

## Triply Bridged Bimetallic Thiolate Complexes of Oxomolybdenum(V). Formation and Structure of Secondary Ammonium Salts of $[(\mu\text{-OCH}_2\text{CH}_2\text{S-S,O})(\mu\text{-O})(\text{OMo}(\text{OCH}_2\text{CH}_2\text{S}))_2]^{2-}$

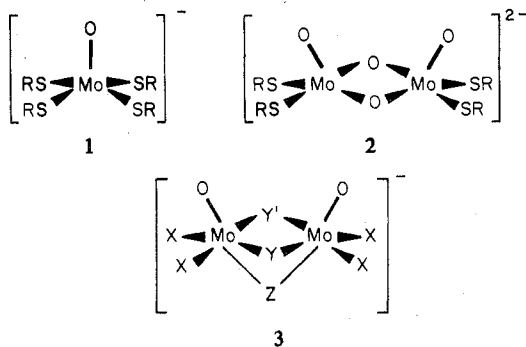
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Red compounds  $(\text{BH}^+)_2[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]^{2-}$  (B = piperidine, morpholine, pyrrolidine) crystallize in moderate yield from reaction mixtures containing  $[\text{MoOCl}_4(\text{OH}_2)]^-$  (or  $[\text{Mo}_2\text{O}_2(\text{SCH}_2\text{CH}_2\text{O})_2\text{Cl}_3]^-$ ),  $\text{HOCH}_2\text{CH}_2\text{SH}$ ,  $\text{H}_2\text{O}$ , and B. Crystal-structure determination for the piperidinium compound reveals that  $[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]^{2-}$  contains two multiply bonded Mo-O groups, each chelated by one  $\text{SCH}_2\text{CH}_2\text{O}^-$  ligand and bridged by three atoms, namely, sulfur (S3, cis to both  $\text{O}_i$ ) and oxygen (OS3, approximately trans to both  $\text{O}_i$ ) of the third  $\text{SCH}_2\text{CH}_2\text{O}^-$  ligand and oxide ( $\text{O}_3$ , cis to both  $\text{O}_i$ ). The coordination stereochemistry of each molybdenum atom is square pyramidal plus distant coordination (OS3) trans to apical  $\text{O}_i$ . One terminal  $\text{SCH}_2\text{CH}_2\text{O}^-$  ligand is cis, and the other trans, relative to the principal bridging atoms S3 and  $\text{O}_3$ . Reactivity information and spectroscopic data are presented. Crystal data:  $a = 8.068$  (1) Å,  $b = 19.904$  (4) Å,  $c = 7.840$  (1) Å,  $\beta = 102.61$  (2)°, space group  $P2_1$ ,  $Z = 2 \times \text{Mo}_2\text{O}_6\text{S}_3\text{N}_2\text{C}_{16}\text{H}_{36}$ ,  $d_{\text{obsd}} = 1.73 \text{ g cm}^{-3}$ , 3080 observed reflections (Mo  $K\alpha$ ),  $R = 0.044$ ,  $R_w = 0.051$ .

### Introduction

Previous papers<sup>1-4</sup> in this series have described the formation and structures of three classes (1, 2, 3) of complexes in which



the oxomolybdenum(V) group is coordinated by thiolate ligands  $\text{RS}^-$ . In 3 the ligands are all monoanionic:  $\text{Y}, \text{Y}' = \text{RS}^-$ ,  $\text{RO}^-$ ;  $\text{X} = \text{RS}^-$ ,  $\text{RO}^-$ ,  $\text{Cl}^-$ ;  $\text{Z} = \text{RS}^-$ ,  $\text{RO}^-$ ,  $\text{Cl}^-$ ,  $\text{R}_2\text{N}^-$ . The new triply bridged structure 3 is formed in a variety of reactions, and we concluded that it is a structure type prevalent in the chemistry of  $\text{OMo}^V$  with monoanionic ligands. Observations of solution reactivity indicate that monometallic complexes 1 are, under certain conditions, thermodynamically unstable with respect to the triply bridged bimetallic complexes 3.

Three type 3 complexes containing the 2-oxoethanethiolate ligand are  $[\text{Mo}_2\text{O}_2(\text{SCH}_2\text{CH}_2\text{O})_2\text{Cl}_3]^-$ ,  $[\text{Mo}_2\text{O}_2(\text{SCH}_2\text{CH}_2\text{O})_3\text{Cl}]^-$ , and  $[\text{Mo}_2\text{O}_2(\text{SCH}_2\text{CH}_2\text{O})_3(\text{SCH}_2\text{CH}_2\text{OH})]^-$ . These all contain the  $\{\text{Mo}_2\text{O}_2(\text{SCH}_2\text{CH}_2\text{O})_2\}$  core, in which one  $\text{SCH}_2\text{CH}_2\text{O}^-$  ligand bridges from Y (S) to Z (O) and the other  $\text{SCH}_2\text{CH}_2\text{O}^-$  ligand chelates from Y' (O) to X (S) in 3. These complexes were isolated from solutions prepared with  $[\text{OMoCl}_4(\text{OH}_2)]^-$ ,  $\text{HOCH}_2\text{CH}_2\text{SH}$ , and hindered tertiary amine as the ligand deprotonating agent.

We now report that analogous reactions using the cyclic secondary amines piperidine, morpholine, or pyrrolidine yield a different triply bridged complex 4 containing an oxido bridging ligand. The crystal structure of the piperidinium salt of 4 has been determined.

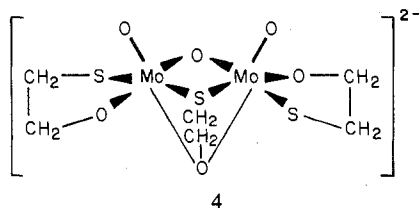


Table I. Observed<sup>a</sup>  $d$  Spacings (Å) for Polycrystalline  $(\text{BH})_2[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]$

B = piperidine	B = morpholine	B = pyrrolidine
10.02 s <sup>b</sup>		
9.90 vvs	9.81 vs	9.63 vs
	9.58 w	
	8.39 ms	
7.91 vvs		
7.67 ms	7.38 vvs	7.59 s
7.29 m		7.29 w
7.14 m	7.13 ms	
	6.53 w	6.87 w
6.16 s	6.24 ms	6.32 s
6.06 m		
5.92 w	5.98 w	
5.26 m	5.13 ms	5.52 m
5.07 m		
5.01 m		
4.83 m		4.75 vw
4.53 w	4.54 w	4.63 mw
4.45 vw		4.31 m
	4.09 vw	4.14 w
	3.99 w	
3.86 ms	3.90 s	3.84 w
	3.86 m	
3.78 m		
3.71 w	3.68 vw	
3.60 w	3.59 w	
3.55 mw		
3.34 w		
3.29 w	3.23 vw	

<sup>a</sup> The values are arranged to emphasize the similarities between the diffraction patterns. <sup>b</sup> Qualitative intensity indicators.

### Experimental Section

Amines and thiols were laboratory reagent grade and were used as received. The molybdenum precursors  $(\text{Et}_4\text{N})[\text{MoOCl}_4(\text{OH}_2)]$ ,  $(\text{Et}_4\text{N})[\text{Mo}_2\text{O}_2(\text{SCH}_2\text{CH}_2\text{O})_2\text{Cl}_3]$ , and the red (thiocyanato)oxomolybdenum(V) compound (formed by reduction of  $(\text{Et}_4\text{N})_2[\text{MoO}_2(\text{NCS})_4]$  in the solid state<sup>5</sup>) were prepared as previously described.<sup>4</sup> Reaction products were routinely identified by polycrystalline X-ray diffraction, using  $\text{Co K}\alpha$  radiation ( $\lambda 1.7915$  Å); diffraction patterns are presented in Table I. Microanalyses were performed by the microanalytical laboratory of this school. Electronic spectra of polycrystalline samples (reflectance) and solutions were obtained with a Cary 17 spectrophotometer. Infrared spectra were recorded on mulls, down to  $300 \text{ cm}^{-1}$ , and are summarized in Table II.

**Piperidinium Salt:**  $(\text{C}_6\text{H}_{10}\text{NH}_2)_2[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]$ . (a) To a solution of 2-hydroxyethanethiol (2.5 g, 32 mmol) and piperidine (7.2 g, 85 mmol) in propanol (35 mL), at room temperature and flushed with dinitrogen, was added water (1 mL) followed by a solution of  $(\text{Et}_4\text{N})[\text{MoOCl}_4(\text{OH}_2)]$  (8.0 g, 20 mmol) in propanol (35 mL) and acetonitrile (5 mL). The mixture immediately developed an intense

Table II. Significant Infrared Frequencies (cm<sup>-1</sup>) for (BH)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>]

BH <sup>+</sup> = C <sub>5</sub> H <sub>10</sub> NH <sub>2</sub> <sup>+</sup>	BH <sup>+</sup> = OC <sub>4</sub> H <sub>8</sub> NH <sub>2</sub> <sup>+</sup>	BH <sup>+</sup> = C <sub>4</sub> H <sub>8</sub> NH <sub>2</sub> <sup>+</sup>	assignmt
	435 sh		
441	447	437	
478	474	477	
503	502	504	
539	531	537	
557	540		
577	576	579	
	597		
664 sh			
676	673	674	
685	687 sh	687	
721	720	723	
730	732	735	
917 sh	905		
922	927	923	} ν(Mo=O)
933	931 sh	929 sh	
	938 sh	942	
1004	1005	1006	
1029			} ν(C-O)
1048	1045	1049	
1059	1058	1058	
1065 sh			
1078 sh			
1550 w	1550 w	1537 br	} ν(N-H)
1592	1596		
1612	1617		
	1632		

red color, which faded within 15 min to a less intense but similar red-yellow color. The mixture was sealed, and the product crystallized slowly at room temperature. After 24 h the red crystals (2.75 g) were separated, washed with propanol, and vacuum dried. The mother liquor, still strongly orange, yielded a further 0.95 g of orange microcrystalline product after partial distillation of solvent at ca. 50 °C. Further recovery of product is complicated by crystallization of piperidinium hydrochloride. Analogous preparations, in which crystallization of the product is induced during slow solvent removal by distillation at ca. 60 °C, yield up to 65% of (C<sub>5</sub>H<sub>10</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>] when 2% solvent water is present and up to 45% when the only water available is that present in the (Et<sub>4</sub>N)[MoOCl<sub>4</sub>(OH<sub>2</sub>)] and laboratory reagent solvents.

(b) To a solution of HOCH<sub>2</sub>CH<sub>2</sub>SH (2.5 g, 32 mmol) and piperidine (7.7 g, 91 mmol) in propanol, flushed with dinitrogen, was added "(Et<sub>4</sub>N)<sub>2</sub>[MoO<sub>2</sub>(NCS)<sub>4</sub>]", red solid (10.0 g), dissolved in warm acetonitrile (30 mL) and methanol (30 mL). A voluminous pale precipitate formed and on heating redissolved to produce an orange-red solution. Room-temperature distillation of the methanol and acetonitrile from this solution caused separation of the orange microcrystalline product (1.9 g), which was identified by X-ray diffraction. The mother liquor, reduced to small volume (ca. 15 mL), produced a further 1.30 g of the orange solid. (C<sub>5</sub>H<sub>10</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>] may be recrystallized from hot methanol or hot pyridine. Anal. Calcd for (C<sub>5</sub>H<sub>10</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>]: C, 30.00; H, 5.66; N, 4.37; S, 15.02. Found: C, 30.09; H, 5.88; N, 4.28; S, 15.14. 10<sup>6</sup>χ<sub>m</sub> = -250 cgsu (291 K); 10<sup>6</sup>χ<sub>m</sub>' = +6 cgsu; μ<sub>eff</sub> = 0.12 μ<sub>B</sub>.

**Morpholinium Salt:** (OC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>]. (a) A solution of (Et<sub>4</sub>N)[MoOCl<sub>4</sub>(OH<sub>2</sub>)] (4.0 g, 10 mmol) in ethanol (95%, 30 mL) was added to a solution of HOCH<sub>2</sub>CH<sub>2</sub>SH (2.5 g, 32 mmol) and morpholine (2.5 g, 29 mmol) in ethanol (70 mL) under dinitrogen. The initially intense red mixture changed to an orange-red solution which deposited the product as an orange microcrystalline precipitate during 24 h. The product was washed with propanol and vacuum dried; yield 1.2 g (37% Mo).

(b) A solution of "(Et<sub>4</sub>N)<sub>2</sub>[MoO<sub>2</sub>(NCS)<sub>4</sub>]" (4.96 g) in methanol (20 mL) and acetonitrile (15 mL) was added to a solution of HOCH<sub>2</sub>CH<sub>2</sub>SH (2.5 g) and morpholine (2.78 g) in methanol (10 mL) under dinitrogen. The red solution was heated and deposited an orange microcrystalline precipitate, which was filtered, washed with propanol, and vacuum dried; yield 1.1 g. Anal. Calcd for (OC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>]: C, 26.09; H, 5.00; N, 4.35; S, 14.93. Found: C, 26.01; H, 5.20; N, 4.37; S, 14.91. 10<sup>6</sup>χ<sub>m</sub> = -249 cgsu (291 K); 10<sup>6</sup>χ<sub>m</sub>' = -7 cgsu.

**Pyrrrolidinium Salt:** (C<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>]. Reactions analogous to those described above, employing solutions of (i) pyrrolidine, HOCH<sub>2</sub>CH<sub>2</sub>SH, H<sub>2</sub>O, and (Et<sub>4</sub>N)[MoOCl<sub>4</sub>(OH<sub>2</sub>)] in propanol, (ii) pyrrolidine, HOCH<sub>2</sub>CH<sub>2</sub>SH, and (Et<sub>4</sub>N)[MoOCl<sub>4</sub>(OH<sub>2</sub>)] in methanol and acetonitrile, or (iii) pyrrolidine, HOCH<sub>2</sub>CH<sub>2</sub>SH, and "(Et<sub>4</sub>N)<sub>2</sub>[MoO<sub>2</sub>(NCS)<sub>4</sub>]" in methanol and acetonitrile, yielded the product as red crystals. Anal. Calcd for (C<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>]: C, 27.45; H, 5.27; N, 4.57; S, 15.71. Found: C, 27.27; H, 5.58; N, 4.78; S, 15.22.

This product is demonstrably soluble in these reaction mixtures, and refrigeration is necessary to obtain appreciable yields (ca. 20% Mo).

**Conversion of (Et<sub>4</sub>N)[Mo<sub>2</sub>O<sub>2</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>Cl<sub>3</sub>] to (C<sub>5</sub>H<sub>10</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>].** To a solution of (Et<sub>4</sub>N)[Mo<sub>2</sub>O<sub>2</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>Cl<sub>3</sub>] (3.1 g, 5.1 mmol) in acetonitrile (100 mL) and propanol (50 mL) at 50 °C, flushed with dinitrogen, was added HOCH<sub>2</sub>CH<sub>2</sub>SH (1.8 g, 23 mmol). The yellow solution slowly developed an orange coloration. Addition of piperidine (5.0 g, 59 mmol) in propanol (30 mL) accelerated the color change to orange-red. Water (0.5 mL) was added. The acetonitrile was distilled from the mixture at ca. 50 °C, causing separation of the product as an orange microcrystalline precipitate. After digestion the product was filtered, washed with propanol, vacuum dried, and identified by X-ray diffraction. A second crop was obtained from the mother liquor; total yield 1.15 g (35% Mo).

**Properties and Reactions.** The three compounds have substantial solubility (>10<sup>-2</sup> M) in water, but their solubility in other pure solvents is small. The low solubility in cold aprotic solvents (pyridine, DMF, Me<sub>2</sub>SO, or acetonitrile) is increased by heating, which yields yellow solutions. The piperidinium salt is appreciably soluble in methanol but sparingly soluble in higher alcohols and in piperidine. Two general observations indicate that solution equilibria involving at least hydrogen bonding exist for these compounds. The pyrrolidinium salt is more soluble in mixtures of acetonitrile and propanol than in the pure solvents, and the pyrrolidinium and piperidinium salts are more soluble in their reaction mixtures (containing excess halide, thiolate, and secondary ammonium cation) than in pure solvents.

None of the compounds (solid or solution) is appreciably oxidized by dioxygen within 1 h at room temperature. When treated with weak base, weak acid, or H<sub>2</sub>S, aqueous solutions of (C<sub>5</sub>H<sub>10</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>] show no change during 10 min at room temperature.

Treatment of (C<sub>5</sub>H<sub>10</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>] with excess HOCH<sub>2</sub>CH<sub>2</sub>SH appears to increase its solubility in hot acetonitrile plus methanol plus propanol, but there is no color change on heating first at reflux with dinitrogen flush and then at 80 °C in a sealed system for 6 h. After cooling and partial evaporation, a substantial amount of the (C<sub>5</sub>H<sub>10</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>] was recovered. Although it cannot be concluded that there is no reaction to form species such as [Mo<sub>2</sub>O<sub>2</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>OH)]<sup>4-</sup>, it is clear that any such reaction is extremely slow.

In contrast, (C<sub>5</sub>H<sub>10</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>] reacts instantly with excess benzenethiol, producing an intense red solution in methanol.

**Analogous Reactions.** A series of reaction mixtures containing piperidine and/or HOCH<sub>2</sub>CH<sub>2</sub>SH in large excess of the 2:3:8 [MoOCl<sub>4</sub>(OH<sub>2</sub>)]<sup>-</sup>:HOCH<sub>2</sub>CH<sub>2</sub>SH:piperidine stoichiometric ratio required for formation of [Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>]<sup>2-</sup> also yielded (C<sub>5</sub>H<sub>10</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>] in comparable yield.

**Reaction Deficient in Piperidine.** A solution containing HOCH<sub>2</sub>CH<sub>2</sub>SH (2.5 g, 32 mmol), piperidine (3.0 g, 35 mmol) and (Et<sub>4</sub>N)[MoOCl<sub>4</sub>(OH<sub>2</sub>)] (8.0 g, 20 mmol) in hot acetonitrile and propanol was colored yellow rather than the intense orange-red characteristic of [Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>]<sup>2-</sup>. Removal of the acetonitrile by distillation at ca. 60 °C precipitated a yellow microcrystalline product, which after washing and drying was identified by X-ray diffraction as (Et<sub>4</sub>N)[Mo<sub>2</sub>O<sub>2</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>Cl<sub>3</sub>]; yield 3.9 g (64% Mo).

**Reactions with Other Amines.** Reactions following the various procedures successful in preparation of (C<sub>5</sub>H<sub>10</sub>NH<sub>2</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>], but using amines (B) other than piperidine, morpholine, or pyrrolidine, did not permit isolation of analogous compounds (B-H)<sub>2</sub>[Mo<sub>2</sub>O<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>]. The amines investigated were tripropylamine (pK<sub>a</sub> = 10.5), dipropylamine (11.0), *N*-methylmorpholine (7.38), *N*-ethylmorpholine (7.67), *N*-methylaniline (4.84), and dicyclohexylamine (11.3). In the case of *N*-methylmorpholine a very small amount of orange product, mixed with amine hydrochloride, was obtained from a concentrated reaction mixture in propanol. Reactions with dicyclohexylamine indicated that a water-insoluble

Table III. Crystallographic Details,  $(C_5H_{10}NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$ 

$a$ , Å	8.069 (1)
$b$ , Å	19.904 (4)
$c$ , Å	7.840 (1)
$\beta$ , deg	102.61 (2)
$V$ , Å <sup>3</sup>	1228.75
space group	$P2_1$
$Z$	2
$d_{obsd}$ , g cm <sup>-3</sup>	1.73
$d_{calcd}$ , g cm <sup>-3</sup>	1.73
radiation	Mo K $\alpha$ , ( $\lambda$ 0.710 69 Å)
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	12.73
crystal faces and separations, mm	{100}, {010}, {001}
no. of intens measmts	3872
$\phi_{max}$ , deg	30
no. of independent reflectns	3635
criterion for obsd reflectn, $I/\sigma(I)$	>2.58
no. of obsd reflectns	3080
criterion for inclusion, and number ( $m$ ), of reflectns in final least-squares refinemt	obsd, ( $\sin \phi$ )/ $\lambda$ > 0.15 3042
no. of parameters refined ( $n$ )	278
$R = \sum^m  \Delta F  / \sum^m  F_o $	0.044
$R_w = [\sum^m w  \Delta F ^2 / \sum^m w  F_o ^2]^{1/2}$	0.051
$[\sum^m w  \Delta F ^2 / (m - n)]^{1/2}$	1.55

orange product, possibly  $((C_5H_{11})_2NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$ , may be isolable after removal of the insoluble amine hydrochloride.

Reaction solutions with these amines underwent the same color changes as those with cyclic secondary amines, indicating that  $[Mo_2O_3(SCH_2CH_2O)_3]^{2-}$  could similarly exist in solution. Additions of piperidinium hydrochloride to solutions prepared with tripropylamine (not more basic than piperidine), in an attempt to crystallize  $(C_5H_{10}NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$  and thereby demonstrate the presence of  $[Mo_2O_3(SCH_2CH_2O)_3]^{2-}$  in solution, were unsuccessful. In view of the complex solubilities of the crystalline cyclic secondary ammonium salts, noted above, this result cannot be regarded as evidence that  $[Mo_2O_3(SCH_2CH_2O)_3]^{2-}$  is not formed with the non-cyclic amines.

**Crystallography.** The crystal of  $(C_5H_{10}NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$  used was selected from a reaction crop. The crystallographic procedures followed were standard, and the same as those previously described.<sup>4</sup> Numerical details are set out in Table III. All methylene hydrogen atoms were included at idealized positions ( $d_{C-H} = 0.95$  Å) with temperature factors equal to those of their bonded carbon atoms and were not refined. The four hydrogen atoms on the two nitrogen atoms were located in difference syntheses and refined with isotropic temperature factors. Anisotropic temperature factors were refined for all nonhydrogen atoms.

The structure and the atom labeling are shown in Figures 1 and 2. The atoms of the 2-oxoethanethiolate ligands are labeled  $Sm-CSm1-CSm2-OSm$  ( $m = 1, 2, 3$ ),  $m = 3$  being the bridging ligand. The piperidinium atoms are  $Nn$  and  $CNnp$  ( $n = 1, 2$ ;  $p = 1-5$ ). The two hydrogen atoms bonded to atom  $xxxx$  are labeled  $Hhxxxx$  ( $h = 1, 2$ ).

During the least-squares refinement the OS2-CS22 bond was anomalously short, and CS22 was abnormally anisotropic. Detailed examination of this region of the structure revealed a minor amount of disordering (not greater than 25% alternative location), mainly at CS22 and with very slight displacement of OS2. A chemically reasonable disorder model did not refine satisfactorily. The ordered model refined and reported possesses flawed dimensions involving CS22.

Neutral atom scattering factors were taken from standard compilations. Anomalous dispersion<sup>6</sup> was included for the molybdenum and sulfur atoms. Friedel pairs were not measured, and no attempt was made to determine the absolute configuration.

The largest peaks in the final difference synthesis were less than  $0.83 e \text{ \AA}^{-3}$  and were in the vicinity of the molybdenum atoms. The largest electron density representing the supposed disorder in ligand 2 was  $0.55 e \text{ \AA}^{-3}$ .

Atomic coordinates are given in Table IV, and bond distances and angles are set out in Table V. A complete listing of the refined temperature factors is archived with the supplementary material. Table

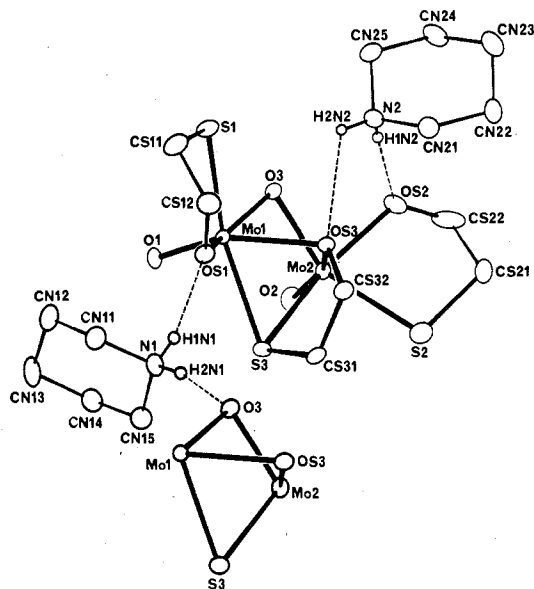


Figure 1. Crystal structure of  $(C_5H_{10}NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$ , showing the hydrogen bonds.

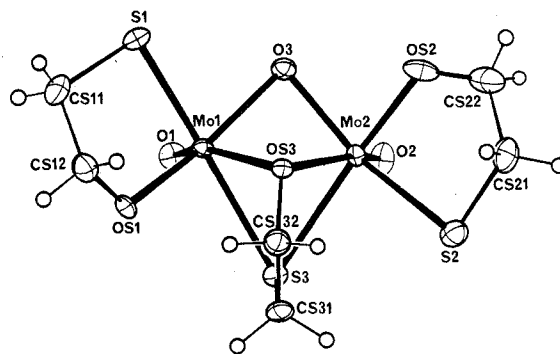
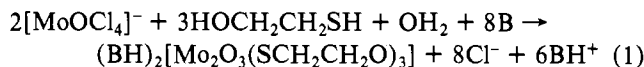


Figure 2. The  $[Mo_2O_3(SCH_2CH_2O)_3]^{2-}$  ion, viewed from the side opposite the terminal oxo ligands.

VI provides details of molecular planes.

## Results and Discussion

The interaction in alcohols of  $(Et_4N)[MoOCl_4(OH_2)]$  or other oxomolybdenum(V) precursors with 2-hydroxyethanethiol and sufficient secondary or tertiary alkylamine generates initially an intense yellow-red solution. At and above room temperature the color of this solution fades to lighter orange-red, and when the base (B) is one of the cyclic secondary amines piperidine, morpholine, or pyrrolidine, orange-red crystals of  $(BH)_2[Mo_2O_3(SCH_2CH_2O)_3]$  can be isolated. Equation 1 represents the overall reaction. Yields of these



products from mixtures based on eq 1 are up to 65% (Mo) and are maximized when water (ca. 1%) is added to that normally present in undried laboratory solvents.

Part of the crystal structure of  $(C_5H_{10}NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$  is shown in Figure 1. The triple bridge between the two MoO groups is comprised of one oxide ligand (O3) and one  $-OCH_2CH_2S-$  ligand doubly bridging at both oxygen (OS3) and sulfur (S3). Each molybdenum atom is terminally chelated by one  $-OCH_2CH_2S-$  ligand. There exist intricate hydrogen bonds involving ammonium protons and molybdenum coordinated oxygen atoms (but not the multiply bonded terminal "molybdenyl" oxygen atoms). The hydrogen bonding involving N1 links anions in the crystal and presumably contributes to the low solubility of the solid.

Table IV. Atomic Coordinates for  $(C_5H_{10}NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$ 

atom <sup>a</sup>	x	y	z	atom <sup>b</sup>	x	y	z
Mo1	0.0266 (1)	0.6483 (0) <sup>c</sup>	0.8586 (1)	H1CS11	0.3627	0.5442	0.7985
Mo2	-0.1380 (1)	0.7528 (0) <sup>c</sup>	0.9586 (1)	H2CS11	0.5126	0.5958	0.8496
S1	0.3095 (3)	0.6169 (1)	1.0114 (3)	H1CS12	0.3590	0.6770	0.6914
S2	-0.2265 (3)	0.8619 (1)	0.8411 (3)	H2CS12	0.3404	0.6159	0.5703
S3	-0.2200 (3)	0.7053 (1)	0.6579 (3)	H1CS21	-0.1680	0.9529	1.0355
O1	-0.1000 (8)	0.5802 (3)	0.8619 (9)	H2CS21	0.0019	0.9279	0.9872
O2	-0.3166 (8)	0.7226 (3)	1.0127 (10)	H1CS22	0.0163	0.8940	1.2687
O3	0.0325 (7)	0.6903 (3)	1.0854 (6)	H2CS22	-0.1622	0.8699	1.2287
OS1	0.1314 (7)	0.6356 (3)	0.6533 (7)	H1CS31	-0.1775	0.8037	0.5153
OS2	-0.0154 (9)	0.8148 (4)	1.1591 (7)	H2CS31	-0.0962	0.7440	0.4362
OS3	0.0805 (6)	0.7559 (3)	0.8288 (6)	H1CS32	0.1493	0.7643	0.6052
N1	-0.0468 (12)	0.6030 (4)	0.3199 (10)	H2CS32	0.0751	0.8293	0.6613
N2	0.3289 (10)	0.7833 (5)	1.1382 (12)	H1CN11	0.1628	0.5464	0.3361
CS11	0.3923 (14)	0.5898 (6)	0.8244 (15)	H2CN11	0.0162	0.5245	0.1848
CS12	0.3125 (13)	0.6329 (6)	0.6742 (13)	H1CN12	0.0291	0.4992	0.5369
CS21	-0.1018 (14)	0.9149 (5)	1.0169 (16)	H2CN12	0.0483	0.4452	0.4030
CS22	-0.0635 (13)	0.8705 (8)	1.1795 (13)	H1CN13	-0.2254	0.4435	0.4529
CS31	-0.1114 (12)	0.7640 (4)	0.5421 (10)	H2CN13	-0.2307	0.4591	0.2595
CS32	0.0627 (12)	0.7819 (5)	0.6569 (11)	H1CN14	-0.2646	0.5553	0.5103
CN11	0.0426 (14)	0.5393 (5)	0.3028 (13)	H2CN14	-0.4070	0.5348	0.3549
CN12	-0.0068 (16)	0.4861 (5)	0.4180 (15)	H1CN15	-0.2838	0.6368	0.3030
CN13	-0.1964 (18)	0.4757 (6)	0.3750 (16)	H2CN15	-0.2738	0.5852	0.1621
CN14	-0.2881 (15)	0.5412 (6)	0.3907 (15)	H1CN21	0.3251	0.8496	0.9425
CN15	-0.2328 (15)	0.5957 (5)	0.2815 (13)	H2CN21	0.5067	0.8319	1.0393
CN21	0.3958 (13)	0.8417 (5)	1.0552 (13)	H1CN22	0.2882	0.9172	1.1628
CN22	0.4012 (13)	0.9031 (5)	1.1638 (16)	H2CN22	0.4528	0.9386	1.1134
CN23	0.4976 (13)	0.8910 (6)	1.3518 (16)	H1CN23	0.4871	0.9300	1.4207
CN24	0.4304 (14)	0.8309 (6)	1.4303 (12)	H2CN23	0.6147	0.8852	1.3549
CN25	0.4295 (13)	0.7689 (5)	1.3174 (13)	H1CN24	0.3176	0.8396	1.4435
H1N1	-0.004 (14)	0.6181 (55)	0.407 (15)	H2CN24	0.4972	0.8226	1.5439
H2N1	-0.000 (18)	0.6326 (76)	0.248 (18)	H1CN25	0.3796	0.7233	1.3656
H1N2	0.261 (15)	0.7894 (70)	1.133 (18)	H2CN25	0.5430	0.7578	1.3114
H2N2	0.3285 (86)	0.7531 (42)	1.0679 (91)				

<sup>a</sup> Refined atoms: estimated standard deviations, in parentheses, refer to the least significant digit(s) listed. <sup>b</sup> Methylene hydrogen atoms: locations calculated but not refined. <sup>c</sup> Origin determined by  $y(\text{Mo1})$ :  $\sigma y(\text{Mo2}) = 0.000\ 04$ .

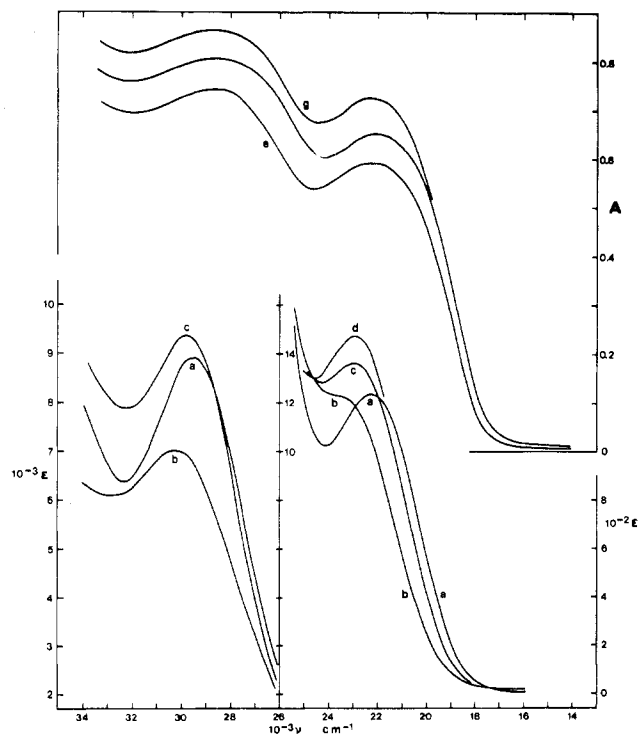


Figure 3. Electronic spectra of  $(\text{BH})_2[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]$  species, for  $(\text{C}_5\text{H}_{10}\text{NH}_2)_2[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]$  in (a) water  $11.0 \times 10^{-3}$  M, (b) propanol  $0.325 \times 10^{-3}$  M, (c) pyridine  $0.955 \times 10^{-3}$  M, and (d) acetonitrile  $0.187 \times 10^{-3}$  M, and reflectance spectra for (e) B = piperidine, (f) B = pyrrolidine, and (g) B = morpholine.

The magnetic properties, infrared spectra, and reflectance spectra (see Figure 3) indicate that the  $[\text{Mo}_2\text{O}_3-$

$(\text{SCH}_2\text{CH}_2\text{O})_3]^{2-}$  ion exists in all three isolated compounds. The polycrystalline diffraction patterns (Table I) are intriguingly similar, and in view of the very similar stereochemistry and volume of the three cyclic amines, it is possible that the three compounds have essentially the same crystal structure.

**Formation of  $[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]^{2-}$  in Solution.** Several observations on the formation of  $[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]^{2-}$  (as monitored by the crystallization of the  $\text{C}_5\text{H}_{10}\text{NH}_2^+$  salt) provide approximate information on the relative acidities of the coordinated ligands involved. Amine base in amount (eq 1) sufficient for deprotonation of coordinated  $\text{HOCH}_2\text{CH}_2\text{SH}$  and the water which forms the bridging oxide ligand is necessary for formation of  $[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]^{2-}$ . When the amine base is deficient, the complex  $[\text{Mo}_2\text{O}_2(\text{SCH}_2\text{CH}_2\text{O})_2\text{Cl}_3]^-$ , containing deprotonated  $\text{HOCH}_2\text{CH}_2\text{SH}$  but no bridging deprotonated water, is isolated. The high acidity of coordinated  $\text{HOCH}_2\text{CH}_2\text{SH}$  in bridging positions has been noted previously<sup>4</sup> in connection with the preparation of  $[\text{Mo}_2\text{O}_2(\text{SCH}_2\text{CH}_2\text{O})_2\text{Cl}_3]^-$ . Three observations demonstrate the acidity of the conjugate acid  $\text{Mo}-\text{O}(\text{H})-\text{Mo}$  of the oxide bridge in  $[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]^{2-}$ . First, the acid  $\text{HOCH}_2\text{CH}_2\text{SH}$  ( $\text{p}K_a = 9.5$  (SH)) in excess of the amount specified by eq 1 does not appear to diminish the formation of  $[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]^{2-}$ . Second, isolated  $[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]^{2-}$  does not react with  $\text{HOCH}_2\text{CH}_2\text{SH}$ . Third, morpholine (conjugate acid  $\text{p}K_a = 8.33$ ) is sufficient for formation of the oxide bridge.

Synthetic reactions with amines other than piperidine ( $\text{p}K_a = 11.1$ ), pyrrolidine ( $\text{p}K_a = 11.3$ ), or morpholine ( $\text{p}K_a = 8.3$ ) have not crystallized analogous compounds  $(\text{BH}^+)_2[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]$ . The amines used were tripropylamine ( $\text{p}K_a = 10.5$ ), dipropylamine ( $\text{p}K_a = 11.0$ ), *N*-methylmorpholine ( $\text{p}K_a = 7.4$ ), *N*-ethylmorpholine ( $\text{p}K_a = 7.7$ ), *N*-methylaniline ( $\text{p}K_a = 4.8$ ), and dicyclohexylamine ( $\text{p}K_a = 11.3$ ). It is sur-

Table V. Bond Distances (Å) and Angles (deg) in  $(C_5H_{10}NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$ 

Molybdenum Coordination			
Mo1-O1	1.700 (5) <sup>a</sup>	Mo2-S3	2.492 (2)
Mo2-O2	1.698 (6)	Mo1-O3	1.956 (5)
Mo1-S1	2.418 (2)	Mo2-O3	1.957 (6)
Mo2-S2	2.406 (3)	Mo1-OS3	2.209 (6)
Mo1-OS1	1.990 (5)	Mo2-OS3	2.220 (5)
Mo2-OS2	2.072 (6)	Mo1-Mo2	2.676 (1)
Mo1-S3	2.521 (2)		
O1-Mo1-S1	107.0 (2) <sup>a</sup>	S2-Mo2-OS2	78.8 (2)
O1-Mo1-OS1	105.9 (3)	S3-Mo1-O3	103.5 (2)
O1-Mo1-S3	88.5 (2)	S3-Mo2-O3	104.6 (2)
O1-Mo1-O3	102.9 (3)	O1-Mo1-OS3	155.1 (3)
O2-Mo2-S2	102.6 (2)	O2-Mo2-OS3	157.9 (3)
O2-Mo2-OS2	108.2 (3)	S3-Mo1-OS1	88.2 (2)
O2-Mo2-S3	92.1 (3)	S3-Mo2-S2	89.1 (1)
O2-Mo2-O3	100.9 (3)	Mo1-O3-Mo2	86.3 (2)
S1-Mo1-OS1	81.2 (2)	Mo1-S3-Mo2	64.5 (1)
		Mo1-OS3-Mo2	74.3 (2)
2-Oxoethanethiolate Ligands			
S1-CS11	1.82 (1)	OS3-CS32	1.42 (1)
S2-CS21	1.85 (1)	CS11-CS12	1.49 (2)
S3-CS31	1.819 (8)	CS21-CS22	1.53 (2) <sup>b</sup>
OS1-CS12	1.44 (1)	CS31-CS32	1.54 (1)
OS2-CS22	1.20 (2) <sup>b</sup>		
Mo1-S1-CS11	98.6 (4)	Mo2-OS3-CS32	121.3 (5)
Mo2-S2-CS21	99.4 (4)	S1-CS11-CS12	107.2 (7)
Mo1-S3-CS31	101.5 (3)	S2-CS21-CS22	105.6 (8)
Mo2-S3-CS31	99.8 (3)	S3-CS31-CS32	109.6 (5)
Mo1-OS1-CS12	120.9 (5)	OS1-CS12-CS11	111.5 (8)
Mo2-OS2-CS22	122.6 (7) <sup>b</sup>	OS2-CS22-CS21	115.9 (0) <sup>b</sup>
Mo1-OS3-CS32	118.1 (5)	OS3-CS32-CS31	111.2 (7)
Piperidinium Cations			
N1-CN11	1.48 (1)	CN21-CN22	1.49 (1)
N1-CN15	1.47 (1)	CN22-CN23	1.53 (2)
N2-CN21	1.49 (1)	CN23-CN24	1.50 (2)
N2-CN25	1.49 (1)	CN24-CN25	1.52 (1)
CN11-CN12	1.50 (1)	N1-H1N1	0.75 (11)
CN12-CN13	1.51 (2)	N1-H2N1	0.95 (15)
CN13-CN14	1.52 (2)	N2-H1N2	0.55 (12)
CN14-CN15	1.51 (2)	N2-H2N2	0.82 (15)
CN11-N1-CN15	113.1 (8)	CN12-CN13-CN14	110.7 (9)
CN21-N2-CN25	112.8 (7)	CN13-CN14-CN15	111.2 (9)
N1-CN11-CN12	110.5 (8)	CN21-CN22-CN23	111.6 (9)
N1-CN15-CN14	111.7 (8)	CN22-CN23-CN24	111.6 (8)
N2-CN21-CN22	111.1 (8)	CN23-CN24-CN25	111.4 (8)
N2-CN25-CN24	109.0 (8)	H1N1-N1-H2N1	97 (11)
CN11-CN12-CN13	110.7 (9)	H1N2-N2-H2N2	105 (15)
Hydrogen Bonds			
H1N1...OS1	2.03 (12)	H2N2...OS3	2.43 (7)
H2N1...O3 <sup>c</sup>	1.78 (15)	H2N2...O3	2.72 (8)
H1N2...OS2	2.34 (12)	H2N2...S1	2.73 (11)
N1-H1N1-OS1	166 (11)	N2-H2N2-OS3	113 (5)
N1-H2N1-O3 <sup>c</sup>	166 (13)	N2-H2N2-O3	100 (7)
N2-H1N2-OS2	171 (17)	N2-H2N2-S1	146 (10)

<sup>a</sup> Esd's in parentheses refer to the least significant digit(s) listed.

<sup>b</sup> Very uncertain dimension, due to crystallographic disorder; see text. <sup>c</sup> Lattice transformation ( $x, y, z - 1$ ).

prising that dipropylamine has not yielded a crystalline product. However, in all cases the solution colors which developed during the reactions are very similar to the color of mixtures containing cyclic secondary amines. Therefore it is probable that  $[Mo_2O_3(SCH_2CH_2O)_3]^{2-}$  is at least partially formed in all such solutions and that the noncrystallization of the expected ammonium salts is a consequence of their greater solubility. Addition of piperidinium hydrochloride to these solutions does not lead to crystallization of appreciable amounts of  $(C_5H_{10}NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$ . All indications are that complex hydrogen bonding upsets expected solubilities

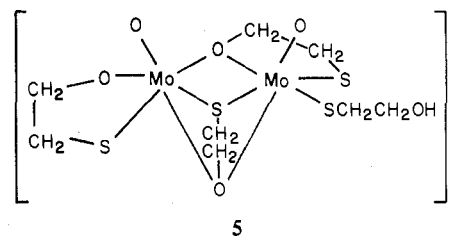
Table VI

Atom Displacements (Å) from Molecular Planes			
atom	plane		
	Mo1 equator	Mo2 equator	bridging chelate ligand
Mo1	(+0.39) <sup>a</sup>		
Mo2		(+0.40) <sup>a</sup>	
S1	+0.07		
S2		0.0	
S3	+0.06	0.0	-0.02
O3	-0.06	-0.01	(+0.06) <sup>a</sup>
OS1	-0.07		
OS2		+0.01	
OS3			+0.03
CS31			+0.04
CS32			-0.05
plane coeff <sup>b</sup>	plane		
	Mo1 equator	Mo2 equator	bridging chelate ligand
<i>l</i>	-0.4709	-0.9056	-0.5359
<i>m</i>	-0.8792	-0.2595	0.7853
<i>n</i>	0.0728	0.3355	0.3101
<i>p</i>	-10.665	0.669	14.163

<sup>a</sup> Values in parentheses were excluded from least-squares plane calculations. <sup>b</sup> Planes  $lX + mY + nZ - p = 0$  are defined for the orthogonal system  $X \parallel a, Y \parallel b, Z \parallel c^*$ .

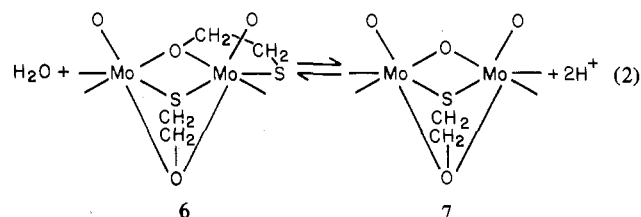
in solutions with mixed solvents and/or mixed amines and their conjugate acids. It cannot be concluded that  $[Mo_2O_3(SCH_2CH_2O)_3]^{2-}$  is not formed in these solutions. Spectrophotometric investigation of the content of these solutions has not been conclusive, because the possible complexes have similar spectra, and the spectrum of  $[Mo_2O_3(SCH_2CH_2O)_3]^{2-}$  is solvent dependent (Figure 3, see below).

More than one type of complex is formed in these preparative solutions. Thus, the 2:12:12  $[MoOCl_4(OH_2)]^- - HOCH_2CH_2SH - C_5H_{10}NH$  mixture in propanol crystallizes  $(C_5H_{10}NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$ , while the comparable mixture with tripropylamine in place of piperidine crystallizes instead  $(Et_4N)[Mo_2O_2(SCH_2CH_2O)_3(SCH_2CH_2OH)]$  in small yield. Crystal structure determination<sup>7</sup> has established that the anion in this latter complex has the same triply bridged structure, **5**, as that previously described for  $(Pr_3NH)[Mo_2O_2(SCH_2CH_2O)_3(SCH_2CH_2OH)]$ .



Similar reactions with other bases, including  $K_2CO_3(s)$ ,  $OH^-(solvent)$ , and  $^-OCH_3(solvent)$ , generate different products which are still uncharacterized.

Interconversion between the two types of triple bridge, eq 2, has so far been effected only in one direction. Reaction of



$(Et_4N)[Mo_2O_2(SCH_2CH_2O)_2Cl_3]$  with  $HOCH_2CH_2SH$  and

piperidine has produced  $(C_5H_{10}NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$ . However, there is no evidence yet that  $HOCH_2CH_2SH$  as acid is able to remove the oxo bridge in  $[Mo_2O_3(SCH_2CH_2O)_3]^{2-}$ .

**Structure of  $[Mo_2O_3(SCH_2CH_2O)_3]^{2-}$ .** Details of the structure are provided in Figures 1 and 2 and Tables V and VI. The structurally significant component of the complex anion is the linkage of the pair of multiply bonded Mo–O<sub>t</sub> groups by three chemically different bridging functions, thiolate sulfur (S3), alkoxide oxygen (OS3), and oxide (O3). The dominating influence of the terminal oxygen atom O<sub>t</sub> on each molybdenum atom is seen in the elongation (ca. 0.2 Å) of the bonds to the bridging atom (OS3) trans to both O<sub>t</sub>. The coordination stereochemistry of each molybdenum atom is best described as square pyramidal with more distant coordination trans to the apical atom O<sub>t</sub>. Similarly the bridge is described best in terms of the basal-edge fusion of two coordination square pyramids. The molybdenum atoms are displaced 0.39 and 0.40 Å from their well-defined basal coordination planes. The external dihedral angle between these basal coordination planes (previously<sup>4</sup> denoted β) is 227°, and the external dihedral angle between the planes Mo1, O3, S3 and Mo2, O3, S3 (α<sup>4</sup>) is 193°.

The three bridging atoms S3, OS3 and O3, together with the two carbon atoms of the bridging ligand, are coplanar within 0.06 Å, and the Mo–Mo vector is 2° from the perpendicular to this plane. Within this bridging plane OS3 is displaced 0.40 Å from the Mo1, Mo2, O1, O2 plane, on the same side as S3.

Each molybdenum atom is asymmetrically coordinated by six different functions: one bridging and one terminal thiolate (at mean distances 2.51 and 2.41 Å, respectively); one bridging and one terminal alkoxide (mean distances 2.21 and 2.04 Å, respectively); one bridging and one terminal oxide (mean distances 1.96 and 1.70 Å, respectively). A curious feature is the difference in the geometrical isomers adopted by the two terminally chelating  $^-OCH_2CH_2S^-$  ligands. In the Mo1 basal plane S1 is trans to S3, whereas in the Mo2 basal plane S2 is cis to S3. Possibly the energies of interion hydrogen bonding (particularly that of OS1 and O3) and associated lattice packing outweigh the energy advantages of coordination geometrical isomers. There exist three well-defined hydrogen bonds involving H1N1, H2N1, H1N2 and OS1, O3, OS2, respectively. Although H2N2 is closest to OS3 (see Figure 1), the N2–H2N2 bond is directed between OS3, O3, and S1 (see Figure 1 and Table V), and any hydrogen bonding by H2N2 must be regarded as very weak.

There are two structure types with which the geometry of  $[Mo_2O_3(SCH_2CH_2O)_3]^{2-}$  should be compared, namely,  $[Mo_2O_3(SCH_2CH_2O)(ox)_2]$  (Hox = 8-hydroxyquinoline),<sup>8</sup> which has the same triple-bridge structure 7, and the three  $^-OCH_2CH_2S^-$  complexes<sup>4</sup> with the triple-bridge structure 6. There are no significant geometrical differences between the bridges in  $[Mo_2O_3(SCH_2CH_2O)_3]^{2-}$  and  $[Mo_2O_3(SCH_2CH_2O)(ox)_2]$ . However, both ox ligands in  $[Mo_2O_3-$

$(SCH_2CH_2O)(ox)_2]$  have nitrogen trans to the bridging sulfur atom. The difference between oxide and alkoxide oxygen in the bridge is a shortening of 0.07 Å in the Mo–O distance and ca. 0.06 Å in the Mo–Mo distance.

**Spectra.** The infrared spectra (Table II) contain numerous absorptions, in agreement with the low symmetry of the complex, and detailed assignments cannot yet be made. It is noted that a 755-cm<sup>-1</sup> frequency in  $[Mo_2O_3(SCH_2CH_2O)(ox)_2]$ , assigned<sup>8</sup> as Mo–O–Mo, is not present in the infrared spectra of  $(BH)_2[Mo_2O_3(SCH_2CH_2O)_3]$  which show no absorption between 740 and 830 cm<sup>-1</sup>.

The electronic spectra of solid and solution phases contain essentially two bands, at ca. 23 000 cm<sup>-1</sup> ( $\epsilon(Mo_2) \sim 1400 M^{-1} cm^{-1}$ ) and at ca. 30 000 cm<sup>-1</sup> ( $\epsilon(Mo_2) \sim 9000 M^{-1} cm^{-1}$ ). Both bands are slightly solvent dependent, occurring at lowest energy in water. This fact, together with the absorption intensity, indicates charge-transfer character for the transitions involved. The 30 000-cm<sup>-1</sup> band is similar in energy and intensity to an analogous band<sup>4</sup> in  $[Mo_2O_2(SCH_2CH_2O)_2Cl_3]^-$  and  $[Mo_2O_2(SCH_2CH_2O)_3Cl]^-$ . Abbreviated information only is available for  $[Mo_2O_3(SCH_2CH_2O)(ox)_2]$ ; namely, a broad band occurs at 390 nm (25 600 cm<sup>-1</sup>) ( $\epsilon \sim 600$ ) and a peak at 252 nm (39 700 cm<sup>-1</sup>) ( $\epsilon \sim 2000$ ).<sup>8</sup> It is probable that the 25 600-cm<sup>-1</sup> band corresponds to the 23 000-cm<sup>-1</sup> band in  $[Mo_2O_3(SCH_2CH_2O)_3]$  and that absorption in this vicinity is characteristic of the type 4 bridge. Absorption of comparable intensity in this region is not present in  $[Mo_2O_2(SCH_2CH_2O)_2Cl_3]^-$ . Further investigations in progress should provide more information about the electronic transitions of this system.

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**Registry No.**  $(C_5H_{10}NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$ , 71382-10-0;  $(OC_4H_8NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$ , 71484-71-4;  $(C_4H_8NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$ , 71424-36-7;  $(Et_4N)[Mo_2O_2(SCH_2CH_2O)_2Cl_3]$ , 71382-12-2;  $(Et_4N)[MoOCl_4(OH)_2]$ , 57127-49-8;  $(Et_4N)_2[MoO_2(NCS)_4]$ , 52486-94-9.

**Supplementary Material Available:** Supplementary Table 1, refined atom thermal parameters, and supplementary Table 2, structure factor amplitudes,  $\times 10$ , for  $(C_5H_{10}NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$  (13 pages). Ordering information is given on any current masthead page.

## References and Notes

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