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Note

First Cubane-like Polysulfidomolybdate: Synthesis and Crystal Structure of $Cs_6[Mo_4S_{23.6}]$

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Introduction

Many polysulfidomolybdate anions, $[Mo_nS_m]^{z-}$, are known for $n < 4$,[1] but none with a Mo_4S_4 cubane core appear to be known for $n = 4$. On the other hand, many compounds containing the Mo_4S_4 cubane core have been synthesized and structurally characterized.[2] Here we present a simple synthesis and the structure of the first cubane-like polysulfidomolybdate, $Cs_6[Mo_4S_{23.6}]$.

Experimental Section

Materials and Syntheses. All reagents were used as purchased. Mo_6Br_{12} was synthesized through the reaction of Mo with Br_2 at 750 °C.[3] Cs_2S_3 was synthesized by the reaction of Cs with S in liquid ammonia. $Cs_6[Mo_4S_{23.6}]$ was obtained from the reaction of 0.10 g (0.065 mmol) of Mo_6Br_{12} and 0.60 g (1.65 mmol) of Cs_2S_3 in 20 mL of water at 25 °C. When the solution and orange precipitate of Mo_6Br_{12} were held for 1 h at 60−80 °C, the orange precipitate was replaced by a dark-red one and the solution turned dark red. The solution was filtered and cooled to 5 °C. The black tetrahedral-shaped crystals that formed were filtered off, washed with methanol, and dried. Unoptimized yield: 0.040 g (21% based on Mo). Anal. Calcd for $Cs_6Mo_4S_{23.6}$: Mo, 19.80. Found: Mo, 18.98. Microanalysis for Mo was performed by Oneida Research Services, Whiteboro, NY. The uncharacterized orange precipitate is probably $Cs_2[Mo_3S_{13}]$.

X-ray Crystallography. Diffraction data were collected on a tetrahedrally shaped black crystal with the use of graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer with the program SMART.[4] The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by re-collecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in ω in groups of 606 frames at φ settings of 0°, 90°, 180°, and 270°. The exposure times was 15 s/frame. Cell refinement and data reduction were carried out with the use of the program SAINT,[4] and face-indexed absorption corrections were performed numerically with the use of the program XPREP.[5] Then the program SADABS[5] was employed to make incident beam and decay correction.

Table 1. Crystal Data and Structure Refinement Details for $Cs_6[Mo_4S_{23.6}]$

fw	1939.12	ρ_{calc}, g cm^{-3}	3.239
space group	$F\bar{4}3m$	T, K	153
a, Å	15.8436(7)	μ, cm^{-1}	78.9
V, Å^3	3977.1(3)	$R(F)^a$	0.036
Z	4	$R_w(F_o^2)^b$	0.087

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. [b] $R_w(F_o^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.034F_o^2)^2$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

The compound crystallizes with four formula units in space group $F\bar{4}3m$ of the cubic system. Its structure was solved by means of the direct methods program SHELXS of the SHELXT-PC suite of programs[5] and was refined by full-matrix least-squares techniques. The structure comprises an anionic Mo_4S_4 cluster and three independent Cs^+ cations. The cluster itself has crystallographically imposed $\bar{4}3m$ (T_d) symmetry, which leads to disorder of the S_n^{2-} ligands that bridge the Mo atoms. Indeed, not only are these ligands disordered, but examination of electron density maps revealed that these bridges consist of superimposed S_3^{2-} and S_4^{2-} ligands. The data were of sufficient quality to permit the refinement of both of these ligands, and the resultant composition is $Cs_6Mo_4S_4(S_3)_6$:$Cs_6Mo_4S_4(S_4)_6$ = 0.73(2):27(2) or $Cs_6[Mo_4S_{23.6}]$. No supercell was apparent on the diffraction frames. The final refinement, which involved anisotropic displacement parameters for all atoms, converged satisfactorily and resulted in sensible bond distances and displacement ellipsoids. Further details are given in Table 1 and in Supporting Information.

Results and Discussion

Synthesis. The synthesis of $Cs_6[Mo_4S_{23.6}]$ is remarkably simple, involving as it does the reaction of Mo_6Br_{12} with Cs_2S_3 in water. Although water remains an unusual solvent in polysulfidometalate chemistry, it was employed originally in the preparation of the $[Mo_3S(S_2)_6]^{2-}$ and $[Mo_2(S_2)_6]^{2-}$ anions.[6] $Cs_6[Mo_4S_{23.6}]$ is stable in air and soluble in H_2O.

Structure. The structure of $Cs_6[Mo_4S_{23.6}]$ comprises well-separated Cs^+ cations and cluster anions. The anion, which

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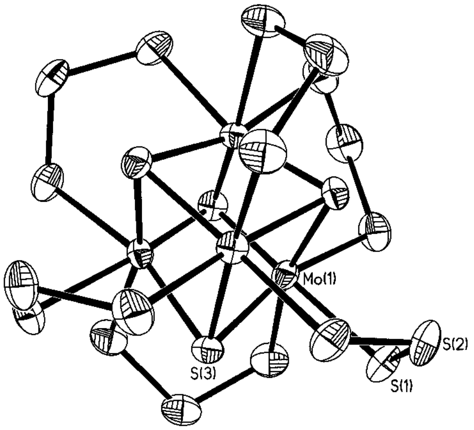

Figure 1. $[Mo_4S_4(S_3)_6]^{6-}$ component of the $[Mo_4S_{23.6}]^{6-}$ anion, with displacement ellipsoids drawn at the 50% probability level. Neither the disorder of the S_3^{2-} ligands nor the presence of S_4^{2-} ligands is shown.

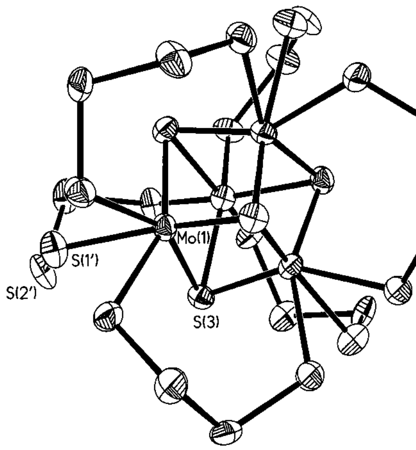

Figure 2. $[Mo_4S_4(S_4)_6]^{6-}$ component of the $[Mo_4S_{23.6}]^{6-}$ anion, with displacement ellipsoids drawn at the 50% probability level. Neither the disorder of the S_4^{2-} ligands nor the presence of S_3^{2-} ligands is shown.

has crystallographically imposed $\bar{4}3m$ symmetry, comprises a regular tetrahedral cubane-like Mo_4S_4 core with the six Mo−Mo edges of the tetrahedron bridged by S_n^{2-} chains (n = 3, 4). It is important to note that whereas the X-ray diffraction data enable us to determine the ratio of 0.73(2): 0.27(2) of S_3^{2-}:S_4^{2-} they do not permit us to distinguish a structure in which on average S_3^{2-} and S_4^{2-} rings are randomly mixed in a 0.73:0.27 ratio to lead to the “average” anion, $[Mo_4S_4(S_3)_{4.38}(S_4)_{1.62}]^{6-}$, from one in which $[Mo_4S_4(S_3)_6]^{6-}$ anions (Figure 1) are randomly mixed among $[Mo_4S_4(S_4)_6]^{6-}$ anions (Figure 2) in that same ratio. Of course, these are two extremes and some combination of them is possible. Moreover, the possibility of various confomers exists depending on the direction of folding of individual S_3^{2-} rings or the direction of crossing of individual S_4^{2-} rings. Since the anion lacks useful NMR nuclei, it is not possible to investigate these various possibilities through solution NMR studies, as was the case, for example, for $[Re_6(Te_{8-n}Se_n)(CN)_6]^{4-}$ clusters (n = 0−8).[7]

The regular tetrahedral Mo_4S_4 cluster has a Mo−Mo distance of 2.8642(19) Å and a Mo−μ_3-S distance of 2.358(2) Å. These may be compared with the range of Mo−Mo distances of 2.740(1)−2.872(1) Å and Mo−μ_3-S distances of 2.324(2)−2.388(3) Å in $Na_2[Mo_4S_4(edta)_2]\cdot 6H_2O$,[8] where Mo, as in the present compound, has an average oxidation state of 3.5. Distances in the $n = 3$ component of the $[Mo_4S_{23.6}]^{6-}$ anion are S1−S2 = 2.080(11) Å, Mo1−S1 = 2.573(6) Å. The S1 atoms lie in a plane with the Mo1 atoms, whereas the S2 atom disorders over two crystallographically equivalent positions, 1.8 Å apart. Distances in the $n = 4$ component are S1′−S2′ = 2.09(2) Å, S2′−S2′ = 2.11(2) Å, Mo1−S1′ = 2.45(2) Å. The S1′ atoms lie in a plane with the Mo1 atoms, but the S2′−S2′ segment crosses this plane. Furthermore, the S2′−S2′ segment disorders over two crystallographically equivalent paths.

The structure of the anion is similar to that of the $[Re_4S_4(S_3)_6]^{4-}$ anion in $[NH_4]_4[Re_4S_{22}]\cdot 2H_2O$.[9,10] Although their structures are similar, the electronic states of their M_4S_4 cores (M = Re, Mo) are different. The Re core, $[Re_4S_4]^{8+}$, is a 12-electron cluster of Re(IV); the Mo core, $[Mo_4S_4]^{6+}$, is an electron-deficient 10-electron cluster with equal numbers of Mo(III) and Mo(IV) centers.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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