The Adamantane Structure in Polynuclear Cu_4S_6 Cores: The Crystal and Molecular Structures of $Cu_4[SC(NH_2)_2]_6(NO_3)_4{\cdot}4H_2O$ and $Cu_4[SC(NH_2)_2]_9(NO_3)_4{\cdot}4H_2O$

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Summary The compounds $Cu_4[SC(NH_2)_2]_6(NO_3)_4{\cdot}4H_2O$ and $Cu_4[SC(NH_2)_2]_9(NO_3)_4{\cdot}4H_2O$ have been prepared, their structures determined, and are shown to contain a central Cu_4S_6 core with four trigonal planar Cu atoms in the former, but only one trigonal planar Cu in the latter.

CONSIDERABLE chemical interest has been shown in recent years concerning polynuclear Cu^I species, particularly those containing a tetrahedron,[1] cube,[2] or octahedron[3] of metal atoms. The Cu_4X_4 (cubane or step)[4] structures have recently been investigated. We here report the previously unknown Cu_4S_6 adamantane core in two structures, one of which contains Cu^I in two different geometric environments.

Both compounds of the title were prepared from low pH (*ca.* 1) aqueous solutions of thiourea (tu) and copper(II) nitrate. *Crystal data:* $Cu_4(tu)_6(NO_3)_4{\cdot}4H_2O$, orthorhombic $P2_12_12_1$, $a = 7{\cdot}908(3)$, $b = 18{\cdot}381(4)$, $c = 24{\cdot}099(5)$ Å, $Z = 4$, $D_c = 1{\cdot}95$ g cm^{-3}, $D_m = 1{\cdot}97$ g cm^{-3}, Mo-K_α ($\lambda = 0{\cdot}71068$ Å, $\mu = 29{\cdot}0$ cm^{-1}), $N = 1764$ (N = number of independent *hkl* intensities used in structure determination); $Cu_4(tu)_9(NO_3)_4{\cdot}4H_2O$, monoclinic $I2/c$, $a = 25{\cdot}248(5)$, $b = 15{\cdot}365(2)$, $c = 25{\cdot}778(5)$ Å, $\beta = 107{\cdot}67(5)$ °, $Z = 8$, $D_c = 1{\cdot}71$ g cm^{-3}, $D_m = 1{\cdot}79$ g cm^{-3}, Mo-K_α ($\lambda = 0{\cdot}71068$ Å, $\mu = 22{\cdot}8$ cm^{-1}), $N = 2720$. Absorption corrections were made. Intensity data were collected for both compounds on a Picker card-controlled automatic diffractometer to $2\theta \leqslant 60°$. The structures were solved by a combination of direct and heavy atom methods and refined by full-matrix least-squares with anomalous dispersion corrections and anisotropic temperature factors for copper and sulphur atoms and isotropic temperature factors for all other atoms (excluding hydrogen). Refinement gave a conventional R value of 0·074 for $Cu_4(tu)_6(NO_3)_4{\cdot}4H_2O$ and 0·095 for $Cu_4(tu)_9(NO_3)_4{\cdot}4H_2O$. While this is a relatively high value for diffractometer data, it is understandable in terms of the nitrate group and waters of hydration showing considerable disorder as well as the instability of the crystals in the X-ray beam.

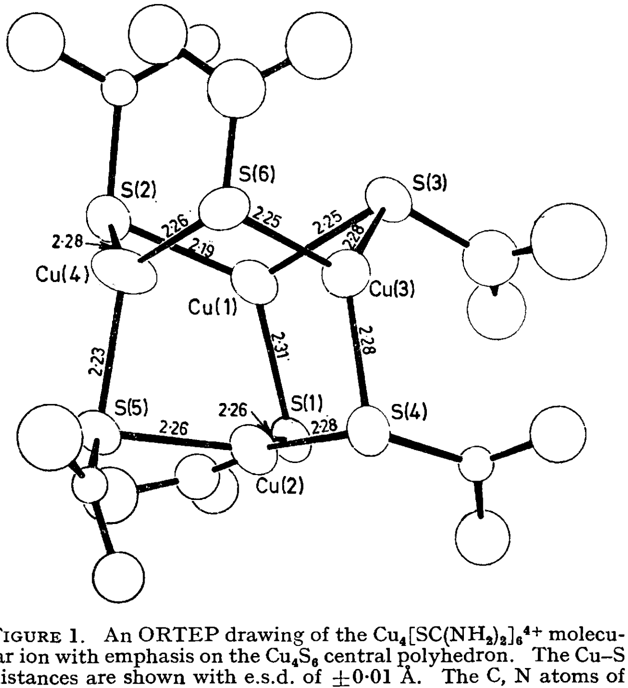

FIGURE 1. An ORTEP drawing of the $Cu_4[SC(NH_2)_2]_6{}^{4+}$ molecular ion with emphasis on the Cu_4S_6 central polyhedron. The Cu–S distances are shown with e.s.d. of ±0·01 Å. The C, N atoms of the $SC(NH_2)_2$ groups are shown as open isotropic circles. The atoms were drawn at the 50% probability level.

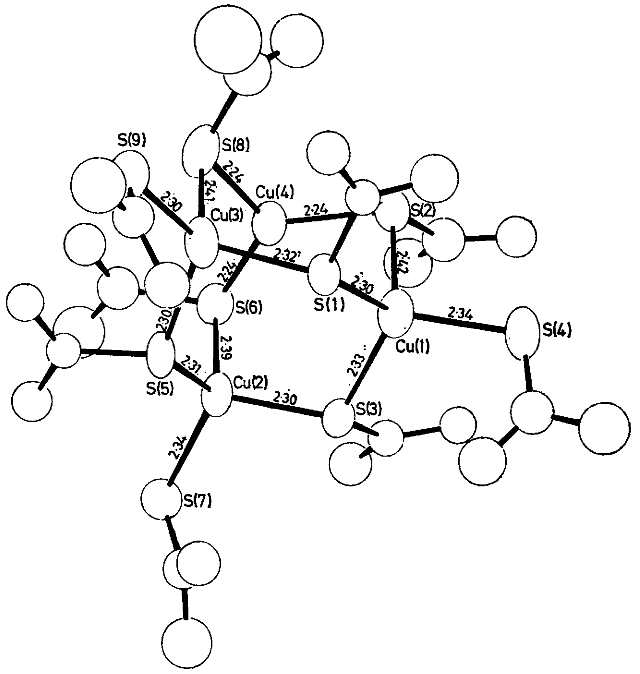

FIGURE 2. An ORTEP drawing of the $Cu_4[SC(NH_2)_2]_9{}^{4+}$ molecular ion, again with emphasis on the central polyhedron. Other details as in Figure 1.

The structures of $Cu_4[SC(NH_2)_2]_6(NO_3)_4{\cdot}4H_2O$ and $Cu_4[SC(NH_2)_2]_9(NO_3)_4{\cdot}4H_2O$ are made up of discrete ionic units $Cu_4(tu)_6{}^{4+}$ and $Cu_4(tu)_9{}^{4+}$, respectively (Figures 1 and 2). These units are then only loosely inter-connected by weak hydrogen bonding with water molecules and $NO_3{}^-$ groups, as well as ionic interactions with the $NO_3{}^-$ groups.

In each case the four Cu atoms are arranged in a distorted tetrahedral array within six bridging sulphur atoms of an approximate octahedral array. This arrangement leads to the inter-connected chair form of six-membered rings characteristic of adamantane.

In the $Cu_4(tu)_6^{4+}$ ion (Figure 1) each copper(I) atom is in an approximately trigonal planar environment. Cu(1) is 0·07, Cu(2) 0·20, Cu(3) 0·23, and Cu(4) 0·36 (all ±0·01 Å), out of the plane defined by their three bonded sulphur neighbours. The S–Cu–S angles vary from 106 to 126(1)° and the Cu–Cu distances vary from 2·833(2) to 3·093(2) Å. The Cu–Cu–Cu angles vary from 55·6° to 64·9° compared to 60° for a regular tetrahedron of Cu atoms. All the interatomic distances and angles in the thiourea groups are normal.

The $Cu_4(tu)_9^{4+}$ ion can be viewed as derived from the $Cu_4(tu)_6^{4+}$ ion by adding three non-bridging (terminal) thiourea groups, resulting in three very distorted 'tetrahedral' copper species and one trigonal planar copper (Figure 2). This results in a general lengthening of Cu–Cu distances that range from 3·842 to 3·925(2) Å for the four-co-ordinate copper atoms, and from 3·202 to 3·425(2) Å for the three-co-ordinate copper, *i.e.*, the Cu_4S_6 core expands. It should be noted that the range of Cu–Cu–Cu angles about the four-co-ordinate copper atoms continues in the same range as in the $Cu_4(tu)_6^{4+}$ species, 52·3—60·8(3)°, but the Cu–Cu–Cu angles about the three-co-ordinate Cu are 70·8, 71·8, and 72·3(3)°. The Cu(4) (the trigonal planar copper) atom is only 0·04 ± 0·01 Å displaced from the plane of its neighbouring sulphur atoms.

It is worthy of note that the trigonal planar Cu–S distances in $Cu_4(tu)_6^{4+}$ range from 2·19 to 2·31 Å, and in $Cu_4(tu)_9^{4+}$ they are all 2·24 Å; however, the 'tetrahedral' Cu–S distances in $Cu_4(tu)_9^{4+}$ range from 2·30—2·42 Å.

A particularly interesting aspect of these Cu_4S_6 polynuclear species is the fact that the fourth copper atom in the cluster seems to be particularly resistant to becoming four-co-ordinate. We have been unable to prepare $Cu_4(tu)_{10}^{4+}$ which would correspond to a Cu_4S_6 core with four tetrahedral Cu^I atoms.

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