The Preparation and Crystal Structure of the Unusual Copper–Sulphur Cage Complex $Cu_8(SC_5H_{11})_4(S_2CSC_5H_{11})_4$

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The electrochemical oxidation of anodic copper in an acetonitrile solution of RSH (R = Ph, $C_{10}H_7$, CPh₃, C_6F_4H , *o*-MeC₆H₄, CMe₂Et) yields CuSR; treatment of CuSCMe₂Et with CS₂ produces Cu₈(SR)₄(S₂CSR)₄, whose structure is based on an unusual Cu₈S₁₂ cage.

The electrochemical oxidation of a sacrificial anode in a non-aqueous cell is a convenient room-temperature route to thiolato complexes of metals such as zinc, cadmium, mercury,^{1,2} tin, lead,³ cobalt, nickel,⁴ *etc*. We have now extended this work to copper, silver, and gold, each of which can be oxidized to give the M^I thiolates in excellent yield. For copper, a variety of thiols (RSH; R = Ph, C₁₀H₇, CPh₃, C₆F₄H, *o*-MeC₆H₄, C₄H₉ⁿ, CMe₂Et) in acetonitrile gave CuSR as insoluble, colourless to yellow, air stable compounds. When 1,10-phenanthroline (phen) was added to the cell prior to electrolysis, the products were the red adducts CuSR ·phen; in the case of R = *o*-MeC₆H₄, the product was shown by *X*-ray crystallography to be a dimer based on a folded Cu₂S₂ ring, with a CuN₂S₂ co-ordination kernel and bridging sulphur atoms.⁵

The copper(1) thiolates are generally insoluble in organic solvents, but a sample of $CuSC_5H_{11}$ (0.5 g) dissolved almost immediately in carbon disulphide (50 ml). This mixture was stirred at room temperature for periods up to 12 h (the time had no effect on the nature of the final product), the solvent was removed *in vacuo*, and the solid residue recrystallized from tetrahydrofuran-methanol. This material is Cu_8 -(SC_5H_{11})₄($S_2CSC_5H_{11}$)₄; crystals for X-ray studies were obtained from carbon disulphide–n-pentane mixtures.

The crystal structure determination followed the methods described earlier,^{3,6} using a fully automated single crystal diffractometer. *Crystal data:* a = 31.532(26), b = 20.700(6), c = 23.725(10) Å, $\beta = 114.16(5)^{\circ}$, space group C2/c, Z = 8, $D_c = 1.54$ g cm⁻³, R = 0.0745 for 4203 observed reflections, radiation Mo- K_{α} , data collected at room temperature. The structure was refined in blocks during the least squares analysis, with Cu(1) and Cu(2) in every cycle, Cu(3)—Cu(8) and S(1)—S(14) (199 variables) in alternate cycles with S(15), S(16) and C(1)—C(44) (213 variables).†

The molecular structure consists of a complex cage of eight copper atoms linked through thiolato (RS) and alkyl trithiocarbonato (RSCS₂) ligands. Figure 1 shows the overall structure, and Figure 2 gives an outline of the Cu₈S₁₂ cage. There are a number of interesting features to this unusual structure. The eight copper atoms form a series of distorted tetrahedra [Cu(1),(8),(4),(5); (4),(8),(2),(6); (2),(6),(3),(7)] joined along the appropriate edges [Cu(4)–Cu(8) and Cu(2)– Cu(6)], giving a structure of lower symmetry than those observed in polymeric organocopper compounds.⁷ This Cu₈ framework is then capped by sulphur atoms which may be mono-, bi-, or tri-dentate. Thus the thiolate sulphur atoms S(1),(3),(5),(7) each bridge three copper atoms [*e.g.*, S(1)– Cu(1), –Cu(4), –Cu(2)] in an approximately tetrahedral CSCu₃ array. The ligating sulphur atoms of the alkyl trithiocarbonate groups are of two kinds: S(9), (12), (13), and (15) are monodentate, while S(2), (4), (6), and (8) are bidentate and bridging [*e.g.*, S(2)–Cu(2,3)]. The geometry at each bidentate sulphur is pyramidal. The average sum of the bond angles about the copper atoms is $359 \pm 1^{\circ}$, so that there is a slightly distorted CuS₃ trigonal planar geometry.

Another interesting feature of the Cu₈S₁₂ cage is the presence of a series of six-membered rings, some of which [*e.g.* Cu(2)–S(1)–Cu(4)–S(3)–Cu(3)–S(2) and Cu(1)–S(9)–C(1)–S(4)–Cu(4)–S(1)] are clearly in the boat form. The cage is capped by two eight-membered rings [*e.g.* Cu(3)–S(15)–C(19)–S(6)–Cu(7)–S(13)–C(13)–S(2)]. Finally, we note that the Cu–S bond distances lie between 2.237(5) and 2.301(5) Å (see Figure 1), substantially shorter than those found⁸ in the complex (Ph₃P)₂Cu(μ -S₂CSCH₂SCS₂)Cu(PPh₃)₂ for which the range is 2.411(5)–2.479(5) Å, or in (Ph₃P)₂CuS₂COEt, where the values are 2.404(2) and 2.451(2) Å. The compound



Figure 1. The structure of $Cu_8(SC_5H_{11})_4(S_2CSC_5H_{11})_4$. Copper and sulphur atoms are drawn with 50% probability ellipsoids. The carbon atoms are represented as spheres; the pentyl carbon atoms are of arbitrary radius. The Cu–S(thiolate) and Cu–S(alkyl trithiocarbonate) distances range from 2.237(5) to 2.301(5) Å and from 2.263(5) to 2.292(5) Å respectively. The Cu \cdots Cu distances lie between 2.652(3) and 3.200(3) Å, with an average value of 2.92(12) Å.



Figure 2. The outline of the Cu_8S_{12} cage.

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

 $Cu_4(dppm)(CS_3)_2$ (dppm = diphenylphosphinomethane) has a structure⁹ involving six-membered CuSCuPCP and CuSCSCuS rings, and here the Cu–S bond lengths are in the range 2.308–2.406 Å, again larger than those in the present structure.

This Cu₈S₁₂ cage is another example of a structure involving d¹⁰ metal ions and various sulphur donor ligands. The molecule is formed by the insertion of CS₂ into M–SR bonds; the insertion reactions of this molecule with inorganic and organometallic compounds have been the subject of a number of studies.¹⁰ The present results are unusual in that only half the CuSR units of the presumed (CuSR)₈ starting material react, which may well reflect stabilizing factors in the crystalline product. It is worth noting that in the case of CS₂ and Cd(SR)₂ (R = C₄H₉ⁿ), the product in the presence of phen is Cd(S₂CSR)₂·phen in which the ligand is again an alkyl trithiocarbonate anion.¹¹

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