

## Synthesis and Structure of the Hexanuclear Copper(I) Cluster Compound $\text{Cu}_6[\mu_3\text{-S}_2\text{P(OEt)}_2]_6$

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A copper(I)-dithiophosphate cluster compound  $\text{Cu}_6[\mu_3\text{-S}_2\text{P(OEt)}_2]_6$  (I) was synthesized and its crystal structure characterized by X-ray crystallography. Compound I crystallizes in the triclinic system, space group  $P\bar{1}$ , and the resulting centrosymmetric geometry of the six copper atoms in the molecule is intermediate between the distorted octahedron and the chair conformation of cyclohexane. In Compound I, the two S-atoms of dithiophosphate are coordinated to three Cu atoms, and one is monodentate to one Cu and another bridges two Cu atoms.

**Key Words:** Cluster compound, Copper, Dithiophosphate, Crystal structure.

### INTRODUCTION

Transition metal-sulfur cluster chemistry, an important subject in inorganic and metalloprotein chemistry, is currently receiving much attention<sup>1</sup>. The chemistry of trinuclear and cubic Mo and W sulfido clusters has been extensively studied<sup>2</sup> and heterometallic cubic derivatives reported<sup>3</sup>. Biologically relevant Fe/sulfido clusters have been synthesized<sup>4</sup>. In nitrogenase, the Fe/Mo/S cofactor is believed to be the site of substrate activation and reduction<sup>5</sup>. As a part of these studies the dithiophosphate clusters,  $\text{Mo}_3(\mu_3\text{-S})(\mu_2\text{-S})_3[\mu_2\text{-S}_2\text{P(OEt)}_2][\text{S}_2\text{P(OEt)}_2]_3(\text{H}_2\text{O})$ , with three  $d^2$  Mo(IV) forming localized electron-pair Mo-Mo bonds<sup>6</sup>,  $\text{Cu}_8[\text{S}_2\text{P(O-}i\text{-Pr)}_2]_6(\mu_8\text{-S})$ , a sulfide-centred  $\text{Cu}_8$  cube and  $\text{Cu}_6[\text{S}_2\text{P(OEt)}_2]_6(\text{H}_2\text{O})_2$ , a distorted octahedron<sup>7</sup>, have been prepared. Clusters containing Cu(I) with chalcogenide ligands have taken on renewed interest through their commercial use and their possible antioxidant properties in life systems and their photophysics<sup>8,9</sup>. The compound CuDDP (DDP = dialkyl dithiophosphate) has been described to be an important antioxidant when added with ZnDDP in the compounding of lubricating oils<sup>10</sup>. Dithiophosphate, having two P-attached sulfur atoms that can coordinate to metal ions by different modes, is an important ligand in promoting the formation of new types of clusters. In the present paper, the synthesis and structure of the copper(I)-dithiophosphate cluster  $\text{Cu}_6[\mu_3\text{-S}_2\text{P(OEt)}_2]_6$  (I) is reported.

### EXPERIMENTAL

$\text{Na}[\text{S}_2\text{P(OEt)}_2]$  was synthesized according to literature method<sup>11</sup>. All commercially available chemicals were of analytical reagent grade and used directly

without further purification. The C and H contents were determined by using an Elementar Vario EL analyzer. Infrared spectra were recorded from KBr pellets on a Midac Prospet IR spectrometer. All operations were carried out under ambient conditions.

### Synthesis of $\text{Cu}_6[\mu_3\text{-S}_2\text{P(OEt)}_2]_6$ (I)

Reaction of an aqueous solution of  $\text{Na}[\text{S}_2\text{P(OEt)}_2]$  with an aqueous solution of  $\text{CuCl}_2$  gave a black precipitate. The precipitate was redissolved in ethanol and after three weeks the filtered solution afforded a pale yellow hexanuclear cluster  $\text{Cu}_6[\mu_3\text{-S}_2\text{P(OEt)}_2]_6$  (I) in 40% yield. Anal. data for  $\text{C}_{24}\text{H}_{60}\text{O}_{12}\text{P}_6\text{S}_{12}\text{Cu}_6$ , Calcd.: C, 19.31; H, 4.05; Found: C, 19.40; H, 4.02%. Main IR absorption bands (KBr,  $\text{cm}^{-1}$ ): 2980 (s), 1385 (s) ( $\text{—CH}_3$ ), 2925 (m) ( $\text{—CH}_2\text{—}$ ), 1454 (w), 1439 (m), 1154 (m), 1100 (m), 1039–1017 (vs), 775 (s), 645 (s), 533 (s) ( $[\text{S}_2\text{P(OEt)}_2]^-$ ); 454 (w), 426 (w) (Cu—S). These syntheses are simple, reproducible and can be carried out easily at room temperature.

### X-ray crystallography

Single-crystal X-ray diffraction data for I were collected on a Nonius CAD4 diffractometer using  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.071073$  nm) with a graphite monochromator at 293(2) K. The structures were solved by the Patterson method and subsequent difference by Fourier techniques and refined by full-matrix least-squares procedures based on  $F^2$  by using the SHELXTL software package<sup>12</sup>. All non-hydrogen atoms were refined anisotropically. All calculations were performed with the program SHELXL-97. The molecular graphics were created by SHELXTL. Atomic scattering factors and anomalous dispersion correction were taken from International Table for X-Ray Crystallography<sup>13</sup>. Fig. 1 shows the perspective view of I with atomic numbering scheme.

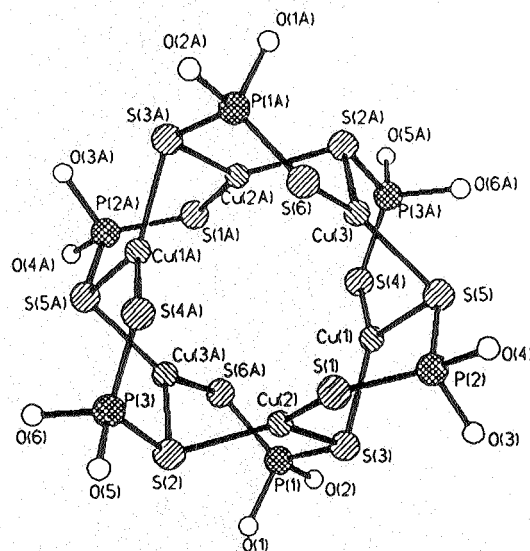


Fig. 1. ORTEP drawing of I which lies on inversion centre  $\bar{1}$  ( $C_i$ ). Thermal ellipsoids are shown at 50% probability and all hydrogen and carbon atoms are omitted for clarity

A summary of the key crystallographic data and structural refinements is presented in Table-1. Selected bond lengths and angles are presented in Table-2.

TABLE-1  
SUMMARY OF CRYSTALLOGRAPHIC INFORMATION FOR COMPOUND I

|  |  |
|--|--|
| Formula                                    | C <sub>24</sub> H <sub>60</sub> O <sub>12</sub> P <sub>6</sub> S <sub>12</sub> Cu <sub>6</sub> |
| Formula weight                             | 1492.5   |
| Temperature (K)                            | 293 (2)  |
| Crystal system                             | triclinic  |
| Space group                                | P-1  |
| Unit cell dimensions:                      |  |
| a (nm)                                     | 1.1381 (2)   |
| b (nm)                                     | 1.2672 (3)   |
| c (nm)                                     | 1.2679 (3) Å   |
| α (°)                                      | 111.36 (3)   |
| β (°)                                      | 107.43 (3)   |
| γ (°)                                      | 107.43 (3)   |
| V (nm <sup>3</sup> )                       | 1.4428 (5)   |
| Z  | 2  |
| D <sub>calcd.</sub> (g.cm <sup>-3</sup> )  | 1.718  |
| Absorption coefficient (mm <sup>-1</sup> ) | 2.82   |
| F (000)                                    | 756.0  |
| Crystal size (mm)                          | 0.2 × 0.4 × 0.6  |
| θ ranges (°)                               | 1.94–25.01   |
| Reflections collected                      | 2735   |
| Independent reflections                    | 2729 (R <sub>int</sub> = 0.0246)   |
| Restraints/parameters                      | 0/246  |
| GOF  | 1.061  |
| Final R indices [I > 2σ(I)]                | R <sub>1</sub> = 0.0864<br>wR <sub>2</sub> = 0.2459 <sup>a</sup><br>R <sub>1</sub> = 0.0896    |
| R indices (all data)                       | wR <sub>2</sub> = 0.2508 <sup>a</sup>  |

<sup>a</sup>w = 1/[σ<sup>2</sup>(F<sub>0</sub><sup>2</sup>) + (0.1592P)<sup>2</sup> + 9.0992P], P = (F<sub>0</sub><sup>2</sup> + 2(F<sub>c</sub><sup>2</sup>))/3.

TABLE-2  
SELECTED BOND DISTANCES (nm) AND BOND ANGLES (°) OF COMPOUND I

|               |           |                  |             |
|---------------|-----------|------------------|-------------|
| Cu(1)···Cu(2) | 0.3117    | S(3)-Cu(1)-S(4)  | 123.75 (16) |
| Cu(2)···Cu(3) | 0.3122    | S(3)-Cu(1)-S(5)  | 116.66 (15) |
| Cu(1)···Cu(3) | 0.3121    | S(4)-Cu(1)-S(5)  | 118.10 (19) |
| Cu(1)-S(4)    | 0.2234(5) | S(1)-Cu(2)-S(2)  | 123.87 (14) |
| Cu(1)-S(3)    | 0.2251(5) | S(1)-Cu(2)-S(3)  | 118.04 (12) |
| Cu(1)-S(5)    | 0.2272(3) | S(2)-Cu(2)-S(3)  | 116.57 (14) |
| Cu(2)-S(1)    | 0.2233(3) | S(2)-Cu(3)-S(5)  | 116.62 (14) |
| Cu(2)-S(2)    | 0.2259(4) | S(2)-Cu(3)-S(6)  | 117.99 (15) |
| Cu(2)-S(3)    | 0.2266(3) | S(5)-Cu(3)-S(6)  | 123.93 (15) |
| Cu(3)-S(6)    | 0.2231(4) | Cu(1)-S(5)-Cu(3) | 87.13 (10)  |
| Cu(3)-S(5)    | 0.2256(3) | Cu(1)-S(3)-Cu(2) | 87.28 (14)  |
| Cu(3)-S(2)    | 0.2269(5) | Cu(2)-S(2)-Cu(3) | 87.19 (16)  |

## RESULTS AND DISCUSSION

The crystal structure of I contains one  $\text{Cu}_6[\text{S}_2\text{P}(\text{OEt})_2]_6$  molecule lying on an inversion centre in a triclinic unit cell such that the crystallographically independent unit is composed of one-half molecule. The resulting centrosymmetric geometry of the six copper atoms in the molecule is intermediate between the distorted octahedron and the chair conformation of cyclohexane. Two triangles formed by Cu1-Cu2-Cu3 and Cu1A-Cu2A-Cu3A are on the parallel planes and the distance between the planes is 0.270 nm. The distance of Cu-Cu bond is 0.3117–0.3122 nm with a mean value 0.3120 nm and that of Cu-S bond 0.2231–0.2272 nm with the 0.3120 nm mean value. Each of the six Cu atoms has a trigonal planar coordination composed of one mono-coordinated S atom and two  $\mu_2$ -S atoms from three  $[\text{S}_2\text{P}(\text{OEt})_2]^-$  ligands. The resulting localized sulfur coordination about each Cu(I) is corresponding to the formation of three electron-pair Cu-S bonds. The sum of the three S-Cu-S bond angles around one Cu atom is close to  $360^\circ$ , e.g.,  $358.51$ ,  $358.48$  and  $358.40^\circ$  for Cu(1), Cu(2) and Cu(3), respectively and the mean value of these nine bond angles is  $119.50^\circ$  ( $116.57$ – $123.93^\circ$ ). It must be pointed out that a similar structure of I dihydrate  $\text{Cu}_6[\text{S}_2\text{P}(\text{OEt})_2]_6(\text{H}_2\text{O})_2$  has been reported by Fackler *et al.*<sup>7</sup>, but  $\text{Cu}_6[\text{S}_2\text{P}(\text{OEt})_2]_6(\text{H}_2\text{O})_2$  was obtained by the addition of  $\text{NH}_4[\text{S}_2\text{P}(\text{OEt})_2]$  to the  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  (1 : 1) solution of  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  and two cluster compounds are different in crystal systems, space group and unit cell parameters.

In conclusion, the hexanuclear copper(I) cluster compound formally arises from each monoanionic dithiophosphate  $[\mu_3\text{-S}_2\text{P}(\text{OEt})_2]^-$  ligand effectively functioning as a six-electron tridentate donor. The reaction of Cu(II) with dithiophosphate in an aqueous solution at room temperature gave reduced Cu(I) hexanuclear cluster. This is of significance in spite of not knowing the composition and structure of oxidation product. These will be a focus of future attention.

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