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Hydrothermal Synthesis of a Mixed-Cluster Molybdenum Polysulfide: $Cs_4[Mo_3S(S_2)_6][Mo_3S(S_2)_5(S_4)]\cdot 0.5H_2O$

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There is a rich history in the polysulfide chemistry of metals.[1] In particular, the chemistry of molybdenum polysulfides has deep bonding[2] and in hydrodesulfurization catalysis.[3] There is indeed unique chemical reactivity found within molecular polysulfide compounds.[4] A number of papers have reviewed metal polychalcogenide chemistry in recent years which illustrate the continuing interest in new metal chalcogenide materials.[5–9] The highlights of this chemistry have been the development of unique synthetic methods to prepare new compounds and materials, including molten salt and solvatothermal synthesis. Sheldrick has illustrated the utility of the solvatothermal method using carbonate mineralizers to prepare new main-group-metal chalcogenides[10,11] and Kanatzidis has prepared several new transition-metal chalcogenides from solutions of alkali-metal polychalcogenides.[12–15] We have also illustrated the utility of hydrothermal synthesis as an alternative method to prepare one- and two-dimensional copper polychalcogenide materials.[16,17] In this communication, we report the first hydrothermal synthesis[18] and unique structure[19–22] of a mixed-cluster molybdenum sulfide, $Cs_4[Mo_3S(S_2)_6][Mo_3S(S_2)_5(S_4)]\cdot 0.5H_2O$.

The structure comprises alternate stacking layers of clusters between glide planes of the unit cell. The clusters are divided into two classes, type A and type B, as shown in Figure 1. The type A cluster, $[Mo_3S(S_2)_6]^{2-}$, is identical to the clusters observed by Müller in $(NH_4)_2[Mo_3S(S_2)_6]\cdot 2H_2O$.[3,23–27] It is also similar to the $[Mo_3Se_{14}]^{3-}$ subclusters observed in Kanatzidis' $[Mo_{12}Se_{56}]^{12-}$ cluster of clusters.[12] The cluster is composed of a $Mo^{IV}{}_3$ triangle whose edges are bridged by $(\mu_2\text{-}S_2)^{2-}$ units and whose triangular face is capped by one $(\mu_3\text{-}S)^{2-}$ atom. Each molybdenum is also terminally bound to one $S_2{}^{2-}$ disulfido ligand. Most of the bond distances and angles correlate well with the previously reported $[Mo_3S(S_2)_6]^{2-}$ structure.[3,27] There are several bonding roots in the history of metal–metal

The type B cluster, $[Mo_3S(S_2)_5(S_4)]^{2-}$, is a unique mixture of the type A cluster with an $S_4{}^{2-}$ ligand substituted for one $S_2{}^{2-}$ ligand in the terminal position. The $S_4{}^{2-}$ ligand assumes the envelope geometry seen in other $S_4{}^{2-}$-containing anions such as $[MoS(S_4)_2]^{2-}$ and $[Mo_2(S)_4(S_4)_2]^{2-}$.[4,28] features worth noting here. The $Mo(3)S_4$ ring does not rigorously conform to previously described bonding pictures wherein the ligand provides substantial π-back-bonding from the π^*-orbitals in the sulfur ring to generate an alternating S—S-S—S, long–short–long bonding picture. Instead, there appears to be a weaker Mo–S π-bonding interaction. This effect is also seen in bonding to the apical sulfur, S(15), from Mo(3) where the bond length is longer by 0.040(6) Å than the bonds to either Mo(1) or Mo(2) and longer by 0.043(6) Å than in the previously reported $[Mo_3S(S_2)_6]^{2-}$ compound.[3,26] The average Mo–Mo distances in cluster B are longer by ~0.02 Å than those in cluster A but are comparable to those of the previously reported $[Mo_3S(S_2)_6]^{2-}$.[3,27] These bonding effects may be manifestations of changes in the HOMO orbital, which is π^*-terminal-$S_2{}^{2-}$ in $[Mo_3S(S_2)_6]^{2-}$,[27,29] or of long intercluster interactions.

The two cluster types are packed within the unit cell as shown in Figures 2 and 3. Figure 2 illustrates the layering of the two cluster types, perpendicular to [100], in an -A-B-A-A′-B′-A′- packing of clusters. Interlayer distances are A–A′ = 5.33 Å and A–B = 6.35 Å. Cesium atoms are located within the layers. Waters of hydration are located between A-layers, closely associated with Cs(2); Cs(2)–O(1) = 3.038(12) Å. The cesium atoms are coordinated to sulfur and water, with coordination environments of between 9 and 11 sulfur (oxygen) atoms per cesium atom and Cs–S bond distances between 3.407(6) and 4.114(5) Å. Type A clusters are arranged with their Mo_3 rings canted off perpendicular to the *x*-axis and twisted between A- and A′-layers by the 2-fold axes. The type B clusters are arranged such that their Mo_3 rings are nearly perpendicular to the type A clusters and the MoS_4 rings are directed alternately "up" and "down" into the A-planes.

Figure 3 illustrates how the clusters interact through weak

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(18) $Cs_4Mo_6S_{28}\cdot 0.5H_2O$ was prepared by reacting 47.5 mg of Mo powder (99.999%, Johnson Matthey) and an excess (236.7 mg) of K_2S_5 powder, as prepared in ref 13, in a quartz ampule (loaded in an inert atmosphere) with 0.50 mL of a 2.0 M CsCl (99.9%, Fisher) aqueous solution. The ampule was sealed under vacuum, heated in a furnace to 150 °C (10 °C/h) for 72 h, and then cooled to 25 °C at 10 °C/h. The product (quantitative yield in Mo by powder X-ray diffraction) was filtered from solution and washed with deionized water and allowed to dry. Qualitative EDS measurements confirmed the Cs:Mo:S ratios.

(19) A well-diffracting, ruby-red faceted rod (0.08 × 0.07 × 0.44 mm) was selected from the filtrate. Crystal data for $Cs_4Mo_6S_{28}\cdot 0.5H_2O$: orthorhombic *Aba*2 (No. 41), $Z = 8$, $a = 31.498(3)$ Å, $b = 20.227(1)$ Å, $c = 12.785(1)$ Å, $V = 8145.5(11)$ Å^3, at 298 K. $D_{calc} = 3.283$ g/cm^3, $\mu = 6.760$ mm^{-1}, and 2θ range (θ–2θ scan) = 4.0–50.0° with Mo Kα radiation. The structure was solved by direct methods (SHELXTL UNIX[20]) and refined (SHELXL-93,[21] full-matrix least squares on F^2) from 4537 reflections ($-1 \le h \le 37$, $-24 \le k \le 1$, $-1 \le l \le 15$) and 4119 independent reflections. Number of variables: 348. Final $R = 0.044$ and $R_w = 0.1020$; GOF = 1.066. Largest residuals are ~2.9 Å from Cs (1.53 to -2.14 e/Å^3). The absolute structure was checked by the method of Flack.[22]

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(29) A detailed, comparative molecular orbital diagram is forthcoming.

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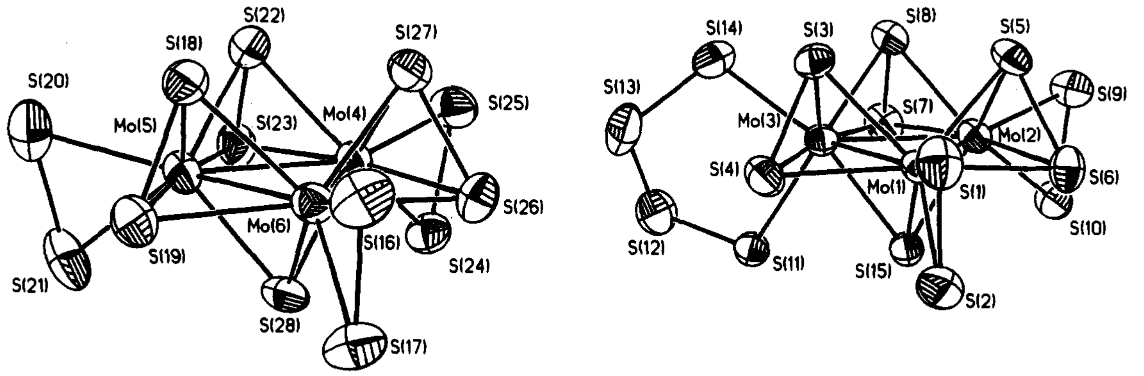

Figure 1. Individual molecular structures (70% thermal ellipsoids) and labeling scheme of the Mo/S trinuclear subclusters. Selected bond distances (Å) and angles (deg) for each cluster are as follows. Type A (left): Mo(4)–Mo(5) 2.715(2), Mo(4)–Mo(6) 2.726(2), Mo(5)–Mo(6) 2.716(2), Mo(4)–S(28) 2.366(5), Mo(5)–S(28) 2.381(6), Mo(6)–S(28) 2.379(5), S(26)–S(27) 2.053(7), S(16)–S(17) 2.063(7), S(22)–S(23) 2.031(7), S(18)–S(19) 2.023(7), S(24)–S(25) 2.092(7), S(20)–S(21) 2.072(9), Mo(5)–Mo(4)–Mo(6) 59.89(6), Mo(4)–Mo(5)–Mo(6) 60.27(6), Mo(4)–Mo(6)–Mo(5) 59.85(6). Type B (right): Mo(3)–Mo(2) 2.740(2), Mo(2)–Mo(1) 2.724(2), Mo(3)–Mo(1) 2.747(2), Mo(1)–S(15) 2.371(5), Mo(2)–S(15) 2.370(4), Mo(3)–S(15) 2.410(5), Mo(3)–S(11) 2.507(5), Mo(3)–S(14) 2.536(6), S(11)–S(12) 2.082(7), S(12)–S(13) 2.040(10), S(13)–S(14) 2.046(8), S(9)–S(10) 2.091(8), S(1)–S(2) 2.049(8), S(8)–S(7) 2.039(7), Mo(2)–Mo(3)–Mo(1) 59.54(6), Mo(3)–Mo(2)–Mo(1) 60.36(6), Mo(3)–Mo(1)–Mo(2) 60.11(6), S(11)–Mo(3)–S(14) 87.1(1), S(12)–S(11)–Mo(3) 110.2(3), S(13)–S(12)–S(11) 100.0(3), S(14)–S(13)–S(12) 100.8(3), S(13)–S(14)–Mo(3) 101.4(2).

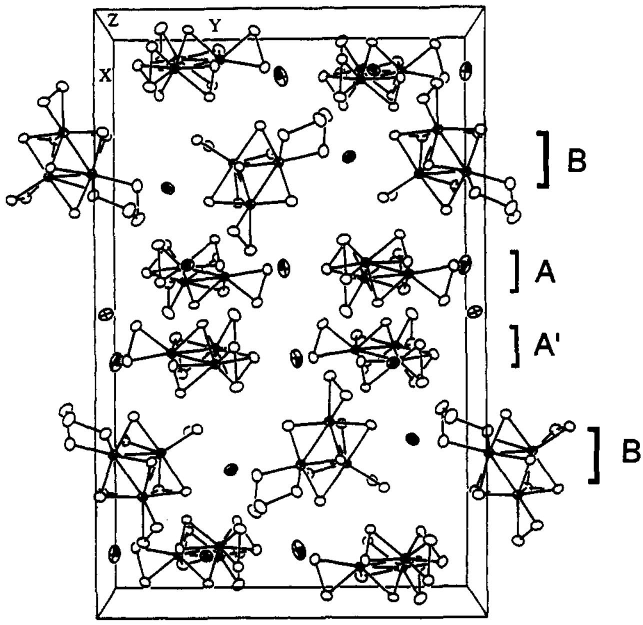

Figure 2. Packing diagram of the unit cell viewed down [001]. Atom types are as follows (50% thermal ellipsoids): Mo, small, shaded thermal ellipsoids; S, open ellipsoids, Cs, large, shaded thermal ellipsoids; O, principal axis thermal ellipsoids.

S–S interactions. The S(11) atoms of the MoS_4 rings in the type B clusters are directed toward the S(3)–S(5)–S(8) triangle formed from the μ_2-S_2 bridging units.[30] This interaction forms one-dimensional chains of type B clusters along the [001] direction. The type A clusters are linked through similar bonding via the S(2) of the S_2^{2-} "paddles" to S(18), S(22), and S(27).

Hydrothermal synthesis has once again yielded a uniquely bonded molybdenum chalcogenide compound. This new compound may offer insight into polychalcogenide bonding to electron-poor d^2 metals such as Mo(IV) and opens a new door to directed synthesis of molybdenum sulfide compounds.

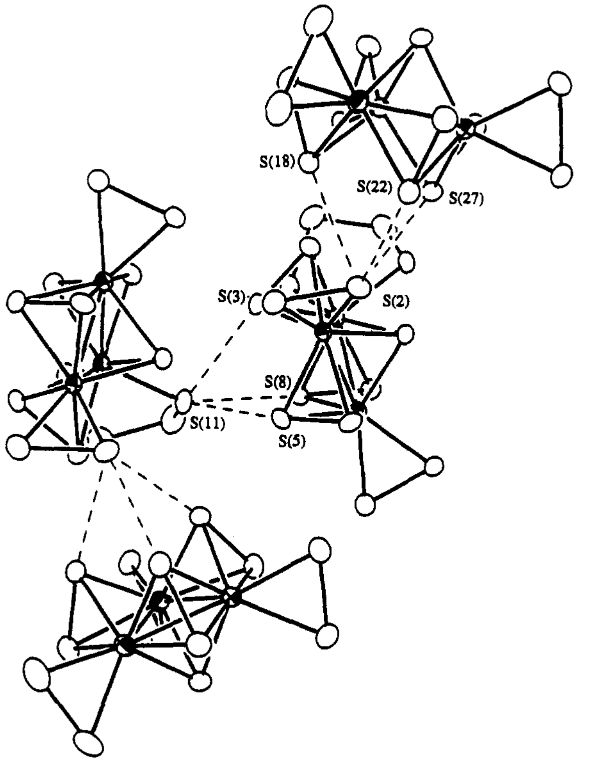

Figure 3. Intercluster interactions as viewed down [010]: Mo, shaded thermal ellipsoids; S, open ellipsoids. Selected bond distances (Å): S(11)–S(3) 3.222(7), S(11)–S(5) 3.145(7), S(11)–S(8) 3.337(7), S(2)–S(18) 3.223(7), S(2)–S(22) 3.114(7), S(2)–S(27) 3.198(7).

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Supplementary Material Available: Tables of crystal data and structure refinement parameters, atomic coordinates of all atoms, anisotropic thermal parameters, and all bond distances and angles for $Cs_4Mo_6S_{28}\cdot 0.5H_2O$ (11 pages). Ordering information is given on any current masthead page.

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(30) This intercluster bonding has been observed, for example, in: Meienberger, M. D.; Hegetschweiler, K.; Ruegger, H.; Gramlich, V. *Inorg. Chim. Acta* **1993**, *213*, 157–169.