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$[C_5H_{14}N_2][(MoO_3)_3(SO_4)]\cdot H_2O$: Sulfated α-Molybdena Chains

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Recent work in the preparation of organically templated metal sulfates under hydrothermal conditions has been extended to include the sulfation of α-molybdena through the synthesis of $[C_5H_{14}N_2][(MoO_3)_3(SO_4)]\cdot H_2O$. Single crystals were grown under hydrothermal conditions from molybdenum oxide, water, sulfuric acid, and an enantiomerically pure (*R*)-2-methylpiperazine source and characterized using both single-crystal X-ray diffraction and infrared spectroscopy. One-dimensional $[(MoO_3)_3(SO_4)]_n^{2n-}$ chains, based on a neutral α-molybdena backbone, are connected through an extensive hydrogen-bonding network containing $[C_5H_{14}N_2]^{2+}$ cations and occluded water molecules. The direction of the hydrogen bonding is primarily dictated by the nucleophilicity of the respective oxide ligands, as determined using bond valence sums.

The reaction of inorganic species with organic structure-directing agents under hydrothermal conditions is a versatile technique for the preparation of novel solid-state materials.[1] The structural diversity and desirable physical properties of these materials are well-known.[2] Metal phosphates comprise a large number of these compounds.[3] Despite the breadth of phosphate chemistry, incorporation of organic structure-directing agents into metal sulfate systems has been explored in depth only during the past few years.[4] Layered α-molybdena is an attractive candidate for sulfation in the presence of organic cations because of its ability to undergo structural rearrangement[5] and literature precedence using mineral acids.[6] We report the synthesis, structure, and characterization of $[C_5H_{14}N_2][(MoO_3)_3(SO_4)]\cdot H_2O$,[7] which contains, to the best of our knowledge, the first sulfated α-molybdena compound in the presences of organic cations.

Three unique Mo^{6+} centers are observed in $[C_5H_{14}N_2][(MoO_3)_3(SO_4)]\cdot H_2O$,[8] each of which is coordinated to six oxide ligands in a distorted octahedral geometry. The presence of these distortions can be understood in the context of the second-order Jahn−Teller theorem,[9] in which a near degeneracy in electron configurations, the product of mixing between empty metal d orbitals and filled oxide p orbitals, is removed through spontaneous distortion. Each Mo^{6+} ion distorts in a C_2 fashion in its respective coordination octahedron. Two “short” bonds to oxide ligands, with distances ranging between 1.686(5) and 1.714(4) Å; two

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(7) $[C_5H_{14}N_2][(MoO_3)_3(SO_4)]\cdot H_2O$ was synthesized by combining MoO_3 (0.497 g, 3.45×10^{-3} mol), (*R*)-2-methylpiperazine (0.149 g, 1.49×10^{-3} mol), H_2SO_4 (0.151 g, 0.157×10^{-3} mol), and deionized water (1.004 g, 5.58×10^{-2} mol) in a 23-mL Teflon-lined autoclave and heating at 180 °C for 24 h, followed by a slow cool to room temperature at 6 °C/h. Autoclaves were opened in air, and colorless crystals were recovered by filtration. IR data: N−H, 3015, 1613 cm^{-1}; C−H, 1464 cm^{-1}; S−O, 1104, 1200 cm^{-1}.

(8) Crystal data: $C_5H_{16}Mo_3N_2O_{14}S$, fw = 647.95, a = 8.5388(6) Å, b = 10.7467(7) Å, c = 118.1127(11) Å, V = 1662.1(2) Å^3, Z = 4, space group $P2_12_12_1$ (No. 19), T = 153(2) K, λ = 0.71069 Å, D_{calc} = 2.525, μ = 2.427, mm-1, Flack parameter = 0.06(6), $R(F_o^2)$ = 0.0243, $R_w(F_o^2)$ = 0.0585. No hydrogen atoms were located from difference maps.

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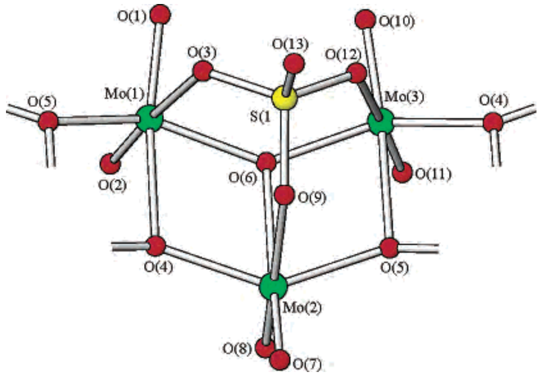

Figure 1. Distorted octahedral Mo^{VI} coordination environments. Red, yellow, and green circles represent oxygen, sulfur, and molybdenum atoms, respectively.

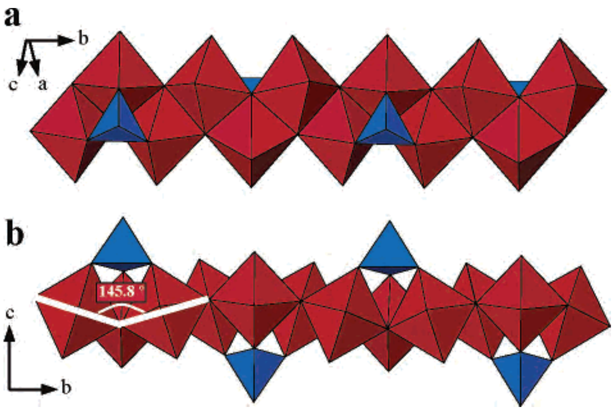

Figure 2. Chains in $[C_5H_{14}N_2][(MoO_3)_3(SO_4)]\cdot H_2O$, viewed along the (a) [−1 0 1] and (b) [1 0 0] directions. Red octahedra and blue tetrahedra represent MoO_6 and SO_4, respectively.

Table 1. Selected Bond Lengths (Å) in $[C_5H_{14}N_2][(MoO_3)_3(SO_4)]\cdot H_2O$

Mo1−O1	1.705(5)	Mo3−O4	1.932(5)
Mo1−O2	1.686(5)	Mo3−O5	2.320(6)
Mo1−O3	2.332(5)	Mo3−O6	1.940(6)
Mo1−O4	2.321(5)	Mo3−O10	1.693(5)
Mo1−O5	1.942(5)	Mo3−O11	1.702(5)
Mo1−O6	1.971(6)	Mo3−O12	2.347(4)
Mo2−O4	1.961(5)	S1−O3	1.485(5)
Mo2−O5	1.955(5)	S1−O9	1.526(4)
Mo2−O6	2.301(4)	S1−O12	1.478(4)
Mo2−O7	1.700(4)	S1−O13	1.455(4)
Mo2−O8	1.714(4)		
Mo2−O9	2.184(3)		

"intermediate" bonds, 1.932(5)−1.971(6) Å; and two "long" bonds, 2.184(3)−2.347(4) Å, are observed for each metal center. See Figure 1. In each MoO_6 coordination octahedron, the two short Mo−O bonds are each trans to the long Mo−O bonds, with the two intermediate Mo−O bonds trans to one another. Selected bond lengths are listed in Table 1.

Three of the oxide ligands in each MoO_6 octahedron bridge between adjacent Mo^{6+} centers in a μ^3 fashion, forming $MoO_{3/1}O_{3/3}$ chains that exhibit a structure analogous to α-molybdena.[10] See Figure 2a. Three oxide ligands, O3, O9 and O12, bridge from three adjacent Mo^{6+} centers to the same S^{6+} ion, which is at the center of a SO_4 tetrahedron. S1 exhibits three long bonds to the bridging oxides, with a range of 1.478(4)−1.526(4) Å, while the terminal S−O13 bond is significantly shorter at 1.455(4) Å. The orientation of successive sulfate tetrahedra alternates in an "up−down−up" motif. See Figure 2b. This chain topology has been reported previously in the compound $Rb_2SMo_3O_{13}$.[11] The $[(MoO_3)_3(SO_4)]_n^{2n-}$ anionic chains are significantly buckled, owing to contraction of the MoO_6−MoO_6 tilt angle by the SO_4 tetrahedra to 145.8 °, in an analogous fashion to $[MoO_3(C_2N_3H_3)]$.[12]

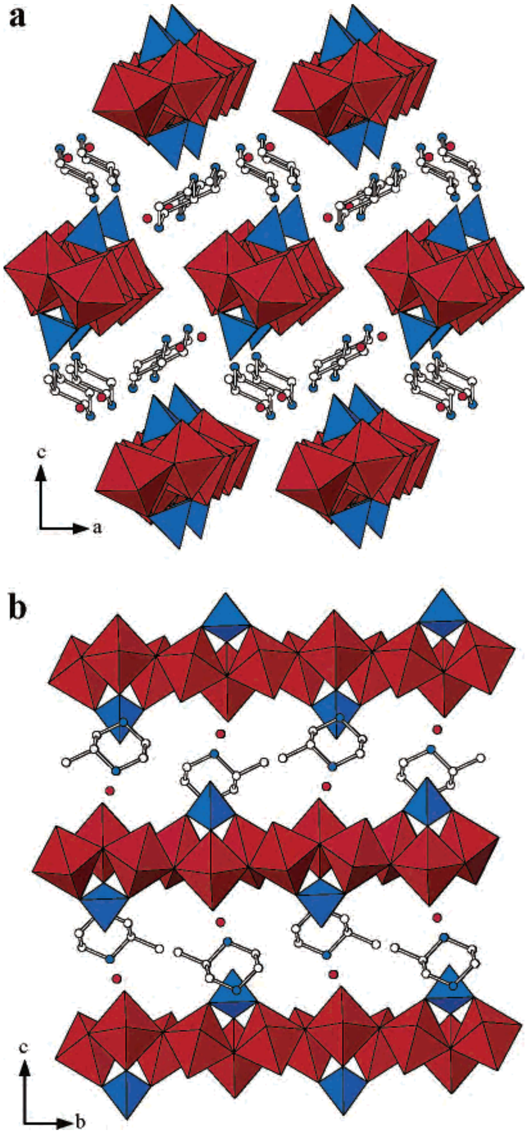

Figure 3. Packing in $[C_5H_{14}N_2][(MoO_3)_3(SO_4)]\cdot H_2O$, viewed along the (a) [0 1 0] and (b) [1 0 0] directions. Red octahedra and blue tetrahedra represent MoO_6 and SO_4, respectively. White, blue, and red circles represent carbon, nitrogen, and oxygen atoms, respectively.

The extensive hydrogen bonding in $[C_5H_{14}N_2][(MoO_3)_3(SO_4)]\cdot H_2O$ can be understood when discussed in the context of bond valence sums,[13] a concept that is used to quantify both the relative strength and residual charges of each bond and respective ligand. All calculations were performed using parameters compiled by Brese and O'Keeffe.[14] The valence

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Table 2. Bond Valence Sums[a] for $[C_5H_{14}N_2][(MoO_3)_3(SO_4)]\cdot H_2O$

S_i	Mo1	Mo2	Mo3	S1	$\sum S_i$	$V - \sum S_i$
O1	1.73				1.73	−0.27[b]
O2	1.69				1.69	−0.31
O3	0.32			1.46	1.78	−0.22
O4	0.33	0.85	0.94		2.12	0.12
O5	0.91	0.85	0.33		2.09	0.09
O6	0.84	0.35	0.92		2.11	0.11
O7		1.75			1.75	−0.25[b]
O8		1.69			1.69	−0.31[b]
O9		0.47		1.30	1.77	−0.23[b]
O10			1.78		1.78	−0.22
O11			1.74		1.74	−0.26
O12			0.30	1.48	1.78	−0.22
O13				1.58	1.58	−0.42[b]
$\sum S_i$	5.82	5.96	6.01	5.82		

[a] Valence sums calculated with the formula $S_i = \exp[(R_0 - R_i)/B]$, where S_i is the bond valence of bond i, R_0 is a constant that depends on the bonded elements, R_i is the bond length of bond i, and B equals 0.37. $\sum S_i$ is the bond valence sum for each atom. V is the predicted valence for a site. R_0 ($Mo^{VI}-O$) = 1.907, R_0 ($S^{VI}-O$) = 1.624. [b] Hydrogen-bond acceptor (determined by N−O and O−O distances).

of each Mo−O and S−O bond was calculated, as reported in Table 2. The overall charge on each Mo and S center can be calculated by adding the appropriate bond valences. In each case, the Mo and S valences are close to 6+, the expected value. The relative residual negative charge of each oxide ligand can be calculated by adding the valences of each Mo−O and S−O bond in which a given ligand participates. The total bond valence ($\sum S_i$) is subtracted from the predicted valence of an oxide ligand, −2, to give the residual negative charge. The relative nucleophilicity of each ligand, which relates to the propensity to accept a hydrogen bond from either the $[C_5H_{14}N_2]^{2+}$ cations or occluded water molecules, is directly proportional to the residual negative charge. The residual negative charges on the oxide ligands vary considerably. The small positive values of O4, O5, and O6 are not surprising as each of these ligands acts as a μ^3 bridge between adjacent molybdenum centers.

Every $[C_5H_{14}N_2]^{2+}$ cation donates four hydrogen bonds through its four acidic hydrogens to O1, O8, and O9, which reside on three different $[(MoO_3)_3(SO_4)]_n^{2n-}$ chains, and the occluded water molecule O14, which, in turn, donates two hydrogen bonds to O7 and O13, each of which are part of two different $[(MoO_3)_3(SO_4)]_n^{2n-}$ chains. The result is an extensive three-dimensional hydrogen-bonding network. The oxide ligands accepting hydrogen bonds closely match those with the highest nucleophilicities. Deviations in the hydrogen-bonding interactions from those predicted using bond valence sums are most likely a result of the steric constraints of each H−N−H and H−O−H bond angle.

$[C_5H_{14}N_2][(MoO_3)_3(SO_4)]\cdot H_2O$ was synthesized from an enantiomerically pure source of (*R*)-2-methylpiperazine, resulting in a compound that contains only (*R*)-2-methylpiperazinium. This compound crystallizes in the noncentrosymmetric space group $P2_12_12_1$ (No. 19), which has the enantiomorphic crystal class 222 (D_2).[15,16] The $[(MoO_3)_3(SO_4)]_n^{2n-}$ chains contain 2_1 screw axes at (0, y, $^3/_4$) and ($^1/_2$, y, $^1/_4$). $Rb_2SMo_3O_{13}$ contains $[(MoO_3)_3(SO_4)]_n^{2n-}$ chains that exhibit the same connectivity. This compound crystallizes in the centrosymmetric space group $P2_1/n$ (No. 14), in which the chains reside on a series of inversion centers at (0, 0, z) and ($^1/_2$, $^1/_2$, z), not along 2_1 screw axes, as observed in $[C_5H_{14}N_2][(MoO_3)_3(SO_4)]\cdot H_2O$.

The sulfation of α-molybdena in the presence of (*R*)-2-methylpiperazinium cations had yielded a novel compound containing $[(MoO_3)_3(SO_4)]_n^{2n-}$ chains. The potential for the formation of additional sulfated molybdates containing organic cations is great, owing to precedence in systems containing other metal centers. Experiments probing the nonlinear optical properties of $[C_5H_{14}N_2][(MoO_3)_3(SO_4)]\cdot H_2O$ and the inclusion of different organic cations are ongoing.

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Supporting Information Available: Complete lists of crystallographic details, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles are available in an X-ray Crystallographic Information File (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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