

The Crystal and Molecular Structure of the Hexa- $(\mu_2$ -Benzenethiolato)tetracuprate(I) Dianion

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We recently reported¹ the existence of a pale yellow complex of empirical formula $(\text{Me}_4\text{N})\text{Cu}_2(\text{SPh})_3$ in two crystalline forms, one of which contains $(\text{Me}_4\text{N})_4\text{Cu}_8(\text{SPh})_{12}$ per asymmetric unit.* We suggested that a $[\text{Cu}_8(\mu_2\text{-SPh})_{12}]^{4-}$ molecular cluster might occur, with a structure composed of an icosahedron or cuboctahedron of doubly-bridging monodentate ligands enveloping a cube of copper(I) atoms, each located in a triangular face of the ligand polyhedron.

Crystal structure determinations have now revealed that both crystalline forms of $(\text{Me}_4\text{N})_n\text{Cu}_2(\text{SPh})_{3n}$ contain only the $[\text{Cu}_4(\mu_2\text{-SPh})_6]^{2-}$ molecular cluster shown in Figure 1. The cluster

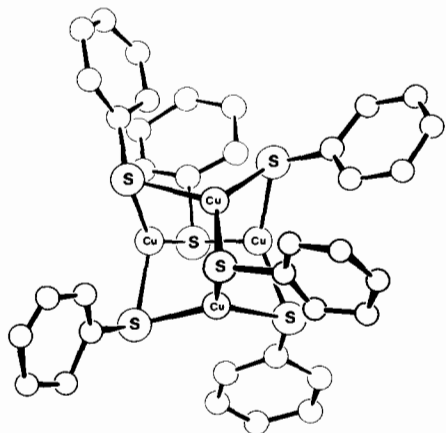


Figure 1. Structure of the $[\text{Cu}_4(\mu_2\text{-SPh})_6]^{2-}$ cluster.

polyhedron is best visualized as an octahedron of doubly-bridging benzenethiolate ligands intersected by a tetrahedron of copper(I) atoms, each of which lies close to the centre of a face of the octahedron and possess trigonal planar coordination. The most important dimensions of the three crystallographical independent clusters are summarized in the Table.

*The crystalline compound $(\text{Ph}_4\text{P})\text{Cu}_2(\text{SPh})_3$ has also been mentioned. D. G. Holah and D. Coucouvanis, *J. Am. Chem. Soc.*, 97, 6917 (1975).

Although no crystallographic symmetry is imposed on the cluster, its Cu_4S_6 core approximates the symmetry of point group T_d .

This repeated occurrence of the $[\text{Cu}_4(\mu_2\text{-SPh})_6]^{2-}$ cluster structure raises the question of the stability and existence of an octametallic copper(I) cluster with monothiolate ligands, $[\text{Cu}_8(\text{SR})_{12}]^{4-}$, at least for $\text{R} = \text{Ph}$. The question gains pertinence from the known cubic $[\text{Cu}_8(\text{S-donor})_{12}]$ cluster structures in two related systems. With chelating 1,1- or 1,2-dithiolate ligands $(\text{S-S})^{2-}$, three clusters $[\text{Cu}_8(\text{S-S})_6]^{4-}$ are known:² the structure consists of a Cu_8 cube surrounded by an S_{12} icosahedron (slightly distorted) with six edges bridged by the chelate ligands as shown diagrammatically in Figure 2. The dimensions of the

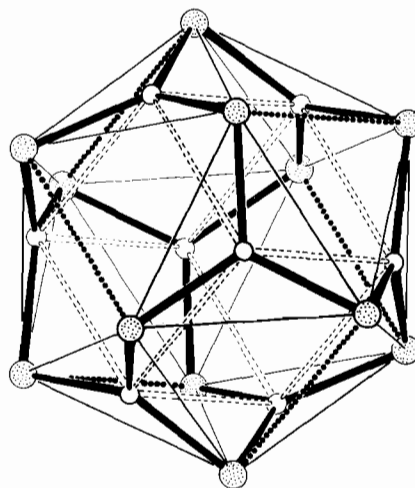


Figure 2. The idealised $\text{Cu}_8(\text{S-donor})_{12}$ cluster structure. The cube of copper atoms and its enclosing icosahedron of sulphur atoms (stipled) are viewed along a direction close to an S_6 symmetry axis. The six linkages between sulphur atoms are denoted as ●●●●.

Cu_8 cube are essentially invariant with the ligand bite distance, a fact which has led to the postulation of substantial copper-copper bonding (at $\text{Cu-Cu} = 2.8 \text{ \AA}$) in these three clusters. Very recently the Cu_8^{I} cube enclosed within an S_{12} icosahedron has been found by Birker and Freeman³ in the copper penicillamine complex $[\text{Cu}_8\text{L}_{12}\text{Cu}_6^{\text{II}}]^{5-}$, $\text{L} = \text{-S-C(Me)}_2\text{-CH(NH}_2\text{)-COO}^-$. The main structural framework in this complex is again that shown in Figure 2, the six icosahedron-edge bridges being formed by copper(II) atoms whose $\text{cis-S}_2\text{N}_2$ square planar coordination is completed with chelation by the amine functions of the penicillamine ligands. The single chloride ion in the Birker-Freeman structure is located at the centre of the cluster.

In view of these data we offer the hypothesis that some linking of sulphur donor atoms along the

TABLE. Summary of Dimensions in $[\text{Cu}_4(\mu_2\text{-SPh})_6]^{2-}$ Clusters.

Dimension	No. of values per Cluster	Crystal I				Crystal II	
		Cluster A		Cluster B		Cluster C	
		Mean	E.s.d. ^a	Mean	E.s.d. ^a	Mean	E.s.d. ^a
Cu-Cu (Å)	6	2.75	0.02	2.74	0.02	2.76	0.04 ^b
S-S (Å)	12	3.94	0.06	3.95	0.05	3.94	0.06
Cu-S (Å)	12	2.29	0.01	2.29	0.01	2.29	0.01
Cu-S-Cu angle (°)	6	73.9	0.4	73.5	0.6	74.3	1.2 ^b
Cu Deviation ^c from S ₃ Plane (Å)	4	0.08	0.02	0.07	0.01	0.09	0.01

^a Estimated standard deviation of the sample mean value. ^b There is a significant D_{2d} distortion of the Cu₄S₆ core in cluster C: two Cu-Cu = 2.64 Å, four Cu-Cu = 2.81-2.85 Å. ^c All copper atoms are outside the faces of the S₆ octahedra.

icosahedron edges is required to confer self-sufficient rigidity on a molecular Cu₈(SR)₁₂ cluster subject to only van der Waals crystal forces. A corollary hypothesis is that copper-copper bonding alone is insufficient for this stabilization.

We note that both crystalline forms of $[\text{Cu}_4(\mu_2\text{-SPh})_6]^{2-}$ crystallized from solutions containing chloride or bromide ion in excess of the amount needed to form $[\text{XCu}_8(\text{SPh})_{12}]^{5-}$ (X = Cl or Br) or a similar species stabilized by an internal anion.

Crystal Data

Crystal I, $(\text{Me}_4\text{N})_2\text{Cu}_4(\text{SPh})_6$: $a = 23.733$, $b = 12.428$, $c = 35.853$ Å, $\beta = 106.84^\circ$, spacegroup $P2_1/c$, $Z = 8$ (two formula units per asymmetric unit), 4918 diffractometer ($\text{CuK}\alpha$) observed reflections. At the present stage of refinement (112 non-hydrogen atoms included with isotropic temperature factors) $R = 0.14$.

Crystal II, $(\text{Me}_4\text{N})_2\text{Cu}_4(\text{SPh})_6\text{C}_2\text{H}_5\text{OH}$: $a = 19.125$, $b = 15.433$, $c = 17.500$ Å, $\beta = 103.73^\circ$, spacegroup $P2_1/a$, $Z = 4$, 3364 diffractometer ($\text{MoK}\alpha$) observed reflections $R = 0.04$.

Full details will be published.

Acknowledgment

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References

- 1 I. G. Dance, *Chem. Comm.*, 103 (1976).
- 2 F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc.*, **96**, 5646 (1974), and references cited therein.
- 3 P. J. M. W. L. Birker and H. C. Freeman, *Chem. Comm.*, 312 (1976).