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$[Mo_{16}O_{53}F_2]^{12-}$: a New Polyoxofluoromolybdate Anion

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Single crystals of a new β-octamolybdate salt containing protonated 1,4-diazabicyclo[2.2.2]octane cations were prepared under mild hydrothermal conditions. This compound, $[C_6H_{13}N_2]_2[C_6H_{14}N_2][Mo_8O_{26}]$, was then used as a starting material in the synthesis of $[C_6H_{13}N_2]_6[Mo_{16}O_{53}F_2]\cdot 4H_2O$, which contains previously unreported $[Mo_{16}O_{53}F_2]^{12-}$ anions. The structure-directing properties of γ-$[Mo_8O_{26}]^{4-}$, a likely intermediate in this pH-dependent transformation, are responsible for the site selection of the fluoride incorporation. $[Mo_{16}O_{53}F_2]^{12-}$, the largest reported polyoxofluoromolybdate cluster, expands upon the limited number of such anions in the literature. The structures of both compounds were determined using single-crystal X-ray diffraction.

Molybdenum oxide fluoride anions have long been studied owing to a host of desirable physical properties that they can exhibit, such as ferroelectricity.[1] These compounds often contain second-order Jahn–Teller active d^0 Mo^{VI} cations,[2] which are generally found in distorted octahedral coordination environments. The distortions in these anions mimic those present in the famous mixed-metal oxides $LiNbO_3$[3] and $KTiOPO_4$[4] and so make oxofluoromolybdates attractive candidates for inclusion in novel functional materials.

Despite the possibility of technological importance, the oxofluoromolybdates in the literature are mainly in the form of monomeric[5−8] and dimeric[9−14] molecular anions. Far fewer large or extended structures are known; reported examples include $[Mo_3O_4F_9]^{5-}$,[15] $[Mo_4O_{12}F_2]^{2-}$,[16] $[Mo_4O_{12}F_3]^{3-}$,[17] $[Mo_6O_{18}F_6]^{6-}$,[18] $[Mo_7O_{22}F_3]^{5-}$,[18] and $[Mo_8O_{26}F_2]^{6-}$[19] molecular anions and $[MoO_3F]_n^{n-}$,[20] *cis*-$[MoO_2F_3]_n^{n-}$,[21] *trans*-$[MoO_2F_3]_n^{n-}$,[22] and $[MoO_3F_2]_n^{2n-}$ chains.[23]

In our search for new polyoxofluoromolybdate clusters, three reaction variables known to directly influence the structure of molybdates were considered: reaction conditions, starting material selection, and pH. Reactions conducted under hydrothermal conditions have been shown to be much more likely to produce compounds containing large polyoxomolybdate clusters with respect to high-temperature solid-state reactions.[24] Under hydrothermal conditions, reactions containing molybdate sources with extended structures, such as MoO_3, favor products with extended structures, such as $[Mo_3O_{10}]_n^{2n-}$ chains. In contrast, the use of molybdate clusters, such as heptamolybdate anions, tends to lead to reaction products that contain molecular polyoxomolybdate anions.[25] Also, the direct link between the reaction pH and molybdate speciation is well-known.[26]

In order to promote the formation of new polyoxofluoromolybdate anions, pH-controlled reactions using molybdate clusters were conducted under hydrothermal conditions. The well-known β-$[Mo_8O_{26}]^{4-}$ anion[27] was selected for use as a

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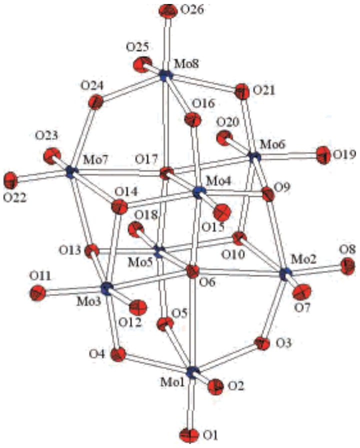

Figure 1. Thermal ellipsoid plot (50% probability) of the $[Mo_8O_{26}]^{4-}$ anions in **1**.

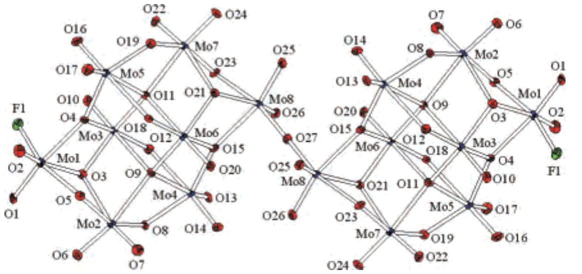

Figure 2. Thermal ellipsoid plot (50% probability) of the $[Mo_{16}O_{53}F_2]^{12-}$ anion in **2**.

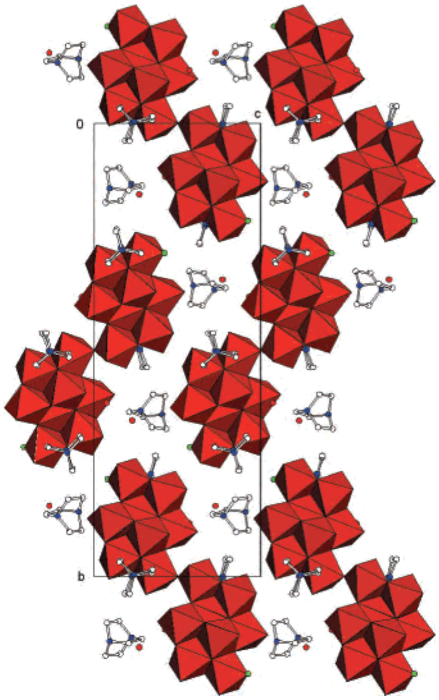

Figure 3. Three-dimensional packing of **2**. Red octahedra represent either MoO_6 or MO_5F, while white, red, green, and blue circles represent C, O, F, and N atoms, respectively. H atoms have been removed for clarity.

starting material because the ability of octamolybdates to interconvert[28,29] and transform is well-known.[30] Single crystals of $[C_6H_{13}N_2]_2[C_6H_{14}N_2][Mo_8O_{26}]$[31,32] (**1**) were grown under mild hydrothermal conditions at a pH of 5 (see Figure 1). This compound was then used as a starting material in a series of reactions designed to probe the effects of the pH. The pHs of eight reactions, with values between 1 and 6, were controlled using H_2SO_4. Syntheses conducted between pH 4 and 6 resulted in a recrystallization of **1**, while those run between pH 1 and 2 produced a new compound ($[C_6H_{14}N_2]_6[Mo_{16}O_{53}F_2]\cdot 4H_2O$[33,34] (**2**)) containing previously unreported $[Mo_{16}O_{53}F_2]^{12-}$ molecular anions (see Figures 2 and 3).

Distinguishing between oxide and fluoride ligands using diffraction data alone is difficult, owing to the similarities in their atomic scattering factors. For this reason, an analysis of the bond valence sums[35,36] in $[Mo_{16}O_{53}F_2]^{12-}$ was performed. The length and valence of the Mo1−F1 bond are appropriate for a terminal fluoride bond, 1.941(3) Å and 0.70, respectively. However, this bond is too long to be a Mo−O bond because it would result in an unreasonably low total valence of 0.91 on the terminal oxide. Elemental analyses were used to confirm the fluoride content of **2**.[33] While Mo^{VI}−OH bonds tend to be only slightly longer (lengths of 1.97 Å are common),[37,38] hydroxide ligands would be expected to act as hydrogen-bond donors. No such interactions are observed in **2**. In addition, $Mo-F_{terminal}$ stretches are clearly observed in the IR spectrum at 482 and 531 cm^{-1}.[9,13]

As stated above, the ability of octamolybdates to transform into other polyoxomolybdate species is well-known; an important intermediate in many of these transformations is

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(31) $[C_6H_{13}N_2]_2[C_6H_{14}N_2][Mo_8O_{26}]$ (**1**) was synthesized in 48% yield by combining MoO_3 (0.4015 g, 2.789×10^{-3} mol), DABCO (0.2124 g, 1.068×10^{-3} mol), H_2SO_4 (0.0887 g, 9.05×10^{-4} mol), aqueous HF (1 drop), and water (1.0118 g, 5.621×10^{-2} mol) in a 23 mL Teflon-lined stainless steel autoclave and heating the mixture to 180 °C for 24 h, before cooling slowly to room temperature at 6 °C/h. Elem anal. Obsd (calcd): C, 14.22 (14.17); H, 2.60 (2.62); N, 5.55 (5.51). IR (cm^{-1}): ν_{N-H} 1511, 1599, 3448; ν_{C-H} 3147; ν_{Mo-O} 709, 842, 920, 948.

(32) Crystal data: crystal size 0.05 × 0.10 × 0.14 mm, triclinic, space group $P\bar{1}$ (No. 2) with $a = 10.1506(9)$ Å, $b = 10.8733(9)$ Å, $c = 18.2157(14)$ Å, $\alpha = 101.369(7)°$, $\beta = 102.8633(17)°$, $\gamma = 100.601(7)°$, $V = 1866.2(3)$ Å^3, $Z = 2$, $\rho_{calc} = 2.712$ g/cm^3, $\theta_{max} = 33.826$, $\lambda = 0.710\,69$ Å, $T = 110(2)$ K, total data 22 166, unique data 12 117, observed data 7128, $\mu = 2.700$ mm^{-1}, 523 parameters, $R/R_w = 0.0365$, 0.0927 on $|F^2|$.

(33) $[C_6H_{14}N_2]_6[Mo_{16}O_{53}F_2]\cdot 4H_2O$ (**2**) was synthesized in 31% yield under conditions identical to those of **1** but with $[C_6H_{13}N_2]_2[C_6H_{14}N_2]$-$[Mo_8O_{26}]$ (0.4690 g, 3.08×10^{-4} mol), DABCO (0.0248 g, 2.21×10^{-4} mol), H_2SO_4 (0.0229 g, 2.34×10^{-4} mol), aqueous HF [48%, 1 drop (∼0.01 g)], and water (0.5436 g, 3.02×10^{-2} mol). Elem anal. Obsd (calcd): C, 14.27 (13.59); H, 2.67 (2.89); N, 5.49 (5.29); F, 1.33 (1.19). IR (cm^{-1}): ν_{N-H} 1473, 1599, 3448; ν_{C-H} 3022; ν_{Mo-O} 614, 710, 923, 937; ν_{Mo-F} 482, 531.

(34) Crystal data: crystal size 0.01 × 0.04 × 0.05 mm, monoclinic, space group $P2_1/n$ (No. 14) with $a = 9.6315(10)$ Å, $b = 33.417(3)$ Å, $c = 12.5367(11)$ Å, $\beta = 103.167(8)°$, $V = 3928.9(6)$ Å^3, $Z = 2$, $\rho_{calc} = 2.686$ g/cm^3, $\theta_{max} = 30.086$, $\lambda = 0.710\,69$ Å, $T = 110$ K, total data 62 465, unique data 11 411, observed data 5538, $\mu = 2.579$ mm^{-1}, 556 parameters, $R/R_w = 0.0256$, 0.0587 on $|F^2|$.

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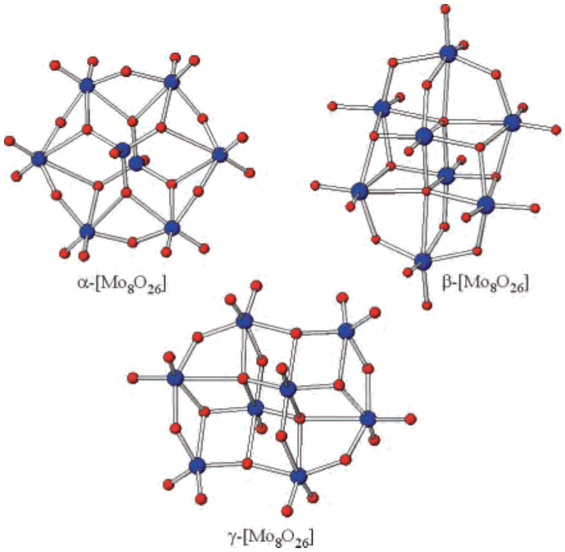

Figure 4. Ball-and-stick representation of the α, β, and γ forms of $[Mo_8O_{26}]^{4-}$. Blue and red spheres represent Mo and O atoms, respectively.

γ-$[Mo_8O_{26}]^{4-}$. This proposed bridge[29] in the isomerization of α-$[Mo_8O_{26}]^{4-}$ to β-$[Mo_8O_{26}]^{4-}$ is shown in Figure 4. It has been demonstrated that γ-$[Mo_8O_{26}]^{4-}$ is not present in appreciable amounts in solution over a wide range of experimental conditions.[26] However, these anions have been observed as secondary building units in the extended structures of several other compounds, most notably those that include $[Mo_8O_{27}]_n^{6n-}$ chains.[39] In addition, this cluster connectivity has also been observed in the polyoxofluoromolybdate anion, $[Mo_8O_{26}F_2]^{6-}$.[19]

The structure of $[Mo_{16}O_{53}F_2]^{12-}$ contains two γ-$[Mo_8O_{26}]^{4-}$ cores, suggesting an importance of this octamolybdate isomer in the conversion of β-$[Mo_8O_{26}]^{4-}$ to $[Mo_{16}O_{53}F_2]^{12-}$. The polyoxofluoromolybdate anion in **2** is constructed from two γ-$[Mo_8O_{26}]^{4-}$ anions that share a common oxide ligand. Each “half” of the cluster also contains a single fluoride ligand.

The structure-directing properties of many molybdate and oxofluoromolybdate species are known to be dictated by the internal bonding motifs present.[40−42] The same is true of γ-$[Mo_8O_{26}]^{4-}$. Inspection of $[Mo_8O_{27}]_n^{6n-}$ chains and $[Mo_8O_{26}F_2]^{6-}$ and $[Mo_{16}O_{53}F_2]^{12-}$ molecular anions reveals that modifications to the γ-$[Mo_8O_{26}]^{4-}$ structure occur at specific sites. The fluoride and bridging oxide ligands in $[Mo_8O_{27}]_n^{6n-}$, $[Mo_8O_{26}F_2]^{6-}$, and $[Mo_{16}O_{53}F_2]^{12-}$ are bound to the two five-coordinate molybdenum centers in γ-$[Mo_8O_{26}]^{4-}$. The bonding in these MoO_5 coordination polyhedra creates a substantial overbonding in selected bridging oxides,[43] and subsequent coordination is directed to relieve these bond stresses. A complete table of bond valence sums for γ-$[Mo_8O_{26}]^{4-}$ is listed in the Supporting Information.

Additional F^- was incorporated into $[Mo_{16}O_{53}F_2]^{12-}$ to yield $[Mo_8O_{26}F_2]^{6-}$ because the reaction gel from which crystals of **2** were grown did not contain sufficient amounts of fluoride. The ~10:1 ratio of Mo/F, in the reactions described above, is insufficient for the formation of $[Mo_8O_{26}F_2]^{6-}$, which exhibits a Mo/F ratio of 4:1. These fluoride-deficient conditions favor the formation of species with lower fluoride concentrations, resulting in the formation of $[Mo_{16}O_{53}F_2]^{12-}$. As demonstrated in previous work,[9,14] it is expected that reactions conducted at higher fluoride concentrations would lead to smaller polyoxofluoromolybdate species.

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Supporting Information Available: An X-ray crystallographic file containing complete tables of atomic coordinates, thermal parameters, and bond lengths and angles for **1** and **2** (CIF), bond valence sums tables for **1**, **2**, and γ-$[Mo_8O_{26}]^{4-}$, a three-dimensional packing diagram of **1**, and a description of the hydrogen-bonding in **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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