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Dimerization of the $[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]^{2-}$ Dianions Stabilized by a Quadruply Bridging Sulfate Ligand and Intramolecular Hydrogen Bonding by the $[(CH_3)_2NH_2]^+$ Cations. Structures of the $[(CH_3)_2NH_2]_{6-x}(Et_4N)_x[\{(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)\}_2(SO_4)]$ Aggregates (x = 1, 2, 2.5)

Chang G. Kim and Dimitri Coucouvanis*

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

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The reactivity of the Mo^{IV}–S_n and Mo^V–S_n functional groups (n = 1, 2) toward electrophilic molecules such as activated alkynes[1] or CS_2[2] is well established. In these reactions dipolar molecules add across the polarized Mo–S bond presumably after an initial electrophilic attack at the nucleophilic, Mo-coordinated, sulfur atom. As a result of these reactions Mo complexes of vinyl disulfide,[1a] dithiolene,[1b,c,d] trithiocarbonate,[2a] and perthiocarbonate[2] ligands have been obtained and their syntheses and structures have been the subject of numerous reports.[1,2]

A reactivity study of the Mo–S_n chromophores in various thiomolybdate complexes toward SO_2 has shown that not unlike other electrophilic molecules SO_2 reacts with the Mo–S_n bonds.[3] At ambient temperatures the Mo=S and Mo—S_2 units react with SO_2 to form η^2-thiosulfite, sulfite, and thiosulfate complexes. The generation of μ_2-thiosulfite and thiosulfate ligands by the reactions of SO_2 with μ-S ligands in organometallic sulfur complexes has been investigated previously by Kubas and coworkers.[4] In this communication we report on the high-temperature (100–120 °C) reactions of SO_2 with thiomolybdates in DMF solution and the syntheses of the $(Et_4N)_x((CH_3)_2NH_2)_{6-x}\{[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]_2(SO_4)\}$ complexes, (x = 1–3). These compounds contain a unique μ_4-O_4S^{2-} ligand that, to our knowledge, is unprecedented in the coordination chemistry of the SO_4^{2-} ligand[5] and the structurally essential $((CH_3)_2NH_2)^+$ cations that appear to stabilize the "trapped" μ_4-O_4S^{2-} ligand by strong hydrogen bonding interactions.

The reaction of the Et_4N^+ salts of either the $[(S)(O)Mo(\mu\text{-}S)_2Mo(O)(S_4)]^{2-}$ (I)[6] or $[(S_2)(O)Mo(\mu\text{-}S)_2Mo(O)(S_4)]^{2-}$ (II)[7] anions, with SO_2 in DMF solution at 100–110 °C over a period of 5 h affords yellow crystals of the $(Et_4N)_{2.5}((CH_3)_2NH_2)_{3.5}\{[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]_2(SO_4)\}$ complex[8] (III) in ~60% yield. Elemental sulfur also is obtained in these reactions and accounts for nearly 90% of the total sulfur originally present as S_n^{2-} terminal ligands in the thiomolybdate complexes I and II. A similar complex, $(Et_4N)_2((CH_3)_2NH_2)_4\{[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]_2(SO_4)]\}$·DMF (IV) is obtained[9] by the reaction of $(DMF)_3(O)Mo(\mu\text{-}S)_2Mo(O)(SO_4)]$ (V)[10] with $Et_4N^+HSO_4^-$, in SO_2 saturated DMF solution, in a 1:1.5 molar ratio at a temperature of 100–110 °C. Finally, the reaction of the $(DMF)_3(O)Mo(\mu\text{-}S)_2Mo(O)(SO_4)]$, complex[10] in an SO_2 saturated, DMF solution with H_2SO_4 and recrystallization of the product from CH_3CN solution affords the $((CH_3)_2NH_2)_6\{[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]_2(SO_4)]\}$·$CH_3CN$ complex (VI)[11] as a microcrystalline powder. The crystalline $(Et_4N)((CH_3)_2NH_2)_5\{[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]_2(SO_4)]\}$·$CH_3CN$ complex VII is obtained from solutions of VI in the presence of Et_4N^+. The structures of III, IV, and VII have been determined[12] and all contain the $\{[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]_2(SO_4)\}^{6-}$ hexaanion (Figure 1). The hexaanion is a tetranuclear cluster that contains two $[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]^{2-}$ subunits, bridged by a μ_4-SO_4^{2-} ligand. The four Mo atoms are related by an idealized $\bar{4}$ axis that passes through the central S atom of the μ_4-SO_4^{2-} bridge and the centers of the $Mo(\mu\text{-}S)_2Mo$ rhombic units. The elongated Mo_4 tetrahedron has approximate D_{2d} symmetry with two short (~2.8 Å) and four long (6.8 Å) Mo–

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(8) Anal. Calcd for $Mo_4S_9O_{25}N_7C_{30}H_{85}$, III (MW 1616.5): C, 22.29; N, 6.07; H, 5.26. Found: C, 22.29; N, 5.65; H, 5.10. IR spectra: (KBr, cm^{-1}): (ν(N—H)), 3172, 2781, 2440; (ν(Mo=O)), 954, 903; ($\nu(SO_4^{2-})$), 1278, 1157, 1110, 660, 614, 582.

(9) Anal. Calcd for $Mo_4S_9O_{25}N_7C_{27}H_{79}$, IV (MW, 1574.3): C, 20.60; N, 6.23; H, 5.02. Found: C, 20.18; N, 6.07; H, 4.63. IR spectra: (KBr, cm^{-1}): (ν(N—H)), 3172, 2782, 2440; (ν(Mo=O)), 960, 903; ($\nu(SO_4^{2-})$), 1280, 1157, 1114, 660, 618, 582.

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(11) Anal. Calcd for $Mo_4S_9O_{24}N_7C_{20}H_{63}$, VI (MW, 1458.2): C, 12.24; N, 7.14; H, 3.74. Found: C, 12.63; N, 6.39; H, 3.96. IR spectra: (KBr, cm^{-1}): (ν(N—H)), 3177, 2781, 2442; (ν(Mo=O)), 917, 889; ($\nu(SO_4^{2-})$), 1271, 1155, 1103, 659, 614, 585. The low energy of the Mo=O vibrations in VI by comparison to III and IV at present is difficult to explain. An examination of the immediate environment around the Mo=O group does not show any unusually short contacts and hydrogen bonding does not seem to be an explanation.

(12) Crystal and refinement data: Yellow crystals of $(Et_4N)_{2.5}((CH_3)_2NH_2)_{3.5}\{[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]_2(SO_4)]\}$·(DMF) (III) are orthorhombic, space group *Pnc*2, with a = 16.997(2) Å, b = 16.997(2) Å, c = 22.623(3) Å, and Z = 4. Yellow crystals of $(Et_4N)_2((CH_3)_2NH_2)_4\{[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]_2(SO_4)]\}$(DMF) (IV) are monoclinic, space group $P2_1/n$, with a = 13.551(2) Å, b = 16.780(2) Å, c = 25.563(4) Å, b = 90.79(1)°, and Z = 4. Yellow crystals of $(Et_4N)((CH_3)_2NH_2)_5\{[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]_2(SO_4)]\}(CH_3CN)$ (VII) are orthorhombic, space group *Pncb*, with a = 11.432(5) Å, b = 11.863(5) Å, c = 38.708(15) Å, and Z = 4. Single-crystal X-ray diffraction data for all crystals were collected on a Nicolet P3/F diffractometer using Mo K_α radiation. The solutions of all structures were carried out by a combination of heavy-atom Patterson techniques, direct methods, and Fourier techniques. No systematic absences consistent with a tetragonal space group were observed for III, however the observed, systematic absences were found consistent with a twinned orthorhombic crystal and the space group *Pnc*2. Once the data were corrected to account for the twinning, solution and refinement of the structure was quite satisfactory. An identical type of twinning has been reported earlier.[13] The two anions in III are located on crystallographic 2-fold axes. The anion in VII is also located on a crystallographic 2-fold axis. The refinement of the structures by full-matrix least-squares methods was based on 3806 unique reflections ($2\theta_{max}$ = 45°, $I > 3\sigma(I)$) for III, 5221 unique reflections, ($2\theta_{max}$ = 45°, $I > 3\sigma(I)$), for IV and 1970 unique reflections ($2\theta_{max}$ = 45°, $I > 5\sigma(I)$) for VII. Anisotropic temperature factors were used for all non-hydrogen atoms in III, IV, and VII. At the current stage of refinement on 606 parameters for III, 596 parameters for IV, and 265 parameters for VII with all atoms present in the asymmetric units, R_w = 0.049, 0.047, and 0.044 respectively for III, IV, and VII.

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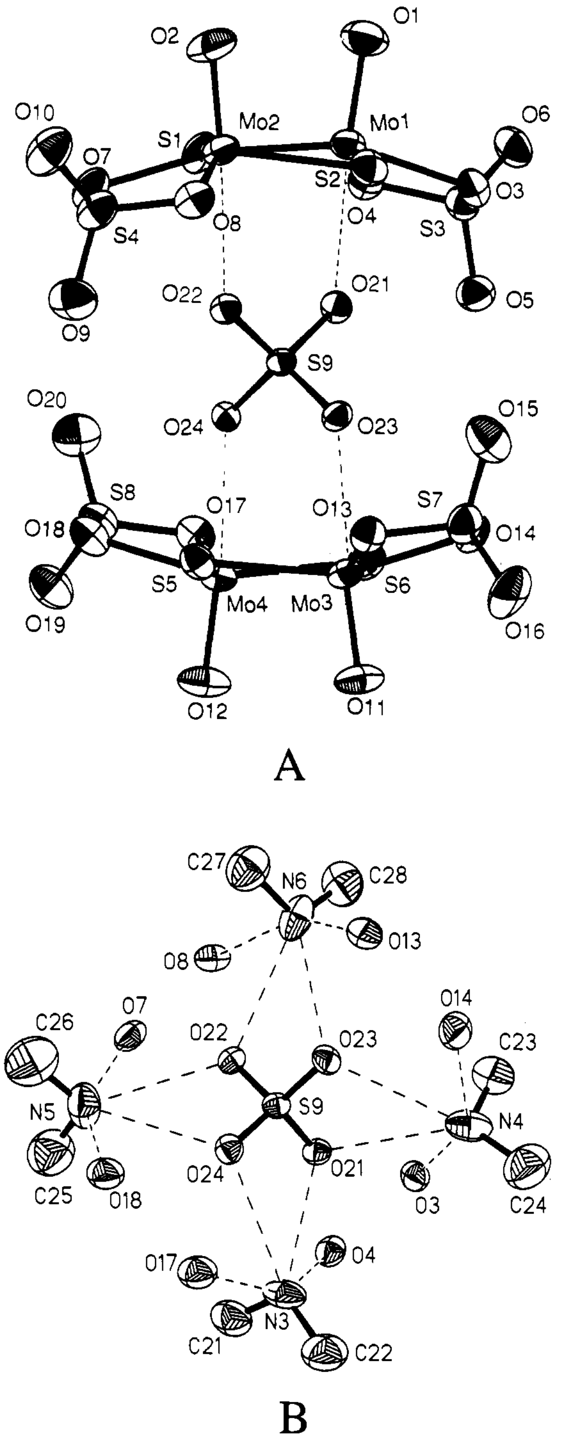

Figure 1. (A) Structure and labeling of $\{[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]_2(SO_4)\}^{6-}$ in IV. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces. The hydrogen bonded $((CH_3)_2NH_2)^+$ cations have been omitted for clarity. The idealized $\bar{4}$ axis lies in the plane of the paper. (B) The central $\mu_4\text{-}SO_4{}^{2-}$ ligand and the hydrogen-bonded $((CH_3)_2NH_2)^+$ cations. The idealized $\bar{4}$ axis lies perpendicular to the plane of the paper. Selected mean bond distances and angles for the anions in III, IV, and VII not reported in the text include the following: Mo–Mo, 2.796(8) Å (range: 2.773(1)–2.822(2) Å); Mo–S$_b$, 2.307(5) Å (range: 2.266(3)–2.326(4) Å) Mo–O$_L$, 2.112(11) Å (range: 2.059(5)–2.151(10) Å); Mo=O, 1.660(11) Å (range: 1.623(7)–1.691(9) Å); Mo–S$_b$–Mo, 74.5(2)° (range: 74.(1)– to 75.0(2)°); S$_b$–Mo–S$_b$, 104.7(2)° (range: 104.3(1)–105.2(2)°). The number in parentheses represents the larger of the individual standard deviations or the standard deviation σ, from the mean value for each class of distances or angles in all three structures.

Mo distances. The individual subunits contain the *syn*-Mo(O)(μ-S)$_2$Mo(O) core. This structural feature is similar to that found in other $[(L)Mo(O)(\mu\text{-}S)_2Mo(O)(L)]^{2-}$ complexes.[14] The structure of III contains two independent $[(Et_4N)_x((CH_3)_2NH_2)_{6-x}\{[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]_2(SO_4)\}\cdot]$ aggregates ($x = 2, 3$) that differ from each other by the number of $((CH_3)_2NH_2)^+$ cations with which they associate via hydrogen bonding. Both anions in III are located on crystallographic 2-fold axes of symmetry. An intriguing feature in the structure of these anions is their regiospecific interactions with the $((CH_3)_2NH_2)^+$ cations. The latter were generated inadvertently by decomposition of DMF.[15] The $((CH_3)_2NH_2)^+$ cations, hydrogen bonded to either of the two independent anions in III and the anions in IV and VII (see the figure in the synopsis of this article in the Table of Contents) lie in a plane that passes through the S atom of the bridging sulfate molecule and is perpenticular to the pseudo-$\bar{4}$ axis of symmetry. In the polymeric VII, four of the five $((CH_3)_2NH_2)^+$ cations lie in the same plane and in the same positions as in III and IV and the other is located between the tetranuclear hexaanions and connects them via hydrogen bonding. The protons in the $((CH_3)_2NH_2)^+$ cations are located so as to make effective use of hydrogen-bonding interactions with the oxygen atoms in both the central μ_4 $\text{-}SO_4{}^{2-}$ ligand and in the η^2, terminal $SO_4{}^{2-}$ ligands. The 16 $N_{(((CH_3)_2NH_2)^+)}\text{–}O_{(SO_4{}^{2-})}$ distances in IV range from 2.86 to 3.13 Å and have a mean value of 2.99(2) Å. Nearly identical anion–cation interactions (both positionally and metrically) prevail in one of the two independent aggregates in III ($x = 2$) and the one in VII ($x = 5$). The $[[((CH_3)_2NH_2)^+]_3\{[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]_2(SO_4)\}]^{3-}$ aggregate in III shows the three $((CH_3)_2NH_2)^+$ cations occupying in an ordered fashion three of the four available locations.

The terminal, η^2-sulfate ligands show Mo–O$_L$ distances of 2.107(5) Å and are shorter than the Mo–O$_{DMF}$ distances in the $[Mo_2(O)_2(\mu_2\text{-}S)_2(\eta^2\text{-}S_2)(DMF)_3]$ complex[6,7] (2.207(14) Å). In III, IV, and VII, the Mo–O distances with the $\mu_4\text{-}SO_4{}^{2-}$ ligands are found in the range from 2.419(8) to 2.469(8) Å). These distances are unusually long and may indicate that the tetranuclear complexes are only weakly held together and very likely owe their existence to effective hydrogen bonding by the $((CH_3)_2NH_2)^+$ cations.

The S–O$_L$ and S–O$_t$ distances within the chelating, terminal sulfate ligands in III, IV, and VII range from 1.513(8) to 1.540(8) Å and from 1.407(7) to 1.431(10) Å, respectively, and compare favorably with distances reported earlier for the $\mu_3\text{-}O_3SO^{2-}$ ligand in the $H_2Os_3(CO)_9(\mu_3\text{-}O_3SO)$ complex.[5h] For the latter S–O$_b$ = 1.51(1), 1.49(1), 1.51(1) Å and S-O$_t$ = 1.42(1) Å. Similar distances also are found with the bridging $SO_4{}^{2-}$ ligand in the $[Mo_2(SO_4)_4]^{3-}$ complex[5c] (S–O$_b$ = 1.521(1) Å and S–O$_t$ = 1.442(2) Å). The S–O distances of the $\mu_4\text{-}SO_4{}^{2-}$ ligands in III, IV, and VII, with a mean value of 1.468(9) Å, not unexpectedly are found nearly halfway between the S–O$_b$ and S–O$_t$ distances.

At present we are exploring the possibility that other oxoanions ($PO_4{}^{3-}$, $AsO_4{}^{3-}$, $SiO_4{}^{4-}$) or tetraoxometalates ($MoO_4{}^{2-}$, $VO_4{}^{3-}$, $WO_4{}^{2-}$) may occupy the locations of any or all of the $SO_4{}^{2-}$ ligands in complexes isostructural to III, IV, or VII, in the presence of $((CH_3)_2NH_2)^+$ cations.

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Supplementary Material Available: Tables S1–S3, containing listings of positional parameters, thermal parameters, and selected distances and angles of II, IV, and VII (33 pages). Ordering information is given on any current masthead page.

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(15) A comment must be made regarding the origin of the $((CH_3)_2NH_2)^+$ cations in III, IV, and VII. Attempts to dry "wet" DMF by refluxing over CaH_2 prior to distillation resulted into an undetected decomposition of some of the $H(CO)N(CH_3)_2$ molecule into CO and dimethylamine. The latter was the source of the $((CH_3)_2NH_2)^+$ cations. The synthesis of the same $(Et_4N)_x((CH_3)_2NH_2)_{6-x}\{[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]_2(SO_4)\}$ complexes, (x = 1, 2, or 3) also can be accomplished in CH_3CN solution from $[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]^{2-}$,[10] $SO_4{}^{2-}$, Et_4N^+, and $((CH_3)_2NH_2)^+$ in the appropriate stoichiometric ratios.