

The Hepta(μ_2 -benzenethiolato)pentacuprate(I) Dianion; X-Ray Crystal and Molecular Structure

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Summary Soluble benzenethiolato-cuprate(I) complexes $[\text{Me}_4\text{N}]_n[\{\text{Cu}_2(\text{SPh})_3\}_n]$ and $[\text{Me}_4\text{N}]_2[\text{Cu}_5(\text{SPh})_7]$ are formed in ethanol; the crystal structure of the latter is composed of $[\text{Cu}_5(\mu_2\text{-SPh})_7]^{2-}$ molecular clusters containing linear and trigonal planar copper co-ordination.

As part of a systematic investigation of metal cluster complexes with monothiolate ligands,¹ we have sought copper

compounds intermediate in molecularity and molecular size between $[\text{Cu}(\text{SR})_2]^-$ (ref. 2) and the insoluble mercaptides $[\text{CuSR}]_n$ (ref. 3) (presumed to be non-molecular in at least one dimension).

From an ethanolic solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (ca. 30 mM), PhSH (ca. 170 mM) and Bu^n_3N (ca. 170 mM), prepared in the absence of dioxygen at 75 °C, two different complexes may be crystallized by slow cooling after addition of tetra-

TABLE. $[\text{Cu}_5(\text{SPh})_7]^{2-}$ cluster mean dimensions.

Dimension	No. of data	Mean	Average deviation from mean ^a	Range
$\text{Cu}^{\text{tri}}\text{g-S}$	12	2.27 Å	0.02 Å	2.23—2.33 Å
$\text{Cu}^{\text{dig}}\text{-S}$	2	2.16 Å	0.002 Å	—
$\angle \text{S-Cu}^{\text{tri}}\text{g-S}$	12	119.6°	8.1°	104.7—137.1°
$\angle \text{Cu-S-Cu}$	7	80.8°	4.9°	75.0—88.0°
Edges of Cu_5 polyhedron	7 ^b	2.92 Å	0.14 Å	2.65—3.12 Å
$\text{Cu}^{\text{tri}}\text{g}$ deviation from S_3 plane	4	0.12 Å	0.09 Å	0.00—0.21 Å

^a Computed crystallographic standard deviations are: Cu—Cu, 0.003 Å; Cu—S, 0.005 Å; $\angle \text{S-Cu-S}$, 0.2°; $\angle \text{Cu-S-Cu}$, 0.2°.

^b Excluding Cu(1)—Cu(2), 4.35 Å, Cu(1)—Cu(5), 4.28 Å, Cu(3)—Cu(4), 3.76 Å.

alkylammonium cation (*ca.* 110 mM). A bright yellow complex has composition $[\text{R}_4\text{N}]_2[\text{Cu}_5(\text{SPh})_7]^\dagger$ and a pale yellow complex, which occurs in at least two different crystal forms, has empirical composition $(\text{Me}_4\text{N})\text{Cu}_2(\text{SPh})_3$.[†] Both compounds are soluble in polar aprotic solvents, and oxidised by air.

The structure of the discrete $[\text{Cu}_5(\mu_2\text{-SPh})_7]^{2-}$ cluster in crystalline $[\text{Me}_4\text{N}]_2[\text{Cu}_5(\text{SPh})_7]^\ddagger$ is shown in the Figure. All the benzenethiolate ligands are doubly bridging, forming a copper(I)—sulphur polyhedron in which four copper atoms ($\text{Cu}^{\text{tri}}\text{g}$) possess trigonal planar co-ordination and the fifth [$\text{Cu}(1)$, Cu^{dig}] almost linear (175°) two-co-ordination. The Cu_5S_7 polyhedron without the phenyl substituents has approximately C_{2v} symmetry. Important cluster dimensions are summarised in the Table: it should be noted that (i) $\text{Cu}^{\text{tri}}\text{g-S}$ is 0.1 Å longer than $\text{Cu}^{\text{dig}}\text{-S}$; (ii) the $\text{Cu}^{\text{tri}}\text{g-S}_3$ co-ordination is closely planar; (iii) average deviations from the mean of comparable angles are very much larger than crystallographic error, indicating substantial angular distortions.

The $[\text{Cu}_5(\mu_2\text{-SPh})_7]^{2-}$ cluster structure may be regarded as derived from an idealised cluster $[\text{Cu}_4(\mu_2\text{-SPh})_6]^{2-}$ in which a tetrahedron of trigonally planar co-ordinated copper atoms is located at the centres of opposite faces of a $(\mu_2\text{-SPh})_6$ octahedron, by replacement of SPh at one vertex by a linear $[(\mu_2\text{-PhS})\text{-Cu}-(\mu_2\text{-SPh})]$ unit, accommodated by increased separation of the Cu(3) and Cu(4) faces of the octahedron. In this idealised $\text{M}_4(\text{SR})_6$ structure the M—M distance is only 15% longer than the M—S distance ($d_{\text{M-M}}/d_{\text{M-S}}$ is independent of $d_{\text{M-S}}$). One such short Cu—Cu distance, 2.65 Å [$\text{Cu}(2)\text{-Cu}(5)$], is retained in $[\text{Me}_4\text{N}]_2[\text{Cu}_5(\text{SPh})_7]$. Although <0.1 Å longer than the interatomic contact in copper metal, this distance is believed to indicate only weak copper-copper bonding.⁴

This is the first crystal structure determination for a binary copper mercaptide complex with an arylthiolate ligand. The cluster architecture is significantly different from the regular trigonal bipyramid of copper atoms in $[\text{Cu}_5(\mu_2\text{-SPh})_6]^{2-}$ (ref. 5). Crystalline $[\text{Me}_4\text{N}]_2[\text{Ag}_5(\text{SPh})_7]$ is isostructural with its copper homologue.⁶

[†] Satisfactory elemental analytical data were obtained.

[‡] Crystal data: $a = 12.250(1)$, $b = 20.151(4)$, $c = 11.531(2)$ Å, $\alpha = 103.50(1)$, $\beta = 90.01(1)$, $\gamma = 83.20(1)^\circ$; space group $\text{P}\bar{1}$; 3682 observed diffractometer data, Mo- K_α radiation; $R = 0.061$.

¹ I. G. Dance and J. C. Calabrese, *J.C.S. Chem. Comm.*, 1975, 762.

² The only well characterized example is $[\text{Et}_4\text{N}][\text{Cu}(\text{SC}_6\text{F}_5)_2]$: W. Beck, K. H. Stetter, S. Tadros, and K. E. Schwarzshans, *Chem. Ber.* 1967, **100**, 3944, 3955.

³ W. E. Duncan, E. Ott, and E. E. Reid, *Ind. Eng. Chem.*, 1931, **23**, 387; D. C. Bradley and C. H. Marsh, *Chem. and Ind.*, 1961, 361.

⁴ The distance pertinent to Cu—Cu overlap considerations would be > 2.65 Å, as the angle between the normals to the planes of trigonal co-ordination for Cu(2) and Cu(5) is *ca.* 110°.

⁵ I. G. Dance, *J.C.S. Chem. Comm.*, 1976, 68.

⁶ I. G. Dance, to be published.

Pale yellow $[\text{Me}_4\text{N}]_n[\text{Cu}_{2n}(\text{SPh})_{3n}]$ is subject to crystal instability which has hindered X-ray structure determination. Nevertheless, it has been determined that one crystal form contains the $[\text{Me}_4\text{N}]_4[\text{Cu}_5(\text{SPh})_{12}]$ unit per asymmetric unit. As the solubility of this compound is

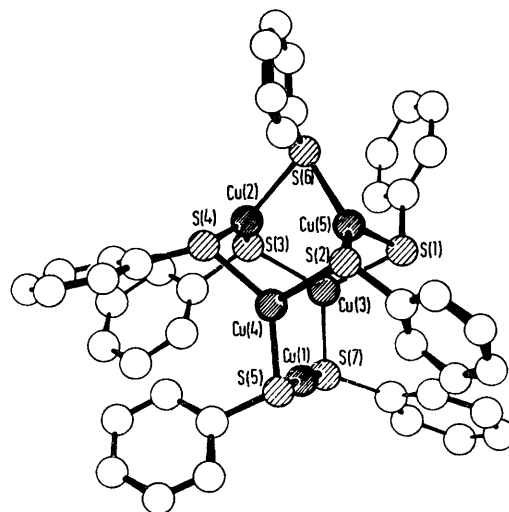


FIGURE. The $[\text{Cu}_5(\mu_2\text{-SPh})_7]^{2-}$ cluster in $[\text{Me}_4\text{N}]_2[\text{Cu}_5(\text{SPh})_7]$.

very similar to that of $[\text{Me}_4\text{N}]_2[\text{Cu}_5(\text{SPh})_7]$ it is most probable that $[\text{Me}_4\text{N}]_4[\text{Cu}_5(\text{SPh})_{12}]$ contains a molecular cluster anion. Two reasonable structures, with doubly bridging benzenethiolate ligands and trigonal copper co-ordination, can be proposed for a $[\text{Cu}_5(\text{SPh})_{12}]^{4-}$ cluster. One contains copper atoms at the centres of 8 non edge-sharing faces of an S_{12} icosahedron ($\angle \text{Cu-S-Cu}$ 97.6°), and the other has copper atoms at the centres of the triangular faces of an S_{12} cubo-octahedron ($\angle \text{Cu-S-Cu}$ 109.5°).

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