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# A Novel Tungsten–Copper–Sulfur Cluster with Dialkyldithiocarbamate: Preparation and Structure of $(Et_4N)_2[W_2Cu_5S_8(S_2CNMe_2)_3]$

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Tetrathiometalates ($MS_4^{2-}$; M = Mo, W) acting as polydentate ligands in the syntheses of mixed-metal clusters have been extensively studied [1–5]. Reactions of $MS_4^{2-}$ with $Cu^+$ afforded various types of M–Cu–S complexes [1]. Dialkyldithiocarbamato ($R_2dtc^-$) is a good bidentate ligand to coordinate with many transition metals. We are interested in M–Cu–S systems and a series of heteronuclear Mo(W)–Cu–S compounds containing $R_2dtc^-$ ligands have been synthesized in our laboratory [6, 7]. Herein we report the synthesis and structure of a novel cluster compound $(Et_4N)_2[W_2Cu_5S_8(S_2CNMe_2)_3]$ consisting of two defective cubane cores, $WCu_2S_4$ and $WCu_3S_4$, bridged by two $Me_2dtc^-$ ligands and jointed by two weak Cu–S bonds.

## Experimental

### Syntheses

All operations were performed under an inert atmosphere in a Schlenk-type apparatus. A mixture of 1.5 g (15 mmol) CuCl and 2.1 g (15 mmol) $NaS_2CNMe_2$ was dissolved in 80 ml DMF and stirred at room temperature for several minutes. To this solution was added 2.9 g (5 mmol) of $(Et_4N)_2WS_4$. The green solution immediately turned red on mixing. After being stirred for 24 h, the reaction mixture was filtered and 50 ml of mixed solvent THF–$Et_2O$–$H_2O$ (2:2:1 by volume) was added to the filtrate. On standing for several days, this solution afforded a red crystalline solid which was collected and washed with 1:4 (vol./vol.) DMF–THF and dried *in vacuo* to give 1.7 g of product. The IR spectrum (KBr) shows characteristic W–$S_t$ absorption at 495 $cm^{-1}$ and W–$S_b$ absorption at 438 and 425 $cm^{-1}$.

### Crystal Data

A single crystal with dimensions 0.4 × 0.4 × 0.5 mm was mounted on a Regaku AFC5R four-circle diffractometer using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The crystal is orthogonal, space group *Pnma* with $a = 23.116(3)$ Å, $b = 17.560(5)$ Å, $c = 12.565(3)$ Å, $V = 5100.3$ Å$^3$, $Z = 4$, $D_c = 2.035$ g/cm$^3$. A total of 5629 reflections were collected in the range $1° < \theta < 24°$, of which 2311 reflections with $I > 6\sigma(I)$ were used in structure determination and refinements after LP and empirical absorption corrections with the AFC5R program. The coordinates of all metal atoms were determined by direct methods and the remaining non-hydrogen atoms were located from successive difference Fourier maps. The structure was refined by full-matrix least-squares technique with anisotropic temperature factors for the tungsten, copper and sulfur atoms, and isotropic temperature factors for the remaining non-hydrogen atoms. The final $R$ and $R_w$ are 0.055 and 0.078, respectively.

## Results and Discussion

The important bond lengths and bond angles are given in Tables 1 and 2, respectively. The structure of the anion of the title compound is depicted in Fig. 1.

As there are four molecules of the title compound in a unit cell, the anion of $[W_2Cu_5S_8(S_2CNMe_2)_3]^{2-}$ is arranged crystallographically in a mirror symmetry and atoms W(1), W(2), Cu(3), S(1), S(3), S(4) and S(5) are located on the mirror plane. The framework $W_2Cu_5S_8$ consists of two 'defective cubanes'

TABLE 1. Selected atomic distances (Å)

| | | | | | |
|---|---|---|---|---|---|
| W1–Cu1 | 2.646(2) | W2–S5 | 2.248(5) | Cu2–S12 | 2.280(5) |
| W2–Cu2 | 2.738(2) | W2–S6 | 2.226(3) | Cu3–S6 | 2.290(4) |
| W2–Cu3 | 2.655(3) | Cu1–S2 | 2.254(4) | Cu3–S21 | 2.364(6) |
| Cu1–Cu2 | 2.784(2) | Cu1–S3 | 2.243(4) | Cu3–S22 | 2.405(6) |
| W1–S1 | 2.116(5) | Cu1–S11 | 2.180(4) | S11–C11 | 1.71(1) |
| W1–S2 | 2.230(3) | Cu2–S2 | 2.507(4) | S12–C11 | 1.71(1) |
| W1–S3 | 2.269(5) | Cu2–S5 | 2.293(3) | S21–C21 | 1.70(3) |
| W2–S4 | 2.126(5) | Cu2–S6 | 2.318(4) | S22–C21 | 1.71(2) |

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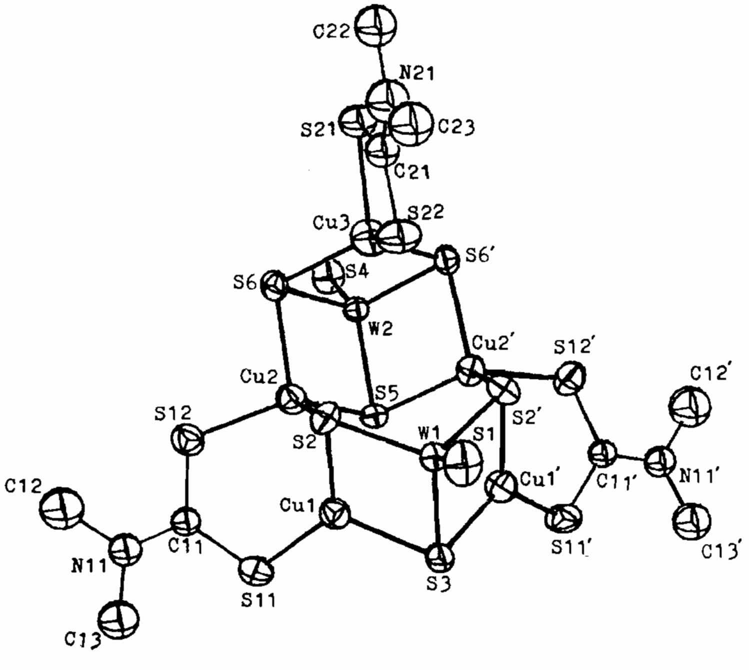

Fig. 1. A perspective view of the anion $(Mo_2Cu_5S_8(S_2CNMe_2)_3)^{2-}$

TABLE 2. Selected bond angles (°)

| | | | |
|---|---|---|---|
| S1–W1–S2 | 109.9(1) | S6–Cu2–S12 | 104.1(1) |
| S1–W1–S3 | 112.0(2) | S6–Cu3–S6′ | 105.7(2) |
| S2–W1–S2′ | 109.5(2) | S6–Cu3–S21 | 121.1(1) |
| S2–W1–S3 | 107.7(1) | S6–Cu3–S22 | 115.5(1) |
| S4–W2–S5 | 113.2(3) | W1–S2–Cu1 | 72.3(1) |
| S5–W2–S6 | 108.2(2) | W1–S2–Cu2 | 114.7(1) |
| S6–W2–S6′ | 110.1(2) | Cu1–S2–Cu2 | 71.3(1) |
| S2–Cu1–S3 | 107.8(2) | W1–S3–Cu1 | 71.9(1) |
| S2–Cu1–S11 | 128.7(2) | Cu1–S3–Cu1′ | 101.4(2) |
| S3–Cu1–S11 | 121.5(2) | W2–S5–Cu2 | 74.1(1) |
| S2–Cu2–S5 | 114.1(2) | Cu2–S5–Cu2′ | 111.4(2) |
| S2–Cu2–S6 | 102.3(1) | W2–S6–Cu2 | 74.1(1) |
| S2–Cu2–S12 | 98.8(1) | W2–S6–Cu3 | 72.0(2) |
| S5–Cu2–S6 | 103.6(2) | Cu2–S6–Cu3 | 106.6(2) |
| S5–Cu2–S12 | 130.6(2) | | |

$[SWS_3Cu_2]$ and $[SWS_3Cu_3]$ facing each other, which are similar to the cores in the literature compounds $[OMS_3(CuPPh_3)Cu(PPh_3)_2]$ and $[OMS_3(CuCl)_3]^{2-}$ (M = Mo, W) respectively [8].. These two 'cubane-like' units are linked by two weak Cu–S bonds (Cu(2)–S(2), 2.507 Å) and two bridging $Me_2dtc^-$ ligands. Structure analysis shows that each of the two tungsten atoms is in an $S_4$ tetrahedral center. The bond angles S–W–S vary from 107.7 to 113.2° (average values 109.4° for $[WCu_2S_4]$ and 109.7° for $[WCu_3S_4]$) and the bond lengths W–S vary from 2.116 to 2.269 Å, of which the terminal W–S distance is the shortest in both units. From the structural point of view, there are three kinds of copper atoms in this molecule: (a) atom Cu(1) essentially in the center of the trigonal plane of atoms S(2), S(3) and S(11); (b) atom Cu(2) in a distorted tetrahedral environment; (c) atom Cu(3) in a highly distorted tetrahedral coordination sphere with an angle S(21)–Cu(3)–S(22) of 75.7°, which is a normal chelate angle for $M(R_2dtc)_n$. Each of the six bridging sulfur atoms is triply bridged and the three $Me_2dtc$ ligands are of two types: two of them are bridging ligands connecting two copper atoms, and the third is a terminal ligand chelating to atom Cu(3).

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