Dawson Clusters

Old Clusters with New Tricks: Engineering S···S Interactions and Novel Physical Properties in Sulfite-Based Dawson Clusters**

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Dedicated to Professor Michael T. Pope
on the occasion of his 71st birthday

Polyoxometalates (POMs) have been subjected to a vast number of studies due to attractive electronic and molecular properties that give rise to a variety of applications, for example, in catalysis,[1] medicine,[2] and materials science.[3] A notable subset of POM-based clusters are those of the very stable Dawson structural type $[M_{18}O_{54}(XO_4)_2]^{m-}$ (M = Mo, W; X = main-group element), first discovered fifty years ago and since then the subject of many hundreds of papers.[4] The conventional Dawson structure incorporates two tetrahedral anions such as PO_4^{3-},[4] AsO_4^{3-},[5] SO_4^{2-},[6] or ClO_4^{-}.[7] Surprisingly, there are only a few examples of $\{M_{18}\}$ Dawson-like clusters that host nontetrahedral anions; examples thereof include a single pyramidal anion (BiO_3^{3-} or AsO_3^{3-}) in each cluster, presumably due to size restrictions,[8,9] or a ditetrahedral anion ($P_2O_7^{4-}$; two tetrahedra sharing one corner).[10]

We are interested in the design of new nonconventional Dawson clusters incorporating two pyramidal anions, as such clusters may exhibit unprecedented properties arising from the intramolecular electronic interactions between the encapsulated anions, and thus provide a novel route to manipulate the physical properties of $\{Mo_{18}\}$ Dawson-type clusters. In the light of previous work[8–10] it appears that the sulfite anion, due to its size and charge, could be a realistic candidate for templating a $\{Mo_{18}\}$ Dawson cage. However, structurally characterized molybdosulfites are rare; some examples include $(NH_4)_4[Mo_5O_{15}(SO_3)_2]\cdot 4H_2O$,[11] $(NH_4)_8[Mo_2O_4(SO_3)_5]\cdot 2H_2O$[12] and the framework structures $(NH_4)_{20}[Mo_{12}O_{24}(SO_3)_{16}]\cdot 4H_2O$[12] and $(NH_4)_{15}\{Na[Mo_6O_{15}(SO_3)_4]_2\}\cdot 5H_2O$.[12] In addition, the biological relevance of molybdenum sulfite chemistry makes access to POM-based sulfite architectures an attractive goal.[13]

By extending our previous work using bulky, "shrink-wrapping" cations[14] we were able to isolate an unprecedented 18-molybdosulfite based on a Dawson-type $\{Mo_{18}\}$ cage using protonated triethanolamine (TEAH). The resulting compound **1** contains the twofold-reduced Dawson anion

$(TEAH)_6[Mo_{18}O_{54}(SO_3)_2]\cdot 4H_2O$ **1**

α-$[\mathrm{Mo}^{V}_{2}\mathrm{Mo}^{VI}_{16}O_{54}(SO_3)_2]^{6-}$ (**1a**),[15] which incorporates the targeted two pyramidal sulfite (SO_3^{2-}) ions as the central cluster templates (Figure 1 a).

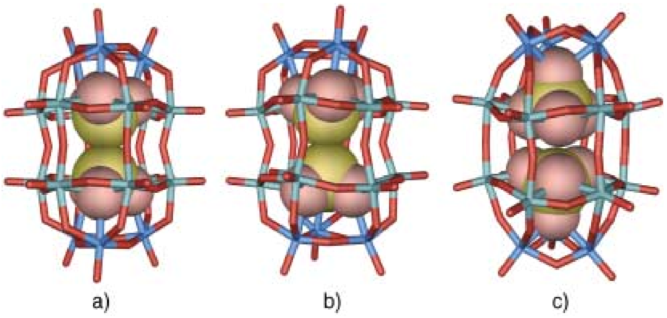

Figure 1. A representation of the structures of the sulfite-based Dawson clusters: a) α-$[\mathrm{Mo}^{V}_{2}\mathrm{Mo}^{VI}_{16}O_{54}(SO_3)_2]^{6-}$ (**1a**), b) β-$[\mathrm{Mo}^{VI}_{18}O_{54}(SO_3)_2]^{4-}$ (**3a**), and c) a comparison with the conventional α-type sulfate-based Dawson anion $[Mo_{18}O_{54}(SO_4)_2]^{4-}$,[6] whereby the central anion templates are shown in a space-filling mode (S: yellow, O: red, capping Mo: blue, "belt" Mo: green).

Anion **1a** has an overall approximate D_{3h} symmetry, with a mirror plane dividing the cage into two equal parts linked together by six equatorial oxo ligands (Figure 1 a). The distinctive peanutlike shape of the $\{Mo_{18}O_{54}\}$ framework was also observed for $\{W_{18}O_{54}\}$ cages in the Dawson-type compounds $(Bu_4N)_6[W_{18}O_{54}(OH)_3(BiO_3)]$[8] and $(H_4N)_7[W_{18}O_{54}(O)(OH)_2(AsO_3)]$.[9] Furthermore, the Mo–O framework of **1a**, as well as the B-type coordination of the heteroatoms within the cage, is very similar to that of 18-molybdopyrophosphate $[Mo_{18}O_{54}(P_2O_7)]^{4-}$, previously reported in $(Bu_4N)_4[Mo_{18}O_{54}(P_2O_7)]$,[10] although in this case connection of the two phosphorus centers by an oxo ligand leads to slight expansion of the O_6 equator compared to **1a**. In

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conventional Dawson clusters, one of the four oxygen atoms of the tetrahedral XO_4 moiety coordinates to the three capping M centers, and the remaining three μ_3-oxo ligands each bridge two of the six remaining M centers of the "belt" part (Figure 1c). However, in **1a** the μ_4-oxo ligands of SO_3 moieties each individually bridge three molybdenum centers, one from the cap and two from the belt. As such, this fundamental difference between the coordination modes of the discrete XO_4 and XO_3 moieties restricts the possible isomers of sulfite-based Dawson clusters to α and β types.[15]

Compound **1** contains the first Dawson $\{M_{18}\}$ cluster incorporating the pyramidal sulfite anion, and the first that includes two such pyramidal anions in the same $\{M_{18}\}$ cage. By employing $Na_2S_2O_4$ as a reducing agent, and thus as the source of SO_3^{2-}, **1** was synthesized in the presence of an excess of triethanolamine (TEA) at pH 4.0 in a yield of about 34%.[16] It was characterized by single-crystal X-ray structure analysis,[17] elemental analysis, IR and UV/Vis spectroscopy, and the oxidation state was additionally confirmed by bond valence sum (BVS) calculations and redox titrations.[18]

To understand the consequences of encapsulating sulfite anions, a synthetic procedure to isolate the unreduced analogue of **1a** was devised, based on the method reported by Hori et al.,[19] which employs an acetonitrile/water solvent mixture for synthesis of the clusters at elevated temperatures and yields the products as Bu_4N^+ salts.[19] This resulted in two new compounds, **2** and **3**.

$(C_{16}H_{36}N)_6[Mo_{18}O_{54}(SO_3)_2][Mo_6O_{19}]$ **2**

$(C_{16}H_{36}N)_4[Mo_{18}O_{54}(SO_3)_2]\cdot C_2H_3N$ **3**

Compound **2** contains the sulfite-based Dawson anion α-$[Mo^{VI}_{18}O_{54}(SO_3)_2]^{4-}$ (**2a**) and the Lindqvist anion $[Mo^{VI}_6O_{19}]^{2-}$, as revealed by single-crystal X-ray analysis.[17] Anion **2a** is a structurally almost identical, but fully oxidized, analogue of **1a** (see Figure 1a). Compound **3** is also unreduced, but contains the β-type Dawson anion β-$[Mo^{VI}_{18}O_{54}(SO_3)_2]^{4-}$ (**3a**) with a staggered arrangement of the SO_3 moieties (in contrast to the eclipsed arrangements in **1a** and **2a**) and approximate D_{3d} symmetry (see Figure 1b).[15]

A novel aspect of this work, common to all sulfite Dawson cluster anions presented here (**1a**–**3a**), is the short S···S contact resulting from the incorporation and relative orientation of the two sulfite ions within the $\{Mo_{18}\}$ cage. The S···S distances of 3.301(2) (**1a**), 3.229(2) (**2a**), and 3.271(5) Å (**3a**) are all much shorter than the sum of the van der Waals radii of two sulfur atoms (ca. 3.6 Å).

Dawson anions are already known to show interesting physical (e.g., electrochemical[6]) properties. Thus, we expected that the incorporation of nontetrahedral sulfite ions in **1**–**3** could further extend their versatility, as the sulfite anions (at least theoretically) can undergo redox processes involving their oxidation to dithionate $S_2O_6^{2-}$ ions [Eq. (1)] (note: sulfur is the only main group element to form $X_2O_6^{n-}$ ions with X–X single bonds).[20]

$$2\,SO_3^{2-} \rightarrow S_2O_6^{2-} + 2\,e^- \qquad (1)$$

Thus, engineering an intramolecular S···S interaction within the Dawson $\{Mo^{VI}_{18}\}$ matrix (as is found in **2** and **3**) results in several intriguing possibilities. For instance, if it were possible to encourage the formation of a dithionate anion, this process could supply two electrons to reduce the surrounding polyoxomolybdate shell to the mixed-valence reduction state $\{Mo^{VI}_{16}Mo^{V}_2\}$, as present in **1a**, with its characteristic blue color. Yet the formation of a S–S single bond within the systems presented here appears to be restricted by the large geometrical changes required of the $\{Mo_{18}\}$ framework, since the S–S distance would have to decrease from about 3.25 to about 2.15 Å. Furthermore, preliminary electrochemical studies[21] showed a difference in properties between sulfite-based Dawson clusters **2a** and **3a** and sulfate analogues.[6] Although the precise nature of the process is not yet understood, it does not clearly indicate the formation of an S–S bond within **2a** or **3a**.[21] However, in preliminary studies we observed striking thermochromic behavior of **2** and **3** between 77 and 500 K (Figure 2), which, to the best of our knowledge, represents the first observation of such behavior for discrete polyoxometalate clusters.[22] These initial investigations also show that the color changes are gradual and are completely reversible between pale yellow (77 K) and deep red (500 K).[23]

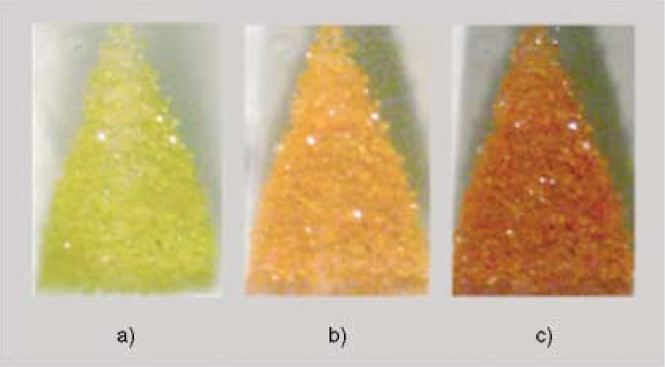

Figure 2. Photographs of crystalline powder samples of compound **3** at a) liquid-nitrogen temperature (77 K), b) at room temperature (298 K), and c) at 500 K.

To explain this observation, and to more generally characterize the electronic structure of this novel family of unreduced and reduced α- and β-type Dawson anions, DFT calculations were performed.[24] These calculations allowed an analysis of the frontier orbitals, which showed that for the unreduced anions **2a** and **3a**, the HOMO is mostly localized on the S and O positions of the sulfite groups, while the LUMO and the following MOs (and the HOMO in the reduced species **1a** and the hypothetical twofold reduced β-type anion, which we have not yet isolated experimentally) are delocalized over all Mo centers (Figure 3). Also, the sum of the Löwdin atomic net charges over the SO_3 groups remains nearly constant on reduction (**2a**/**3a**: 0.02, **1a**: 0.00). Interestingly, despite their relatively wide separation, the two S positions interact electronically: a Mulliken analysis shows

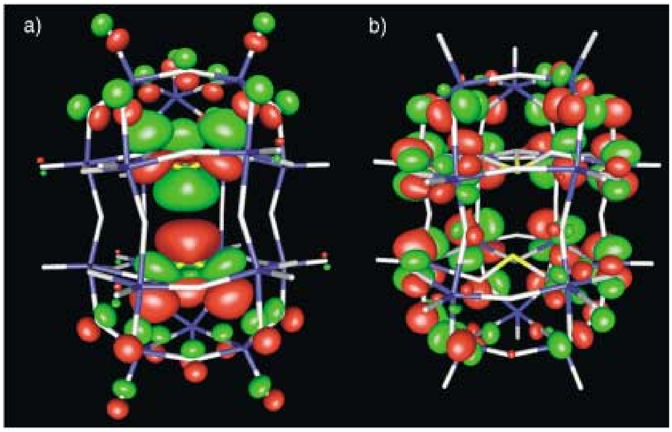

Figure 3. Composition of the HOMO of unreduced **2a** (a) and reduced **1a** (b) α-Dawson anions resulting from DFT calculations superimposed on the molecular geometry (Mo: blue, O: gray, S: yellow; isosurface density value: 0.018). In a) the HOMO is mostly centered on the sulfite positions and antibonding with respect to the S···S contact. On twofold reduction, the HOMO in b) is delocalized over the molybdenum positions, has predominantly Mo(4d) character, and gives rise to the intense charge-transfer absorption band typical of Robin–Day class III polyoxomolybdates.

significant antibonding overlap between orbitals centered on the S positions, and the overlap decreases on reduction of the cluster by a factor of about 0.5, while the net atomic charges on the S atoms remain nearly constant.

If the structural changes due to the geometry optimization calculations are compared to molecular "breathing" vibrations (large amplitudes are observed for the lighter O positions, and small amplitudes for the heavy Mo positions), the shift that is observed with increasing temperature can be understood on the basis of a decreasing HOMO–LUMO gap following optimization, and in the case of the unreduced β-Dawson anion this gap is reduced from 1.63 eV (initial) to 1.40 eV (equilibrated). This change is due to a decrease in energy of the unpopulated molecular orbitals, while the energies of the highest, SO_3-centered populated molecular orbitals remain mostly unchanged.

In summary, a new family of Dawson-type 18-molybdosulfites **1**–**3** that encapsulate two sulfite SO_3^{2-} ions which exhibit interesting supramolecular S···S interactions has been presented. The discovery of these new clusters, in the jubilee year of the discovery of the first Dawson cluster (1953),[4] is particularly exciting because it may provide a new route by which the physical properties of the Dawson-type $\{M_{18}\}$ cage can be manipulated, as well as presenting unprecedented physical properties for Dawson-type cages. Thus, the promise of harnessing the versatile electronic properties associated with Mo-based POMs for use in electron-storage devices and molecular switches has moved a step closer to reality.

Experimental Section

1: Triethanolamine (11.0 g, 73.8 mmol) was dissolved in water (100 mL). Hydrochloric acid (37 %, 10 mL) was added while stirring, followed by the simultaneous addition of $Na_2MoO_4\cdot 2H_2O$ (10.0 g, 41.6 mmol) and $Na_2S_2O_4$ (1.10 g, 6.3 mmol) with stirring and adjustment of the pH value of the solution to 4.0 with dilute hydrochloric acid. The solution was then stirred for 1 h and filtered, and the filtrate was stored in a refrigerator for 3 days, after which dark-blue crystals of **1** were isolated (yield: 2.90 g, 33.9 %). IR (KBr disk): $\tilde{\nu} = 3355$, 1619, 1446, 1377, 1251, 1188, 1093, 1046, 965, 928, 875, 735 cm^{-1}; elemental analysis (%) calcd for $C_{36}H_{104}Mo_{18}N_6O_{82}S_2$: C 11.61, H 2.81, N 2.26; found: C 11.09, H 2.59, N 2.37.

2 and **3**: A solution of $Na_2MoO_4\cdot 2H_2O$ (4.8 g, 20 mmol) and Na_2SO_3 (0.30 g, 2.4 mmol) in H_2O (20 mL) was mixed with acetonitrile (80 mL), and then HCl (37 %, 10 mL) was added. The resulting mixture was refluxed for 2 h and, after cooling, the lower aqueous layer was discarded and the upper layer was treated with Bu_4NBr (2.5 g) in water (50 mL). A yellow sticky solid and pale yellow powder were obtained, and these were collected, washed with water, and dried. Recrystallization of the solid from acetonitrile afforded yellow crystals of **3** (yield: 45 mg, 1.1 %), then light brown crystals of **2** (1.10 g, 26.1 %), and pale yellow crystals of $(Bu_4N)_2[Mo_6O_{19}]$ as the remaining product, which were separated mechanically. Although the α- and β-Dawson anions found in **2** and **3** form in the same reaction system, they can be separated by recrystallization. **2**: IR (KBr disk): $\tilde{\nu} = 3438$, 2961, 2872, 1470, 1379, 963, 904, 785 cm^{-1}; elemental analysis (%) calcd for $C_{96}H_{216}Mo_{24}N_6O_{79}S_2$: C 22.67, H 4.28, N 1.65; found: C 21.66, H 4.18, N 1.82. **3**: IR (KBr disk): $\tilde{\nu} = 3440$, 1479, 969, 904, 786 cm^{-1}; elemental analysis (%) calcd for $C_{66}H_{147}Mo_{18}N_5O_{60}S_2$: C 21.07, H 3.94, N 1.86; found: C 20.91, H 3.85, N 1.54. The purity of the bulk phases of **1**–**3** was confirmed by X-ray powder diffraction, and the oxidation state of the cluster anions was confirmed by a combination of BVS calculations, redox titrations, UV/Vis spectroscopy, and elemental analysis.

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[15] The sulfite-based Dawson cluster isomers are designated α and β in accordance with current literature (see, for example, M. T. Pope, *Inorg. Chem.* **1976**, *15*, 2008; there are additional isomers for conventional Dawson clusters that incorporate two tetrahedral anions). The D_{3h}-symmetric α (**1a** and **2a**) and the D_{3d}-symmetric β (**3a**) types of the sulfite-based Dawson clusters are distinguished both by their polyoxometalate framework and by the relative orientation of the two SO_3 moieties, which are eclipsed in the α type and staggered in the β type. In addition to the arrangement of the anions in the cages, the α and β isomers also differ by the relative linkage of the two $\{SMo_9\}$ half units, which are either mirrored (α) or rotated by 60° with respect to each other (β). DFT calculations on symmetry-idealized geometries for the α and the β isomers revealed the α isomer to be more stable ($\Delta E = 350\,\text{kJ}\,\text{mol}^{-1}$). A further difference in the electronic structure between the oxidized α and β analogues, **2a** and **3a**, concerns the overlap population between the O positions of the sulfite groups and the Mo centers to which they coordinate: despite the only slightly longer (S)O–Mo distances (α: 2.50–2.54 Å, β: 2.49–2.52 Å) the mean (S)O–Mo overlap is significantly reduced (Mulliken overlap integrals: α: 0.013, β: 0.031), hence the sulfite groups in the α isomer have a more isolated character.

[16] Attempts to produce unreduced analogues of **1a** by using Na_2SO_3 instead of $Na_2S_2O_4$ were unsuccessful.

[17] Crystal data and structure refinement for **1**: $C_{36}H_{104}Mo_{18}N_6O_{82}S_2$, $M_r = 3724.29\,\text{g}\,\text{mol}^{-1}$; a lath-shaped crystal ($0.42 \times 0.26 \times 0.15\,\text{mm}^3$) was analyzed with a Kappa CCD diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 160(2) K. Triclinic, space group $P\bar{1}$, $a = 13.84970(10)$, $b = 14.44420(10)$, $c = 27.4121(2)$ Å, $\alpha = 97.0253(2)$, $\beta = 95.2007(2)$, $\gamma = 117.4308(3)°$, $V = 4762.91(6)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 2.597\,\text{g}\,\text{cm}^{-3}$, $\mu(Mo_{K\alpha}) = 2.449\,\text{cm}^{-1}$, $F(000) = 3612$, 142000 reflections measured, of which 21780 were independent, 1273 refined parameters, $R1 = 0.0300$, $wR2 = 0.0799$. **2**: $C_{96}H_{216}Mo_{24}N_6O_{79}S_2$, $M_r = 5085.43\,\text{g}\,\text{mol}^{-1}$; crystal dimensions: $0.42 \times 0.20 \times 0.19$ mm. Monoclinic, space group $P2_1/n$, $a = 22.08540(10)$, $b = 30.09770(10)$, $c = 24.03100(10)$ Å, $\beta = 90.6952(2)°$, $V = 15972.71(11)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 2.115\,\text{g}\,\text{cm}^{-3}$, $\mu(Mo_{K\alpha}) = 1.928\,\text{cm}^{-1}$, $F(000) = 10024$, 250139 reflections measured, of which 36021 were independent, 1881 refined parameters, $R1 = 0.0239$, $wR2 = 0.0519$. **3**: $C_{66}H_{147}Mo_{18}N_5O_{60}S_2$, $M_r = 3761.93\,\text{g}\,\text{mol}^{-1}$; crystal dimensions: $0.14 \times 0.14 \times 0.14\,\text{mm}^3$. Monoclinic, space group $P2_1/n$, $a = 14.3782(2)$, $b = 22.4971(3)$, $c = 18.4127(3)$ Å, $\beta = 91.2590(10)°$, $V = 5954.48(15)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 2.098\,\text{g}\,\text{cm}^{-3}$, $\mu(Mo_{K\alpha}) = 1.947\,\text{cm}^{-1}$, $F(000) = 3692$, 46135 reflections measured, of which 11678 were independent, 814 refined parameters, $R1 = 0.0652$, $wR2 = 0.1422$. CCDC 219454 (**1**), 219455 (**2**), and 219456 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[18] Compound **1** has an intense blue color, characteristic of reduced mixed-valence POMs, and this is also supported by the UV/Vis spectrum of **1** ($\lambda_{\text{max}} = 768$ nm (shoulder), 314 nm (peak) and 238 nm (peak)).

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[20] A search of the CSD revealed that there are over one hundred structures reported for dithionate $S_2O_6^{2-}$ ions, but none of the $X_2O_6^{n-}$ analogues for other main group elements.

[21] Preliminary electrochemical studies show basic electrochemical processes of the $\{Mo_{18}\}$ shell in acetonitrile for **2a** and **3a** similar to those of sulfate Dawson $\{Mo_{18}\}$ clusters.[6]

[22] In a separate study we have also examined the analogous sulfate-based $(C_{16}H_{36}N)_4[Mo_{18}O_{54}(SO_4)_2]$ and discovered that this also displays a similar thermochromic behavior, but over a narrower temperature range and with a less pronounced color change. Surprisingly this has not been reported before.

[23] Variable-temperature crystallographic studies confirmed the absence of phase transitions over the range 150–500 K, but heating the compounds to temperatures above 500 K leads to an interesting irreversible color change to dark blue-green, which indicates possible reduction of the cluster; more details will be reported later.

[24] DFT calculations (including Löwdin and Mulliken population analysis) using the TURBOMOLE package (O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346) employed TZVP basis sets and the Becke–Perdew (BP86) exchange-correlation functional. Equilibrated structures (C_1 symmetry) were obtained from free geometry optimizations starting with crystallographic data; these structures were found to be slightly expanded (due to coulombic repulsion), comparable to vibrational breathing modes. The mean shifts of atomic positions between the initial and equilibrated structures were highest for the equatorial μ_2-O (0.28 Å) centers and the μ_2-O (0.22 Å) positions of the Mo_3O_3 caps, while the O and S sulfite positions remained constant. For a recent review on ab initio calculations on POMs, see also J. M. Poblet, X. López, C. Bo, *Chem. Soc. Rev.* **2003**, *32*, 297.