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Solvothermal Synthesis of a New Mixed-Metal Polysulfide Cluster, $[Me_4N]_3[MoS_4Cu_3(S_5)_2]$

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Introduction

Polychalcogenide compounds are in general useful materials.$^{1-4}$ The polysulfide chemistry of metals has a rich history.^{5} In particular, polysulfide ligands have been implicated as reactive species in the hydrodesulfurization (HDS) of oil and are thought to be present at the surfaces of metal sulfide catalysts.$^{6-8}$ Several literature reviews on metal polychalcogenide chemistry have appeared in recent years, which testify to the continuing interest in this type of new materials.$^{9-14}$ Our interest in exploring unusual conditions for the synthesis of novel metal chalcogenides led us to consider hydro(solvo)thermal techniques. The application of hydro(solvo)thermal methods to prepare metal polychalcogenides is still very restricted in the literature, except with some homometal chalcogenides^{15} such as $K_{12}Mo_{12}Se_{56}$, $K_2Mo_3Se_{18}$, $K_8Mo_9Se_{48}\cdot 4H_2O$, $Cs_4Mo_6S_{28}\cdot 0.5H_2O$, $K_4[Pt_4S_{22}]\cdot 4H_2O$, $[Ph_4P]_2[Pt(S_4)_2]\cdot CH_3OH$, $K_4V_2O_2Se_{10}\cdot 2MeOH$, $K_4V_2O_2Se_8\cdot 0.65MeOH$, K_2PdSe_{10}, and $(Ph_4P)_2[Ru_6(Te_2)_7(CO)_{12}]$. Recently a framework structure composed of adamantane-like Ge_4S_6 and AgS_3 fragments was synthesized hydrothermally and structurally characterized using synchrotron/imaging plate-based X-ray crystallography.^{16} We report here the solvothermal synthesis and structure of the first discrete tetranuclear heterometal polysulfide cluster in the complex $[Me_4N]_3[MoS_4Cu_3(S_5)_2]$.

Experimental Section

Synthesis. $[Me_4N]_3[MoS_4Cu_3(S_5)_2]$ was prepared by reacting 84.32 mg (0.324 mmol) of $(NH_4)_2MoS_4$, 32.08 mg (0.324 mmol) of CuCl, 133.78 mg (0.648 mmol) of K_2S_4,^{17} 99.82 mg (0.648 mmol) of Me_4NBr, and 0.3 mL of EtOH (5.443 mmol) in a Pyrex ampule of about 7 mL capacity. The ampule was sealed under vacuum, heated in a furnace to 100 °C for 72 h, and then cooled to 50 °C at 6 °C/h. Black prismatic crystals of $[Me_4N]_3[MoS_4Cu_3(S_5)_2]$ were isolated and washed with ethanol. These crystals are air-stable and insoluble in water and many organic solvents. XPS measurement on the crystalline sample showed that the compound contain Mo, Cu, and S elements. Semiquantitative analysis performed on a scanning electron microscope (SEM) equipped with an energy-dispersive spectroscopy (EDS) detector gave a ratio of 3:15.1 for Cu/(Mo + S).

Table 1. Crystallographic Data for $[Me_4N]_3[MoS_4Cu_3(S_5)_2]$

chemical formula	$[Me_4N]_3[MoS_4Cu_3(S_5)_2]$	Z	2
formula weight	957.8	T	20 °C
space group	$P2/c$	λ	0.710 73 Å
a	11.873(1) Å	ρ_{calcd}	1.779 g cm^{-3}
b	9.529(1) Å	μ	29.31 cm^{-1}
c	16.511(2) Å	R^a	0.050
β	106.82(1)°	$R_w{}^b$	0.057
V	1788.1(3) Å^3		

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$.

X-ray Crystallography and Structure Solution. A well-developed crystal (0.02 × 0.02 × 0.04 mm) was selected for X-ray crystallographic study. The crystallographic data were collected on a Siemens R3m/V diffractometer equipped graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Three standard reflections were monitored for every 200 reflections. No significant decay was observed. The raw intensities were corrected for Lp effects, and an empirical ψ-scan absorption correction was applied to all data. The structure was solved by direct methods (SHELXTL, PC Version) and refined by full-matrix least squares on *F* using the Siemens SHELXTL PLUS (PC Version) package of crystallographic software. One of the two independent Me_4N^+ ions, which occupies a site of symmetry 2, exhibits orientational disorder; the scattering power of its methyl groups was represented by atoms C(5)−C(8) of half-site occupancy. The hydrogen atoms of the Me_4N^+ cations were allowed to ride on their parent C atoms and were included in structure factor calculations with assigned isotropic thermal parameters. The data processing and structure refinement parameters are summarized in Table 1.

Results and Discussion

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2. The structure of the $[MoS_4Cu_3(S_5)_2]^{3-}$ anion, which has crystallographically imposed C_2 symmetry, is shown in Figure 1. The oxidation states of the metal atoms were checked by the bond valence method, which yielded bond valence sums of 5.69, 1.18, and 1.08 for Mo(1), Cu(1), and Cu(2), respectively.^{18} The MoS_4Cu_3 core in this tetranuclear cluster is similar to that in $[MoS_4(CuCl)_3]^{2-}$.^{19} The MoS_4 unit is essentially tetrahedral with Mo−S distances of 2.231(1) and 2.208(2) Å and S−Mo−S angles in the range 108.1(1)−111.9(1)°. The tetrathiometallate moiety acts as a tetradentate bridging ligand toward three copper(I) atoms with Mo···Cu distances of 2.799(1) and 2.648(1) Å, which are longer than those of 2.615(2) and 2.621(1) Å in $[MoS_4(CuCl)_3]^{2-}$. It is notable that the Cu(1)···Mo(1) distance of 2.799(1) Å is over

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å)[a]

atom	*x*	*y*	*z*	*U*(eq)[b]
Mo(1)	$^1/_2$	0.12943(7)	$^3/_4$	0.0581(2)
Cu(1)	$^1/_2$	0.4231(1)	$^3/_4$	0.0654(3)
Cu(2)	0.72088(6)	0.15386(8)	0.84505(5)	0.0731(3)
S(1)	0.5631(1)	0.2666(2)	0.86369(9)	0.0648(4)
S(2)	0.3506(1)	−0.0003(2)	0.7603(1)	0.0770(4)
S(3)	0.6643(1)	0.5376(2)	0.7395(1)	0.0757(4)
S(4)	0.7851(1)	0.3786(2)	0.7540(1)	0.0758(4)
S(5)	0.9370(1)	0.4228(2)	0.8476(1)	0.0978(5)
S(6)	0.9103(1)	0.3575(2)	0.9597(1)	0.0882(5)
S(7)	0.8888(1)	0.1456(2)	0.9464(1)	0.0795(4)
N(1)	0.6771(4)	0.2589(5)	0.4825(3)	0.0710(6)
N(2)	0	0.1434(5)	$^1/_2$	0.0988(7)
C(1)	0.6773(7)	0.3991(7)	0.5195(5)	0.1429(7)
C(2)	0.5614(7)	0.2342(8)	0.4230(6)	0.1868(7)
C(3)	0.7688(6)	0.2489(7)	0.4402(5)	0.1180(7)
C(4)	0.6975(7)	0.1568(7)	0.5513(5)	0.1514(7)
C(5)	0.0571(7)	0.1782(8)	0.1847(5)	0.1173(7)
C(6)	−0.1077(5)	0.2261(8)	0.2349(7)	0.3029(7)
C(7)	−0.0262(7)	−0.0066(6)	0.2455(7)	0.2681(7)
C(8)	0.0805(8)	0.1771(9)	0.3331(4)	0.5619(7)

[a] Atoms C(5)−C(8) belong to an orientationally disordered Me_4N^+ ion with its center at N(2), and each has half-site occupancy. [a] $U_{eq} = (^1/_3)\sum_i\sum_j U_{ij}a_i a_j \mathbf{a}_i{\cdot}\mathbf{a}_j$.

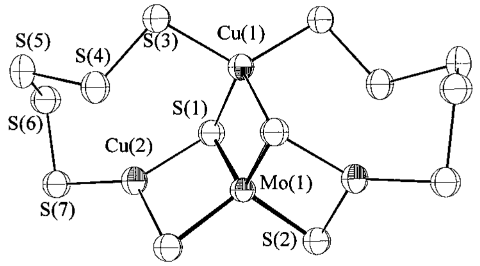

Figure 1. Molecular structure of the $[MoS_4Cu_3(S_5)_2]^{3-}$ cluster showing the atom labeling scheme (30% thermal ellipsoids). Half of the anion (no label) is generated through a crystallographic two fold axis passing through Mo(1) and Cu(1). Selected bond distances (Å) and angles (deg): Mo(1)−Cu(1) 2.799 (1), Mo(1)−Cu(2) 2.648 (1), Mo(1)−S(1) 2.231 (1), Mo(1)−S(2) 2.208 (2), Cu(1)−S(1) 2.344 (2), Cu(1)−S(3) 2.285 (2), Cu(2)−S(1) 2.257 (2), Cu(2)−S(7) 2.202 (1), Cu(2)−S(2A) 2.246 (2); S(1)−Cu(1)−S(3) 106.4(1), S(1)−Cu(1)−S(1A) 101.0(1), S(1)−Cu(2)−S(2A) 105.9(1), S(1)−Cu(2)−S(7) 121.2(1), Mo(1)−S(1)−Cu(1) 75.4(1), Mo(1)−S(1)−Cu(2) 72.3(1), Cu(1)−S(1)−Cu(2) 106.2(1), Mo(1)−S(2)−Cu(2A) 72.9(1), Cu(1)−S(3)−S(4) 102.8(1), S(5)−S(6)−S(7) 104.4(1), and Cu(2)−S(7)−S(6) 96.0(1).

0.1 Å longer than the corresponding distance in $[MoS_4(CuX)_n]^{2-}$.[19,20] The Cu(1)−S(1) bond of 2.344(2) Å is significantly longer than that (2.240(2) Å) in $[MoS_4(CuCl)_3]^{2-}$.

Complexes containing a bridging bidentate μ-S_5^{2-} unit are rare, two examples being $[Mo_2(NO)_2(S_2)_3(S_5)OH]^{3-}$ [21] and $[Nb_2(O)(OMe)_2(S_2)_3(S_5)]^{2-}$.[22] In the present C_2 $[MoS_4Cu_3(S_5)_2]^{3-}$ trianion, two μ-S_5^{2-} units each acts as a bridge across a pair of Cu atoms to form a S_5Cu_2S metallacycle. This eight-membered ring adopts a boat−chair formation (Figure 2) as found in the S_8^{2+} cation[23] and many crystalline derivatives of 1, 5-dithiacyclooctane and 1, 3, 5, 7-tetrathiocane,[24] which is different from the S_8-like crown formation of the $S_5Mo_2(S_2)$ ring in $[Mo_2(NO)_2(S_2)_3(S_5)OH]^{3-}$.[21] The average S−S distance of 2.050(2) Å in the present S_5^{2-} unit is similar to that found in $[Mo_2(NO)_2(S_2)_3(S_5)(OH)]^{3-}$.[21] However, the S−S bond lengths within the S_5^{2-} chain in $[MoS_4Cu_3(S_5)_2]^{3-}$ vary in the pattern "medium−medium−medium−short", in contrast to the "medium−medium−medium−medium" bond motif in $[Mo_2(NO)_2(S_2)_3(S_5)(OH)]^{3-}$.[21]

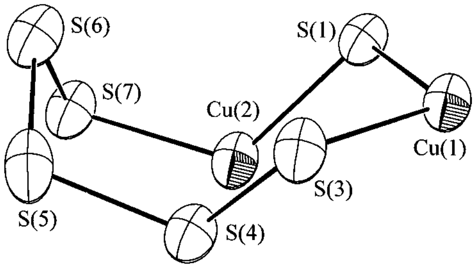

Figure 2. Perspective view of the conformation of the eight-membered S_5Cu_2S ring (30% thermal ellipsoids) in $[Me_4N]_3[MoS_4Cu_3(S_5)_2]$. Selected torsion angles (deg): S(3)−S(4)−S(5)−S(6) 86.0(1), S(4)−S(5)−S(6)−S(7) 63.8(1), S(5)−S(4)−S(3)−Cu(1) −126.8(1), and S(5)−S(6)−S(7)−Cu(2) −66.9(1).

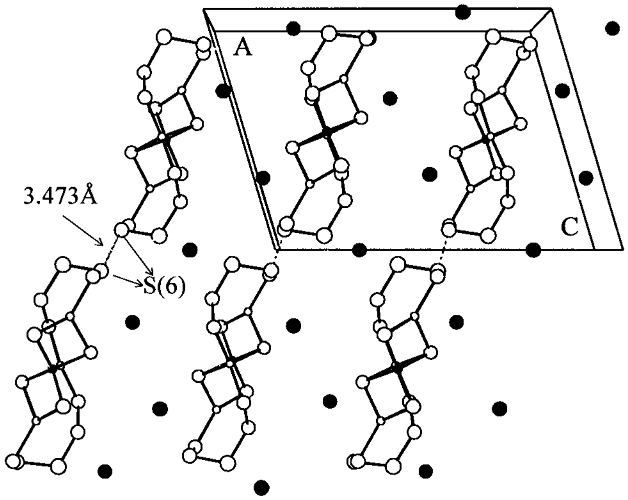

Figure 3. Crystal structure of $[Me_4N]_3[MoS_4Cu_3(S_5)_2]$ viewed along the *b* axis. The atoms are differentiated by size and shading, and for clarity the Me_4N^+ ions are shown as large spheres. The weak interactions between S atoms across inversion centers are represented by broken lines.

A view of the crystal structure of $[Me_4N]_3[MoS_4Cu_3(S_5)_2]$ is shown in Figure 3. The shortest intermolecular S(6)···S(6) contact of 3.473(3) Å exists between each pair of adjacent $[MoS_4Cu_3(S_5)_2]^{3-}$ anions related by a crystallographic center of symmetry. This S···S weak interaction leads to infinite chains of $[MoS_4Cu_3(S_5)_2]^{3-}$ running parallel to the [201] direction with the Me_4N^+ cations located between them. It is interesting to note that a similar weak interaction was observed in several polynuclear molybdenum chalcogenide complexes such as $K_{12}Mo_{12}Se_{56}$,[15a] $K_2Mo_3Se_{18}$,[15b] $K_8Mo_9Se_{48}{\cdot}4H_2O$,[15b] and $Cs_4Mo_6S_{28}{\cdot}0.5H_2O$[15c] synthesized by hydrothermal techniques. The origin of this weak interaction is not clear, but is probably associated with the well-known catenation capacity of the chalcogens. For example, in orthorhombic sulfur there exist intermolecular contacts of 3.37, 3.39, 3.48, and 3.69 Å between the S_8 molecules in the crystal packing.[25] Further explorations

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on hydrothermal synthesis of mixed-metal clusters are in progress in our laboratory.

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Supporting Information Available: Tables of crystal data and structure refinement parameters, all bond distances and angles, anisotropic thermal parameters of non-hydrogen atoms, H-atom coordinates and isotropic displacement coefficients, and bond valence calculation (4 pages).

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