligands are currently being investigated and the redox properties of these products assessed.

We thank the S.E.R.C. for support (to A. J. L.) and Dr. S. R. Cooper for communicating unpublished work to us.

Received, 1st July 1985; Com. 919

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