

Incorporation of Molybdenum Sulfide Cluster Units into a Dawson-Like Polyoxometalate Structure To Give Hybrid Polythiooxometalates**

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In memory of Alfred Geoffrey Sykes

The vast majority of polyoxometalates (POMs)—a class of inorganic compounds remarkable for their impressive size and complexity, as well as important chemical, physical, and biological properties—is derived from rather simple Keggin or Dawson (ultimately Keggin-based) structure types.^[1] The ideal Dawson structural type is represented by the 18-nuclear $[M_{18}O_{54}(XO_4)_2]^{m-}$ POM anions ($M = Mo, W; X = P, As, S, Cl$). Examples of nontetrahedral (or ψ -tetrahedral) anions that are hosted by Dawson-like clusters include derivatives of AsO_3^{3-} , BiO_3^{3-} (a single unit in the cluster, as in $[W_{18}O_{54}-(AsO_3)(H)_2O_3]^{7-}$, in which two protons occupy the site left vacant by the missing As atom).^[2] Two pyramidal SO_3^{2-} units are found in the partially reduced $[Mo^V_2Mo^{VI}_{16}O_{54}(SO_3)_2]^{6-}$ and in the all- Mo^{VI} anion $[Mo_{18}O_{54}(SO_3)_2]^{4-}$.^[3] The adaptability of the Keggin-type structure has been further tested by the preparation of the derivative $[Mo_{18}O_{54}(P_2O_7)]^{4-}$ with encapsulated $P_2O_7^{4-}$.^[4,5] Up to six W atoms can be removed from the parent Dawson structure to give lacunary derivatives such as $[H_2P_2W_{12}O_{48}]^{12-}$, and the initial $[P_2M_{18}]$ structure can be rebuilt by adding Mo^{VI} , $V^{IV/V}$, Nb^V , or various 3d M^{2+} and M^{3+} cations.^[6] Fluoride can replace inner oxygen atoms in Dawson structures, as the preparation of $[H_2NaW_{18}O_{56}F_6]^{7-}$ shows.^[7] Both Keggin and Dawson polyoxometalates are redox-active and can undergo multielectron reduction without decomposition. At a certain stage (uptake of six electrons), this reduction can lead to the formation of a

localized cluster unit $\{W^{IV}_3O_4(H_2O)_3\}^{4+}$ (where t indicates a terminal position) with direct W–W bonding (W–W 2.50 Å), which remains incorporated in the POM structure.^[8] In fact, the $\{W^{IV}_3O_4\}^{4+}$ core belongs to the well-known family of $\{M_3Q_4\}^{4+}$ ($M = Mo, W; Q = O, S, Se, Te$) incomplete cuboidal clusters.^[9] This observation leads to the idea that these chalcogen-containing units also could be incorporated into the Keggin or Dawson-like structures. However, direct exchange of sulfur for oxygen usually leads to breaking of these polynuclear structures. Only one terminal oxygen atom could be replaced by S or Se in Nb-substituted Keggin anions $[PW_{11}\{NbQ\}O_{39}]^{4-}$ ($Q = S, Se$).^[10] Another strategy is based on assembly of the desired POM structure from prearranged building blocks, which of one would bear chalcogen atoms. It has been successfully tested in the preparation of γ -Keggin $[SiW_{10}Mo_2S_2O_{38}]^{6-}$, $[SiW_{12}S_2O_{38}]^{6-}$, and their P-containing analogues from divacant γ - $[XW_{10}O_{36}]^{n-}$ ($X = Si, n = 8; X = P, n = 7$) and $[M_2O_2S_2(H_2O)_6]^{2+}$. In this case, sulfur occupies two μ_2 positions in the isomeric Keggin structure.^[11] Here we report the synthesis of $Cs_{6.5}K(NH_4)_{1.5}[AsW_{15}Mo_3S_4-(H_2O)_3O_{53}] \cdot 14H_2O$ (**1**), a polyoxometalate with the highest sulfur content in the core so far, and $Cs_6-(H_3O)_3[AsW_{15}Mo_3O_2S_2(H_2O)_3O_{53}] \cdot 9.85H_2O$ (**2**), its analogue, the Dawson-based structure of which incorporates incomplete cuboidal $\{Mo_3S_4\}^{4+}$ and $\{Mo_3O_2S_2\}^{4+}$ cluster units.

The synthesis is based on self-assembly from $[AsW_9O_{33}]^{9-}$ and $[Mo_3S_4(H_2O)_9]^{4+}$ or $[Mo_3(\mu_3-S)(\mu-S)(\mu-O)_2(H_2O)_9]^{4+}$ in aqueous solution at pH 2.5 under hydrothermal conditions. Note, however, that the reaction proceeds through degradation and reassembly of the POM, since addition of extra tungstate (as required by the product stoichiometry) leads to different products of low crystallinity which could not be identified. The yield of **1** is essentially quantitative and it is obtained as a single-crystalline phase. Compound **2** is always obtained together with $[H_2AsW_{18}O_{60}]^{7-}$.

According to X-ray analysis,^[12–18] the $[AsW_{15}Mo_3S_4-(H_2O)_3O_{53}]^{9-}$ anion (Figure 1) can be described as derived from the known prototype $[H_2AsW_{18}O_{60}]^{7-}$ ^[2] by replacing one of the six $\{W_3O_{13}\}$ units with common vertices in the As-free hemisphere by a $\{Mo_3S_4O_6(H_2O)_3\}$ unit, so that one of the polar belts will have one Mo atom and the equatorial belt the other two Mo atoms. The three μ_2 -S bridges of the cluster take the place of the three μ_2 -O bridges of the parent arsenotungstate, and the position of the capping μ_3 -S matches the position occupied by one of the μ_3 -O bridges. Just as in

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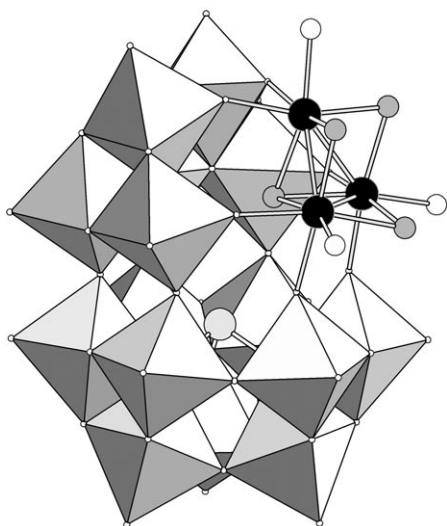


Figure 1. Structure of the cluster anion $[\text{AsW}_{15}\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_3\text{O}_{53}]^{9-}$: $\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_3\}$ fragment in ball-and-stick (Mo black, O white, S gray) and $\{\text{W}_{15}\}$ fragment in polyhedral representation.

$[\text{H}_2\text{AsW}_{18}\text{O}_{60}]^{7-}$, both hemispheres in $[\text{AsW}_{15}\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_3\text{O}_{53}]^{9-}$ belong to the B-type, from the way in which the octahedral units ($15\{\text{WO}_6\}$ and $3\{\text{MoO}_3\text{S}_3\}$) are linked together. An important difference is, however, that the Mo atoms in the POM are in oxidation state IV, not VI, and three Mo–Mo bonds ($2.764(3)$ – $2.763(3)$ Å) are present in the Mo_3 subunit. The bonding is not localized over the rest of the POM structure: closest Mo···W distances are as long as 3.8 Å. The As–(μ_3 -S) distance of $3.648(7)$ Å is shorter than the sum of their van der Waals radii (3.85 Å in the Pauling system)^[19] and, as expected, to ease this strain, two of the Mo–(μ_3 -S) bonds (which are usually quite indifferent to the environment around Mo in other $\{\text{Mo}_3\text{S}_4\}^{4+}$ clusters) are shortened to 2.27 Å from their usual value of around 2.33 – 2.34 Å.^[9,20] The shorter As–O distances ($1.79(1)$ – $1.82(2)$ Å vs. $1.82(2)$ – $1.90(2)$ in $[\text{H}_2\text{AsW}_{18}\text{O}_{60}]^{7-}$) show that the As atom is also pushed away from S. Two $[\text{AsW}_{15}\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_3\text{O}_{53}]^{9-}$ ions are weakly associated in a dimer through four specific μ_2 -S··· μ_2 -S contacts (3.42 – 3.49 Å), as is routinely observed in the structures of $\{\text{Mo}_3\text{S}_4\}$ clusters.^[21]

The structure of the anion in **2** is very similar. Both sulfur atoms are localized in one of the equatorial belts (Figure 2). One of the sulfide ligands is in a μ_3 position inside the POM cage (As···S 3.47 Å, which is even shorter than in **1**, by 0.2 Å), and the other in a μ_2 position on the outer side. This additional shortening is due to the smaller size of the $\{\text{Mo}_3\text{O}_2\text{S}_3\}$ cluster^[22] as compared with the Mo_3S_4 cluster [Mo–Mo 2.64 (oxygen-bridged) and 2.74 Å (sulfur-bridged)]. Shortening of two Mo–(μ_3 -S) bonds ($2.28(1)$ Å) is also evident here. The As···S contacts resemble S···S supramolecular interactions between two pyramidal SO_3^{2-} groups in $[\text{Mo}_{18}\text{O}_{54}(\text{SO}_3)_2]^{4-}$.^[3] Caution must be taken in interpreting the nature of such interactions, since they appear to be caused entirely by the rigidity of the Dawson structure, and may have antibonding character, as in the case of $[\text{Mo}_{18}\text{O}_{54}(\text{SO}_3)_2]^{4-}$. The As–O distances in **2** are $1.78(2)$ – $1.82(2)$ Å, similar to those of **1**. Thus, in both **1** and **2**, unusual shortening of the Mo–(μ_3 -S)

and As–O bonds, together with close As···S contacts, reveal significant strain imposed on the Dawson-like structure by incorporation of the chalcogenide cluster unit. As in the structure of **1**, long Mo···W distances in **2** preclude any metal–metal interaction. Contrary to **1**, the packing of the POM ions in **2** does not involve pairing through μ_2 -S··· μ_2 -S interaction. In both structures the mutual packing of POM anions follows the distorted motif of the face-centered cubic lattice.

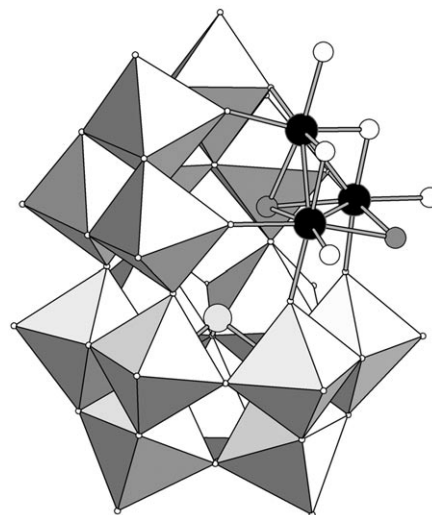


Figure 2. Structure of the cluster anion $[\text{AsW}_{15}\text{Mo}_3\text{O}_2\text{S}_2(\text{H}_2\text{O})_3\text{O}_{53}]^{9-}$: $\{\text{Mo}_3\text{O}_2\text{S}_2(\text{H}_2\text{O})_3\}$ fragment in ball-and-stick (Mo black, O white, S gray) and $\{\text{W}_{15}\}$ fragment in polyhedral representation.

The cyclic voltammograms of **1** and **2** were obtained in 0.4 M NaCl solution (scan rate 100 mV s^{-1} , glassy carbon, E vs. Ag/AgCl). The irreversible oxidation waves at 0.84 V (**1**) and 0.87 V (**2**) correspond to oxidation of As^{III} to As^{V} , which is followed by rapid structural degradation. Two-electron quasi-reversible reduction is observed at -0.43 (**1**) and -0.37 V (**2**). Under the same conditions, the $[\text{AsW}_9\text{O}_{33}]^{9-}$ ion undergoes two-electron quasi-reversible reduction at -0.27 V . We can suppose that in both **1** and **2** reduction is tungsten-centered.

To confirm the retention of the structure in solution, we carried out a ^{183}W NMR study.^[23] According to the idealized C_s point-group symmetry, in the ^{183}W NMR spectrum of **1** eight lines (intensity ratio $2:2:2:2:2:2:2:1$) are expected. In fact, eight lines are observed in the typical region for heteropolytungstates between -100 and -180 ppm ($\delta = -100.7, -112.8, -115.7, -127.9, -142.4, -158.1, -165.3, -175.2\text{ ppm}$).^[24] We thus assume that the solid-state structure of the anion in **1** is retained in solution.

In conclusion, we have prepared the first hybrid polyoxometalates in which a chalcogenide cluster unit is incorporated into a classical POM structure, and thus shown that the Dawson-like structure can accommodate significant distortion by means of shortened M–M bonds and sub-van-der-Waals contacts in the inner space of the complex. Furthermore, this structural type permits substitution of sulfur for oxygen not only at the terminal positions but also in the bridging μ_2 and capping μ_3 positions. The $\{\text{Mo}_3\text{S}_4\}$ cluster can incorporate some 22 transition and post-transition metals to

give in some cases heterometallic cuboidal clusters with remarkable catalytic properties.^[25] Our results indicate a new potential for creating multifunctional hybrid POM-based materials. We have in fact observed that **1** reacts with Cu⁺ to give incorporation product [AsW₁₅Mo₃CuS₄(H₂O)₃O₅₃]⁸⁻, characterization of which is underway.

Experimental Section

1: In a glass tube, K₉[AsW₉O₃₃]·13H₂O^[26] (1.73 g, 0.61 mmol), [Mo₃S₄(H₂O)₉]Cl₄^[27] (0.31 g, 0.43 mmol), CsCl (0.57 g, 3.39 mmol), and NH₄Cl (0.10 g, 1.90 mmol) were dissolved in 2.5 mL of H₂O, and the pH was adjusted to 2.5 with some drops of 1M HCl. The tube was sealed under vacuum and heated at 140 °C for 2 d. After slow cooling to room temperature and opening, brown single crystals of the product were isolated by filtration, washed successively with water/ethanol (1:1), ethanol, and diethyl ether and dried in air. Yield: 1.97 g, 87%. IR (KBr): $\tilde{\nu}$ = 3411, 1616, 953, 844, 802, 766, 658, 476, 449 cm⁻¹; elemental analysis (%) calcd for H₄₀AsCs_{6.50}KMo₃N_{1.50}O₇₀S₄W₁₅: S 2.4, K 0.7, As 1.4, Mo 5.5, Cs 16.4, W 52.2; found: S 2.6, K 0.6, As 1.3, Mo 5.6, Cs 16.6, W 52.6.

2: CsCl (0.03 g, 0.18 mmol) was added to a glass tube filled with a solution of Na₉[AsW₉O₃₃]·13H₂O (0.08 g, 0.027 mmol)^[26] and [Mo₃S₂O₂(H₂O)₉]Cl₄ (0.01 g, 0.015 mmol)^[28] in H₂O (5 mL, pH adjusted to 2.7). The tube was evacuated, sealed and heated at 140 °C for 2 d. Dark gray single crystals of **2** were isolated after slow cooling to room temperature. Some [H₂AsW₁₈O₆₀]⁷⁻ was also produced to give two other crystalline products differing in Cs⁺ content. IR (KBr): $\tilde{\nu}$ = 3411, 1624, 953, 884, 789, 766, 738, 641, 478 cm⁻¹; elemental analysis (%) calcd for H_{34.70}AsCs₆Mo₃O_{70.85}S₂W₁₅: As 1.5, Mo 5.6, Cs 15.5, W 53.5; found: As 1.4, Mo 5.8, Cs 15.1, W 53.4.

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