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Synthesis and Characterization of the Unsymmetrical Trinuclear Oxothiomolybdate Anion $Mo_3O_2S_8^{2-}$

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The synthesis and characterization of polynuclear thiomolybdates and oxothiomolybdates have attracted several research groups during the past decade. Unlike the extensive and varied chemistry of the polyoxomolybdates,[4] the thioanions have so far been limited to small (Mo_2, Mo_3) species that frequently contain oxidation states of molybdenum lower than Mo(VI). Di- and trinuclear oxothiomolybdates have been synthesized, generally in low yield, from $[MoO_xS_{4-x}]^{2-}$ although recently Do, Simhon, and Holm[5] have shown that similar species are formed when polyoxomolybdates are treated with hexamethyldisilthiane. In this paper we report the high-yield synthesis of a trinuclear oxothiomolybdate, $Mo_3O_2S_8^{2-}$, starting from mononuclear species. This anion has previously only been known as a component of the mixed crystal $Mo_3O_{2.55}S_{7.45}^{2-}$.[5]

Experimental Section

Synthesis. Method A. Ammonium dithiodioxomolybdate, $(NH_4)_2MoO_2S_2$ (0.228 g, 1 mmol), was dissolved in 200 mL of methanol at -5 to -10 °C and the solution stirred for 2 h. The color intensified from orange to red. After filtration to remove undissolved solids, a solution of 0.805 g (2.5 mmol) of $(n\text{-}Bu)_4NBr$ in 20 mL of methanol was added. After the mixture had been allowed to stand overnight at 0 °C, a dark red crystalline precipitate formed. This was filtered off, washed with diethyl ether, methanol, and ether, and dried in vacuo: yield 0.21 g (58%); mp 133-134 °C. Anal. Calcd (found) for $[(n\text{-}C_4H_9)_4N]_2Mo_3O_2S_8$ (I): C, 36.38 (36.21); H, 6.90 (6.84); N, 2.83 (2.64); Mo, 27.48 (27.12). The tetraphenylphosphonium (II), *N*-*n*-hexadecylpyridinium (III), and trimethyl-*n*-hexadecylammonium (IV) salts were prepared in an analogous fashion by the addition of 1.05 g (2.5 mmol) of Ph_4PBr, 0.96 g (2.5 mmol) of $C_5H_5NC_{16}H_{33}Br$, and 0.91 g (2.5 mmol) of $Me_3NC_{16}H_{33}Br$, respectively, to the red filtrate. The yields were ca. 50% in each case. Anal. Calcd (found) for $(Ph_4P)_2Mo_3O_2S_8$ (II): C, 45.74 (45.93); H, 3.16 (3.21); Mo, 23.04 (22.93). Mp: 148-149 °C. Anal. Calcd (found) for $(C_5H_5NC_{16}H_{33})_2Mo_3O_2S_8$ (III): C, 42.78 (42.55); H, 6.58 (6.46); N, 2.08 (2.16); Mo 24.23 (24.28). Mp: 133-134 °C. Anal. Calcd (found) for $(Me_3NC_{16}H_{33})_2Mo_3O_2S_8$ (IV): C, 39.81 (39.84); H, 7.67 (7.22); N, 2.44 (2.45); Mo, 24.37 (25.12). Mp: 128 °C.

Method B. Compounds I and II were also prepared by dissolving $[(n\text{-}Bu_4N)]_2MoOS_3$ (0.23 g, 0.33 mmol) and $(Ph_4P)_2MoOS_3$ (0.30 g, 0.33 mmol), respectively, in 150 mL of methanol at room temperature under argon. Glacial acetic acid, 1 mL, was slowly added with vigorous stirring, and the solution became dark red. After the solution had been stirred for 2 h, it was filtered, thereby recovering dark red microcrystals of the desired products. The crystals were washed and dried as in method A. Yields: I, 0.11 g (94%); II, 0.13 g (92%).

Crystallography. Single crystals of I were obtained by recrystallization from dimethylformamide/diethyl ether at -25 °C. Crystal, intensity collection, and refinement data are presented in Table I. All intensity data were collected on an Enraf-Nonius CAD-4 diffractometer, and the structure was solved by using programs from the SDP package. Molybdenum positions were determined from the Patterson map, and all nonhydrogen atoms were located by subsequent structure factor calculation and difference maps. Positional parameters and isotropic and anisotropic thermal parameters were refined by full-matrix least-squares procedures.

Table I. Crystallographic Data for $[(C_4H_9)_4N]_2Mo_3O_2S_8$ (I)

formula: $C_{32}H_{72}Mo_3N_2O_2S_8$
fw = 1061.22
a = 15.910 (2) Å
b = 15.411 (1) Å
c = 20.407 (5) Å
β = 103.40 (1)°
V = 4867.5 Å^3
Z = 4

space group: $P2_1/c$
T = 20 °C
λ = 0.71069 Å
ρ_{calcd} = 1.448 g cm^{-3}
μ = 110 cm^{-1}
$R(F_o)$ = 0.060
$R_w(F_o)$ = 0.066

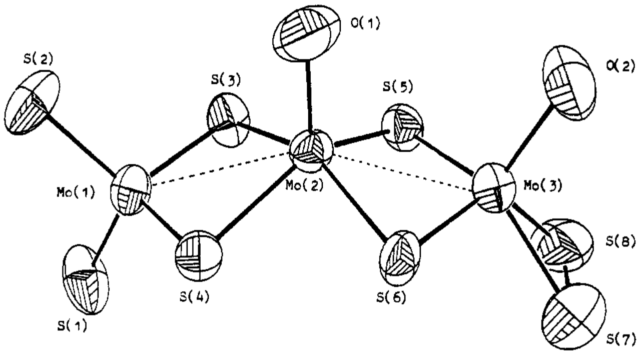

Figure 1.

Results and Discussion

Four salts of the anion $Mo_3O_2S_8^{2-}$ have been prepared in good to excellent yield from the mononuclear anions $MoO_2S_2^{2-}$ and $MoOS_3^{2-}$. The infrared spectrum of compound I shows the following vibrational bands (cm^{-1}): 963 (s), 943 (s) (Mo–O$_t$); 516 (m), 501 (s) (Mo–S$_t$); 477 (m), 425 (w) (Mo–S$_{br}$). The electronic spectrum has the following maxima (nm [$10^3\epsilon$/(M^{-1} cm^{-1})]): 230 [41.0], 270 [18.3], 287 [17.1], 315 [15.4], 378 [8.2], 442 [12.8].

With the exception of the mononuclear species $MoO_xS_{4-x}^{2-}$ (x = 0–4), all previously reported oxothiomolybdates contain at least one molybdenum atom in oxidation state IV or V and one or more η_2-S_2^{2-} ligands. On the basis of the formulas $Mo_2OS_7^{2-}$,[6] $Mo_2O_2S_6^{2-}$,[7] $Mo_2O_4S_7^{2-}$,[8] and $Mo_3OS_8^{2-}$[9] mixed-valence or lower valence states of molybdenum are implied. Although the title anion is no exception on the basis of the structure determination (see below), *in a formal sense* the Mo atoms in $Mo_3O_2S_8^{2-}$ could all be regarded as Mo^{VI}. Indeed, synthesis method B, which leads to a virtually quantitative yield of the polyanion, could be viewed as a nonredox process (cf. eq 1 and 2). These equations are of

$$3MoOS_3^{2-} + 4H^+ \rightarrow Mo_3O_2S_8^{2-} + H_2O + H_2S \quad (1)$$

$$3MoO_4^{2-} + 4H^+ \rightarrow Mo_3O_{10}^{2-} + 2H_2O \quad (2)$$

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(1) Nanjing University.
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(3) Georgetown University.
(4) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983.
(5) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 2827.
(6) Xin, X.; Morris, N. L.; Jameson, G. B.; Pope, M. T. *Inorg. Chem.* **1985**, *24*, 3482.
(7) Clegg, W.; Sheldrick, G. M.; Garner, C. D.; Christou, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2784. Clegg, W.; Mohan, N.; Müller, A.; Neumann, A.; Rittner, W.; Sheldrick, G. M. *Inorg. Chem.* **1980**, *19*, 2066. Rittner, W.; Müller, A.; Neumann, A.; Bather, W.; Sharma, R. C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 530. Müller, A.; Krickemeyer, E.; Reinsch, U. *Z. Anorg. Allg. Chem.* **1980**, *470*, 35.
(8) Müller, A.; Reinsch-Vogell, U.; Krickemeyer, E.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 796.
(9) Simhon, E. D.; Baenziger, N. C.; Kanatzidis, M.; Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1981**, *103*, 1218. Draganjac, M.; Simhon, E.; Chan, L. T.; Kanatzidis, M.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321.

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Table II. Atomic Positional Parameters and Isotropic Thermal Parameters for the $Mo_3O_2S_8^{2-}$ Anion in I

atom	*x*	*y*	*z*	*β*, Å^2
Mo(1)	0.75923 (7)	0.42100 (7)	0.55684 (6)	5.35 (3)
Mo(2)	0.74439 (6)	0.22568 (6)	0.54167 (5)	4.26 (2)
Mo(3)	0.77221 (7)	0.04710 (6)	0.58339 (5)	4.91 (2)
S(1)	0.8193 (3)	0.5103 (3)	0.6329 (3)	8.9 (1)
S(2)	0.6983 (4)	0.4855 (3)	0.4690 (3)	10.6 (2)
S(3)	0.6677 (2)	0.3329 (2)	0.5938 (2)	6.17 (8)
S(4)	0.8576 (2)	0.3297 (2)	0.5341 (2)	5.98 (8)
S(5)	0.6716 (2)	0.1397 (2)	0.6074 (2)	4.83 (7)
S(6)	0.8706 (2)	0.1400 (2)	0.5571 (2)	6.19 (8)
S(7)	0.8873 (3)	–0.0318 (8)	0.6547 (2)	8.3 (1)
S(8)	0.7707 (3)	–0.0376 (2)	0.6813 (2)	7.3 (1)
O(1)	0.6880 (6)	0.2138 (6)	0.4624 (4)	6.5 (2)
O(2)	0.7266 (6)	–0.0132 (5)	0.5152 (4)	6.7 (2)

Table III. Bond Lengths (Å) and Selected Angles (deg) for $Mo_3O_2S_8^{2-}$

Mo(1)–Mo(2)	3.030 (1)	Mo(2)–S(6)	2.363 (2)
Mo(2)–Mo(3)	2.884	Mo(2)–O(1)	1.668 (4)
Mo(1)–S(1)	2.129 (2)	Mo(3)–S(5)	2.281 (2)
Mo(1)–S(2)	2.082 (2)	Mo(3)–S(6)	2.276 (2)
Mo(1)–S(3)	2.246 (2)	Mo(3)–S(7)	2.390 (2)
Mo(1)–S(4)	2.231 (2)	Mo(3)–S(3)	2.392 (2)
Mo(2)–S(3)	2.440 (2)	Mo(3)–O(2)	1.691 (4)
Mo(2)–S(4)	2.442 (2)	S(7)–S(8)	2.053 (3)
Mo(2)–S(5)	2.370 (1)		
Mo(1)–Mo(2)–Mo(3)	156.18 (2)	Mo(1)–S(2)–Mo(3)	80.45 (5)
S(1)–Mo(1)–S(2)	111.12 (9)	Mo(2)–S(5)–Mo(3)	76.63 (5)
S(3)–Mo(1)–S(4)	103.24 (6)		

course only analogous in a formal sense; the trimolybdates contain polymeric anions.[10] Furthermore, the synthesis starting from $MoO_2S_2^{2-}$ must involve a more complex stoichiometry.

The structure determination of I reveals the anion shown in Figure 1. Atomic positional and isotropic thermal parameters are given in Table II, and selected interatomic distances and bond angles are given in Table III. Do, Simhon, and Holm[5] have isolated the salt $(Bu_4N)_2Mo_3O_{2.55}S_{7.45}$ in 11% yield from the reaction of $Mo_8O_{26}^{4-}$ isomers with $(Me_3Si)_2S$ in acetonitrile. The single-crystal x-ray structural investigation of this compound revealed that it contained both $Mo_3O_2S_8^{2-}$ and $Mo_3O_3S_7^{2-}$ anions in an approximately 1:1.22 mole ratio. The structure and dimensions of the first of these are in satisfactory agreement with the present results. As shown in Figure 1, the presence of a disulfide ligand, S(7)–S(8), demonstrates that the molybdenum atoms have been partially reduced. Plausible assignments of oxidation states are VI–IV–VI and VI–V–V for Mo(1)–Mo(2)–Mo(3), respectively. Holm et al.[5] favor the first of these, but there is no compelling evidence in that direction. For example, we note that the anion could be viewed as a derivative of the Mo(V) species $Mo_2O_2S_6^{2-}$, with bidentate MoS_4^{2-} in place of S_2^{2-}. The dimensions of the MoS_4^{2-} moiety in $Mo_3O_2S_8^{2-}$ are close to those of the free tetrahedral anion, and the Mo(2)···Mo(3) separation of 2.884 Å is little changed from the Mo···Mo distance, 2.829 Å, in $Mo_2O_2S_6^{2-}$.[7]

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Registry No. I, 123928-19-8; II, 116634-70-9; III, 123928-13-2; IV, 123928-14-3; $(NH_4)_2MoO_2S_2$, 16150-60-0; $[(n\text{-}Bu_4N)]_2MoOS_3$, 115564-39-1; $(Ph_4P)_2MoOS_3$, 83061-15-8.

Supplementary Material Available: Tables SI–SIII, listing crystallographic data, atomic positional parameters for tetrabutylammonium cations, and anisotropic temperature factors (4 pages); a table of calculated and observed structure factors (25 pages). Ordering information is given on any current masthead page.

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(10) Kreusler, H. R.; Förster, A.; Fuchs, J. *Z. Naturforsch., B* **1980**, *35*, 242.

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Synthesis and Characterization of Derivatives of Pyridine–Borane Adducts

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Syntheses for several amine·BH_2X (X = CN, C(O)NHR, C(S)NHR, C(CN)=NEt, COOR, COOH) adducts have been reported.[1] Primary interest in these compounds arises from their biological activity as antitumor,[2] antiinflammatory,[3] and antihyperlipidemic[4] agents. Pyridine–carboxyborane[5] was also shown to inhibit tumor growth in mice. Because of the interest in the biological activity of new borane adducts and because of difficulty in obtaining high yields of pyridine–carboxyborane, we undertook a study to isolate a variety of intermediates to attempt to determine which intermediates were isolable and under what conditions desired products are formed. This paper reports the isolation and characterization of new pyridine–borane derivatives and a method that improved the yield of pyridine–carboxyborane.

Experimental Section

All IR spectra were recorded on a Perkin-Elmer 1750 FT spectrometer. Samples were prepared as Nujol mulls between NaCl plates. The ^{11}B NMR spectra were obtained on a JEOL FX-90Q FT NMR spectrometer operating at 28.69 MHz; shifts were measured with respect to external $BF_3·OEt_2$; ^1H NMR spectra were obtained on a Varian XL-300 spectrometer. All NMR results are reported in Table I. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ 85018. All melting points are uncorrected.

Materials. Triethyloxonium tetrafluoroborate was prepared according to the procedure of Meerwein.[6] Approximately 1 M Et_3OBF_4 in CH_2Cl_2 was used as a fresh solution.

Safety Note. At no time was the $(BH_2CN)_x$ oligomer handled dry but manipulated as a solution due to potential explosion hazard.[7c,d]

Preparation of $C_5H_5N·BH_2CN$ (1). To a solution of pyridine (39.55 g, 0.50 mol) in 100 mL of CH_2Cl_2 was added a solution of $(BH_2CN)_x$ oligomer[7a,b] (18 g, 0.46 mol) in 100 mL of CH_2Cl_2 at 10 °C during 30 min. The reaction mixture was brought to room temperature and stirring continued for 1 h. The ^{11}B NMR spectrum of the reaction mixture showed no unreacted $(BH_2CN)_x$ oligomer. The solution was washed with water twice and dried over Na_2SO_4. Solvent was removed, and the residue was subjected to vacuum (0.5 mmHg) for 24 h to remove any

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(1) (a) Spielvogel, B. F.; Wojnowich, L.; Das, M. K.; McPhail, A. T.; Hargrave, K. D. *J. Am. Chem. Soc.* **1976**, *98*, 5702. (b) Spielvogel, B. F.; Ahmed, F. U.; Morse, K. W.; McPhail, A. T. *Inorg. Chem.* **1984**, *23*, 1776. (c) Spielvogel, B. F.; Ahmed, F. U.; Silvey, G. L.; Wisian-Neilson, P.; McPhail, A. T. *Inorg. Chem.* **1984**, *23*, 4322. (d) Das, M. K.; Mukherjee, P. *J. Chem. Res., Synop.* **1985**, 66. (e) Speilvogel, B. F.; Ahmed, F. U.; McPhail, A. T. *Synthesis* **1986**, 833. (f) Kemp, B.; Kalbag, S.; Geanangel, R. A. *Inorg. Chem.* **1984**, *23*, 3063. (g) Gyori, B.; Lazar, I.; Emri, J. *J. Organomet. Chem.* **1988**, *344*, 29.

(2) Hall, I. H.; Starnes, C. O.; Spielvogel, B. F.; Wisian-Neilson, P.; Das, M. K.; Wojnowich, L. *J. Pharm. Sci.* **1979**, *68*, 685.

(3) Hall, I. H.; Starnes, C. O.; McPhail, A. T.; Wisian-Neilson, P.; Das, M. K.; Harchelroad, F., Jr.; Spielvogel, B. F. *J. Pharm. Sci.* **1980**, *69*, 1025.

(4) Hall, I. H.; Das, M. K.; Harchelroad, F., Jr.; Wisian-Neilson, P.; McPhail, A. T.; Spielvogel, B. F. *J. Pharm. Sci.* **1981**, *70*, 339.

(5) Spielvogel, B. F.; Harchelroad, F., Jr.; Wisian-Neilson, P. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1223.

(6) Meerwein, H. *Org. Synth.* **1966**, *46*, 113.

(7) (a) Spielvogel, B. F.; Bratton, R. F.; Moreland, C. G. *J. Am. Chem. Soc.* **1972**, *94*, 8597. (b) Modifications are described in: Kaushik, M. P.; Charandabi, M. R. M. D.; Ettel, M. L.; Lofthouse, T. J.; Morse, K. W. *Inorg. Chem.* **1989**, *28*, 897. (c) Spielvogel, B. F. Private Communication. (d) Gyori, B.; Emri, J.; Feher, I. *J. Organomet. Chem.* **1984**, *262*, C7.

(8) (a) Hargrave, K. D.; McPhail, A. T.; Spielvogel, B. F.; Wisian-Neilson, P. *J. Chem. Soc., Dalton Trans.* **1977**, 2150. (b) Bratt, P. J.; Brown, M. P.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1974**, 2161. (c) Emri, J.; Gyori, B. *J. Chem. Soc., Chem. Commun.* **1983**, 1303. (d) Wisian-Neilson, P.; Das, M. K.; Spielvogel, B. F. *Inorg. Chem.* **1978**, *17*, 2327. (e) Uppal, S. S.; Kelly, H. C. *Chem. Commun.* **1970**, 1619. (f) Martin, D. R.; Chiusano, M. A.; Denniston, M. L.; Dye, D. J.; Martin, E. D.; Pennington, B. T. *J. Inorg. Nucl. Chem.* **1978**, *40*, 9. (g) Gyori, B.; Emri, J.; Feher, I. *J. Organomet. Chem.* **1983**, *255*, 17. (h) Peters, J. L.; Norwood, V. M., III; Morse, K. W. *Inorg. Chem.* **1986**, *25*, 3713.

0020-1669/90/1329-0554$02.50/0