

## Oxo/Sulfido Ligand Substitution in $[\text{Mo}_2\text{O}_7]^{2-}$ : Reaction Sequence and Characterization of the Final Product, $[\text{MoS}_3(\text{OSiMe}_3)]^-$

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The oxo/sulfido ligand substitution reactions of one of the simplest polyoxometalates,  $[\text{Mo}_2\text{O}_7]^{2-}$ , were examined in acetonitrile solutions containing  $n = 1-7$  equiv of hexamethyldisilthiane,  $(\text{Me}_3\text{Si})_2\text{S}$ , a reagent previously shown capable of this reaction with monooxo species. Complementary use of multinuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{17}\text{O}$ ,  $^{95}\text{Mo}$ ) revealed formation of the mononuclear products  $[\text{MoO}_{3-x}\text{S}_x(\text{OSiMe}_3)]^-$  ( $x = 0-3$ ). The presence of  $\text{Mo}=\text{S}$  groups was further indicated by absorption spectra. Both  $^{17}\text{O}$  and  $^{95}\text{Mo}$  resonances are monotonically deshielded as  $x$  increases, a behavior analogous to that in the series  $[\text{MoO}_{4-x}\text{S}_x]^{2-}$  ( $x = 0-4$ ) in acetonitrile, whose chemical shifts are also reported. Product distribution and other observations suggest that some  $\text{Mo(VI)}$  is reduced, presumably to dimeric  $\text{Mo(V)-S}$  species. A distribution of products was observed at  $n < 5$ . At  $n = 6-7$  formation of the final product,  $[\text{MoS}_3(\text{OSiMe}_3)]^-$ , was complete. This anion was synthesized and isolated in 31% purified yield as its  $\text{Ph}_4\text{P}^+$  salt.  $(\text{Ph}_4\text{P})[\text{MoS}_3(\text{OSiMe}_3)]^-$  crystallizes in monoclinic space group  $P2_1/n$  with  $a = 15.179$  (5) Å,  $b = 12.067$  (5) Å,  $c = 17.262$  (6) Å,  $\beta = 109.11$  (3)°, and  $Z = 4$ . Structure refinement based on 1883 unique data ( $F_o^2 > 2.5(F_c)^2$ ) gave  $R$  ( $R_w$ ) = 4.8 (4.7)%. The anion is mononuclear and tetrahedral with  $\text{Si}-\text{O}-\text{Mo} = 146.6$  (4)°,  $\text{Mo}-\text{O} = 1.881$  (7) Å, and mean  $\text{Mo}-\text{S} = 2.154$  (6) Å. The compound is a 1:1 electrolyte in acetonitrile, supporting a similar formulation for other salts of the  $[\text{MoO}_{3-x}\text{S}_x(\text{OSiMe}_3)]^-$  series, and has an absorption spectrum with  $\lambda_{\text{max}} = 283, 403,$  and  $534$  nm, similar to that of the trigonal species  $[\text{MoOS}_3]^{2-}$ . Series members are of the general type  $[\text{MY}_3\text{X}]^{9-}$ , in which  $\text{Y}$  is a double- and  $\text{X}$  is a single-bonded ligand;  $[\text{MoS}_3(\text{OSiMe}_3)]^-$  is the only well-characterized  $\text{Mo}$  species of this type.

### Introduction

As observed in our recent report of the syntheses and structures of the unprecedented cage complexes  $[\text{M}_6\text{S}_{17}]^{4-}$  ( $\text{M} = \text{Nb}, \text{Ta}$ ), a new class of transition-element compounds is emerging in the form of soluble salts containing discrete thiometalate anions. Existence of such species is largely confined to the early transition elements. With molybdenum, an extensive series of structurally defined species has already been developed:  $[\text{MoS}_4]^{2-}$ ,  $[\text{MoS}_9]^{2-}$ ,  $[\text{Mo}_2\text{S}_8]^{2-}$ ,  $[\text{Mo}_2\text{S}_{10}]^{2-}$ ,  $[\text{Mo}_2\text{S}_{12}]^{2-}$ ,  $[\text{Mo}_3\text{S}_9]^{2-}$ , and  $[\text{Mo}_3\text{S}_{13}]^{2-}$ .<sup>7,10</sup> In these anions the metal is coordinated by sulfide, persulfide, or polysulfide, the first two of which function as terminal or bridging ligands. In the case of  $[\text{Mo}_2\text{S}_{10}]^{2-}$ , i.e.,  $[\text{Mo}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2)(\text{S}_4)]^{2-}$ , all ligation modes are present. Thiometalate anions of highest nuclearity are  $[\text{M}_6\text{S}_{17}]^{4-}$  followed by  $[\text{W}_4\text{S}_{12}]^{2-}$ .<sup>11</sup> A more restricted set of discrete oxothiometalate anions is known. With molybdenum, these include  $[\text{MoO}_{4-n}\text{S}_n]^{2-}$  ( $n = 1-3$ ),<sup>2,12</sup>  $[\text{MoOS}_3]^{2-}$ ,<sup>3,4</sup>  $[\text{Mo}_2\text{O}_2\text{S}_6]^{2-}$ ,<sup>13</sup> and  $[\text{Mo}_2\text{O}_4\text{S}_7]^{2-}$ .<sup>14</sup> The majority of the two types of anions are derived ultimately from  $[\text{MoS}_4]^{2-}$  by protolysis, thermolysis, or reaction with elemental sulfur, organic trisulfides, or aqueous polysulfide. Certain

of these reactions involve oxidation of sulfide to  $\text{S}_2^{2-}$  and, in all cases, at least partial reduction of  $\text{Mo(VI)}$  to  $\text{Mo(V, IV)}$ .

The foregoing species raise the engaging question as to the existence and stability of thiometalates and oxothiometalates of higher nuclearity possibly analogous to some members of the extensive set of polyoxometalates of molybdenum and other metals.<sup>15</sup> Indeed, Pope<sup>15a</sup> has implicitly raised this question by suggesting that substitution of oxygen by sulfur in oxometalates "should be possible to a limited extent". If the high-nuclearity cage structures of precursor oxometalates are to be maintained, the substitution process must allow oxo replacement in the pervasive terminal and bridging fragments  $\text{M}=\text{O}$  and  $\text{M}_n(\mu_{2,3}\text{-O})$ , respectively, without cage fragmentation and reduction. This suggests the use of a mild, neutral reagent. Recent work in this laboratory has demonstrated that terminal and bridging oxo atoms are replaceable by sulfide under mild conditions with use of hexamethyldisilthiane,<sup>16,17</sup>  $(\text{Me}_3\text{Si})_2\text{S}$ . We have become interested in the utility of this reagent in effecting O/S substitution reactions in polyoxometalates. Reactions at terminal (t) sites are expected to occur more readily than at bridging (b) ligands, and the possibility of  $\text{S}=\text{M}-\text{O}_b^-$  to  $\text{O}=\text{M}-\text{S}_b^-$  rearrangement is raised by the exclusive function of oxo as a terminal ligand in the foregoing oxothiomolybdates.

We have initiated our studies of O/S substitution reactions in polyoxometalates by a detailed examination of the reactions of one of the simplest such species,  $[\text{Mo}_2\text{O}_7]^{2-}$ , with  $(\text{Me}_3\text{Si})_2\text{S}$  in acetonitrile solution. The discrete anion has been structurally characterized in a number of salts in which it has corner-shared  $\text{MoO}_4$  tetrahedra with either linear<sup>18</sup> or nonlinear<sup>19,20</sup>  $\text{Mo}-\text{O}-\text{Mo}$  bridges. Previously described reactions of  $[\text{Mo}_2\text{O}_7]^{2-}$  are limited and include condensation of  $[\text{Mo}_7\text{O}_{24}]^{6-}$  in wet acetonitrile induced by precipitation of insoluble salts of the latter,<sup>19</sup> formation of  $[\text{CpTiMo}_5\text{O}_{18}]^{3-}$  from  $\text{Cp}_2\text{TiCl}_2$  in moist aprotic solvent,<sup>21</sup> hydrolysis to  $[\text{Mo}_5\text{O}_{17}\text{H}]^{3-}$ <sup>22</sup> and formation of  $[\text{RCHMo}_4\text{O}_{15}\text{H}]^{3-}$  with aldehydes.<sup>23</sup> The course of reactions in the system

- (1) Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 7794; *Inorg. Chem.*, in press.
- (2) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934 and references therein.
- (3) Simhon, E. D.; Baenziger, N. C.; Kanatzidis, M.; Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1981**, *103*, 1218.
- (4) Draganjac, M.; Simhon, E.; Chan, L. T.; Kanatzidis, M.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321.
- (5) Pan, W.-H.; Harmer, M. A.; Halbert, T. R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 459.
- (6) Clegg, W.; Christou, G.; Garner, C. D.; Sheldrick, G. M. *Inorg. Chem.* **1981**, *20*, 1562.
- (7) Müller, A.; Bhattacharyya, R. G.; Pfefferkorn, B. *Chem. Ber.* **1979**, *112*, 778.
- (8) Müller, A.; Nolte, W. O.; Krebs, B. *Inorg. Chem.* **1980**, *19*, 2835.
- (9) Pan, W.-H.; Leonowicz, M. E.; Stiefel, E. I. *Inorg. Chem.* **1983**, *22*, 672.
- (10) Müller, A.; Pohl, S.; Dartmann, M.; Cohen, J. P.; Bennett, J. M.; Kirchner, R. M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 434.
- (11) Secheresse, F.; Lefebvre, J.; Daran, J. C.; Jeannin, Y. *Inorg. Chem.* **1982**, *21*, 1311.
- (12) McDonald, J. W.; Friesen, D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205.
- (13) (a) Rittner, W.; Müller, A.; Neumann, A.; Bather, W.; Sharma, R. C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 530. (b) Clegg, W.; Mohan, N.; Müller, A.; Neumann, A.; Rittner, W.; Sheldrick, G. M. *Inorg. Chem.* **1980**, *19*, 2066. (c) Clegg, W.; Sheldrick, G. M.; Garner, C. D.; Christou, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2784. (d) Müller, A.; Krickemeyer, E.; Reinsch, U. *Z. Anorg. Allg. Chem.* **1980**, *470*, 35.
- (14) Müller, A.; Reinsch-Vogell, U.; Krickemeyer, E.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 796.

- (15) (a) Pope, M. T. "Heteropoly and Isopoly Oxometallates"; Springer-Verlag: Berlin, 1983 (cf. p 135). (b) Tsigdinos, G. A. *Top. Curr. Chem.* **1978**, *76*, 1.
- (16) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3809.
- (17) Dorfman, J. R.; Girerd, J.-J.; Simhon, E. D.; Stack, T. D.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 4407.
- (18) Becher, H. J.; Fenske, D. *J. Chem. Res. Synop.* **1978**, 167.
- (19) Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 6146.
- (20) Stadnicka, K.; Haber, J.; Kozłowski, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 3859.
- (21) Klemperer, W. G.; Shum, W. *J. Chem. Soc., Chem. Commun.* **1979**, 60.
- (22) Filowitz, M.; Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1978**, *100*, 2580.

$[\text{Mo}_2\text{O}_7]^{2-}/(\text{Me}_3\text{Si})_2\text{S}$ , as deduced primarily from multinuclear NMR experiments, and full characterization of the final reaction product,  $[\text{MoS}_3(\text{OSiMe}_3)]^-$ , are reported here.

### Experimental Section

**Preparation of Compounds.** All operations were performed under a pure dinitrogen atmosphere. Solvents were freshly dried and distilled before use. Anhydrous diethyl ether (Mallinckrodt), hexamethyldisilthiane (Petrarch Systems, Inc.), and (*n*-Bu<sub>4</sub>N)OH in methanol (Aldrich) were used as received. The compound  $(\text{Ph}_4\text{P})(\text{NO}_3)$  was prepared by metathesis. To a cold concentrated solution of 3.0 g (8.0 mmol) of  $\text{Ph}_4\text{PCl}$  in water was added a concentrated aqueous solution of 0.78 g (9.2 mmol) of  $\text{NaNO}_3$ . Needle-shaped crystals formed immediately and were collected by filtration. This material was washed with cold 9:1 v/v ether/ethanol and ether and was dried in vacuo; 2.22 g (69%) of product was obtained.  $(n\text{-Bu}_4\text{N})_2[\text{Mo}_2\text{O}_7]$  was prepared by the method of Filowitz et al.<sup>24</sup> from  $\alpha\text{-}(n\text{-Bu}_4\text{N})_4[\text{Mo}_8\text{O}_{26}]$  and (*n*-Bu<sub>4</sub>N)OH. Enrichment in <sup>17</sup>O was accomplished by a procedure similar to that previously described.<sup>24</sup> A solution of 6.0 g (7.6 mmol) of  $(n\text{-Bu}_4\text{N})_2[\text{Mo}_2\text{O}_7]$  in 45 mL of acetonitrile was treated with 274  $\mu\text{L}$  (7.6 mmol) of 50% <sup>17</sup>OH<sub>2</sub> (Monsanto Research Corp.). After the solution was stirred for 1 h, sufficient ether was added to cause the separation of 5.4 g of enriched product. The calculated enrichment level is 11% <sup>17</sup>O on the assumption of complete incorporation of added <sup>17</sup>O.

**$(\text{Ph}_4\text{P})[\text{MoS}_3(\text{OSiMe}_3)]$ .** To a vigorously stirred solution of 0.29 g (0.34 mmol) of  $(n\text{-Bu}_4\text{N})_2[\text{Mo}_2\text{O}_7]$  in 60 mL of acetonitrile was added dropwise 0.54 mL (2.60 mmol) of  $(\text{Me}_3\text{Si})_2\text{S}$ . The colorless solution changed sequentially to yellow, orange, and dark red and then to bright red after being stirred for 24 h at room temperature. The red oily residue from solvent removal was treated with a solution of 0.30 g (0.75 mmol) of  $(\text{Ph}_4\text{P})\text{NO}_3$  in 30 mL of acetone. After the bright red solution was stirred for 30 min, solvent was removed. Addition of ~30 mL of ethanol to the residual solid, with stirring gave a finely crystalline, bright red solid. This material was collected by filtration and thoroughly washed with 4:1 v/v ether/ethanol and with ether. The crude product was dissolved in ~30 mL of acetone, and ether was added until the solution became turbid. A small amount of amorphous brown-red solid usually separated when the mixture was maintained at -20 °C for ~2 h. This material was removed by filtration. The bright red filtrate was treated with ether until cloudiness developed. (If more brown-red solid appeared at this point, it was separated by filtration and additional ether was added to turbidity.) Storage at -20 °C for at least 1 day caused separation of red crystals. These were collected, washed with ether, and dried in vacuo, affording 0.14 g (31%) of product. Anal. Calcd for C<sub>27</sub>H<sub>29</sub>MoOPS<sub>3</sub>Si: C, 52.25; H, 4.71; Mo, 15.46; P, 4.99; S, 15.50; Si, 4.52. Found: C, 52.34; H, 4.72; Mo, 15.58; P, 5.10; S, 15.56; Si, 4.70. Absorption spectrum (acetonitrile):  $\lambda_{\text{max}}$  283 ( $\epsilon_{\text{M}}$  11 400), 403 (6000), 534 (1380) nm. IR spectrum (acetonitrile): 1249 (m,  $\nu_{\text{SiC}}$ ), 891 (s,  $\nu_{\text{SiO}}$ ), 845 (m), 750 (w), 741 (w, sh), 512 (s,  $\nu_{\text{MoS}}$ ), 503 (w, sh,  $\nu_{\text{MoS}}$ ) cm<sup>-1</sup>.

**Preparation of Solutions and Spectroscopic Measurements.** The reaction systems  $(n\text{-Bu}_4\text{N})_2[\text{Mo}_2\text{O}_7]/n(\text{Me}_3\text{Si})_2\text{S}$  in acetonitrile have been investigated by several spectroscopic methods. All solutions were prepared and all measurements made under a pure dinitrogen atmosphere. Acetonitrile was freshly distilled from CaH<sub>2</sub>. Typically, ~0.25 g of the Mo compound was dissolved in 30 mL of acetonitrile. The desired number of equivalents  $n = 0.5\text{--}7$  of  $(\text{Me}_3\text{Si})_2\text{S}$  was added, and the solution was stirred at room temperature for 24 h. All volatile components were removed in vacuo at room temperature, affording yellow to red oily residues. For multinuclear NMR experiments the residue was dissolved in 1.2–1.5 mL of CD<sub>3</sub>CN, affording solutions with  $[\text{Mo}] = 0.4\text{--}0.6$  M. For other measurements the residues were dissolved in volumes of acetonitrile sufficient to give solutions with  $[\text{Mo}] = (0.4\text{--}1.7) \times 10^{-2}$  and  $\sim 3 \times 10^{-2}$  M; these were used for UV/visible and FT-IR studies, respectively. NMR spectra were obtained with a Bruker WM-300 spectrometer operating at 300.13 (<sup>1</sup>H), 59.63 (<sup>29</sup>Si), 40.69 (<sup>17</sup>O), and 19.56 (<sup>95</sup>Mo) MHz for the indicated nuclei. Samples containing <sup>95</sup>Mo, <sup>17</sup>O, and <sup>29</sup>Si were measured in 10 mm o.d. NMR tubes equipped with vortex plugs. Chemical shifts are reported vs. external standards: Me<sub>3</sub>Si (<sup>1</sup>H, <sup>29</sup>Si); 3:1 v/v H<sub>2</sub>O (enriched)/CD<sub>3</sub>CN (<sup>17</sup>O); 2 M Na<sub>2</sub>MoO<sub>4</sub> in pH 11 aqueous solution (<sup>95</sup>Mo). Shifts downfield of the references are designated as positive. The <sup>17</sup>O reference is +0.03 ppm different from the signal of tap water. In the cases of <sup>17</sup>O and <sup>95</sup>Mo, whose signals span nearly 1000 and 2000 ppm, respectively, spectral widths and data collection parameters were employed that afforded reliable relative signal

**Table I.** Summary of Crystal Data, Intensity Collection, and Structure Refinement for  $(\text{Ph}_4\text{P})[\text{MoS}_3(\text{OSiMe}_3)]$

formula (mol wt)	C <sub>27</sub> H <sub>29</sub> MoOPS <sub>3</sub> Si (620.72)
<i>a</i> , Å	15.179 (5)
<i>b</i> , Å	12.067 (5)
<i>c</i> , Å	17.262 (6)
$\beta$ , deg	109.11 (3)
cryst syst	monoclinic
<i>V</i> , Å <sup>3</sup>	2988 (2)
<i>Z</i>	4
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.38
<i>d</i> <sub>obsd</sub> , g/cm <sup>3</sup>	1.39 <sup>a</sup>
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
cryst dimens, mm	0.28 × 0.13 × 0.32
radiation	Mo K $\alpha$ ( $\lambda = 0.71069$ Å)
abs coeff, $\mu$ , cm <sup>-1</sup>	7.4
scan speed, deg/min	2.0–29.3 ( $\theta/2\theta$ scan)
$2\theta$ limits, deg	3.0 ≤ $2\theta$ ≤ 43
scan range, deg	1.6 + ( $2\theta_{\text{K}\alpha_1} - 2\theta_{\text{K}\alpha_2}$ )
bkgd/scan time ratio	0.1
data collected	3450 (+ <i>h</i> , + <i>k</i> , ± <i>l</i> )
unique data ( $F_o^2 > 2.5\sigma(F_o^2)$ )	1883
no. of variables	268
goodness of fit (GOF) <sup>b</sup>	1.13
<i>R</i> , % <sup>c</sup>	4.8
<i>R</i> <sub>w</sub> , % <sup>d</sup>	4.7

<sup>a</sup> Determined by the neutral buoyancy technique in CCl<sub>4</sub>/*n*-hexane.

<sup>b</sup> GOF =  $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observs}} - N_{\text{parameters}})]^{1/2}$ ;  $w = [\sigma^2(F) + gF^2]^{-1}$ , with  $g = 0.00087$ . <sup>c</sup>  $R = [\sum ||F_o| - |F_c|| / \sum |F_o|]$ . <sup>d</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ .

intensities in a given spectrum. The <sup>95</sup>Mo FT NMR spectrum of each sample was obtained by taking a wide sweep and a series of sectional measurements. The first measurement provided overall features of the spectrum with regard to number and positions of peaks. These signals were grouped into sets, each set consisting of two adjacent signals and two adjacent sets having a common peak as an internal reference for intensity normalization. A series of sectional measurements were made on these sets. Wide-sweep spectra were recorded over a 55 555-Hz spectral bandwidth by using 140- $\mu\text{s}$  pulse width (90° pulse), 16 384 data words, 4- $\mu\text{s}$  preacquisition delay time, 6.77-Hz pulse repetition rate, 28 000-Hz transmitter offset, and 5000 acquisitions. Parameters for a series of sectional measurements were the following: 14 286–15 625-Hz spectral bandwidth, 8192 data words, 16–17.8- $\mu\text{s}$  pulse width (10.3–11.4° pulse), 17- $\mu\text{s}$  preacquisition delay time, 3.48–3.82-Hz pulse repetition rate, three different transmitter offsets based on the positions of peaks (14 748, 26 562, and 39 149 Hz), and 15 000 acquisitions. In both cases, the first few offending points of FID were discarded to correct the pulse breakthrough, and a 5-Hz exponential line broadening was applied. <sup>17</sup>O NMR spectra were measured at the pulse repetition rate of 3.93 Hz. A spectral bandwidth of 71 429 Hz was digitized by use of 16 384 data words. The pulse width employed, 27  $\mu\text{s}$ , corresponded to a 90° pulse. Acquisition of 2500 data was made with a preacquisition delay of 3  $\mu\text{s}$  and a transmitter offset of 78 715 Hz. Exponential line broadening of 30 Hz was applied as well as the preceding method to correct pulse breakthrough. Electronic spectra were recorded on a Cary Model 219 spectrophotometer. Infrared spectra were obtained with a Nicolet 7000 series Fourier transform spectrophotometer. Conductivity measurements were made with a Radiometer Model CDM3 conductivity meter.

**Collection and Reduction of X-ray Data.** Red rectangular crystals were grown by slow vapor diffusion of ether into a solution of  $(\text{Ph}_4\text{P})[\text{MoS}_3(\text{OSiMe}_3)]$  in acetone at room temperature. A suitable crystal was sealed in a glass capillary under dinitrogen. The orientation matrix and unit cell parameters were determined by least-squares treatment of 25 machine-centered reflections ( $18^\circ \leq 2\theta \leq 25^\circ$ ) with a Nicolet R3m four-circle automated diffractometer and graphite-monochromatized Mo K $\alpha$  radiation. Data were obtained at ~23 °C. Details of the data collection and crystal parameters are summarized in Table I. Intensities of three check reflections monitored every 123 reflections showed average 7% ( $3^\circ \leq 2\theta \leq 30^\circ$ ), 15% ( $3^\circ \leq 2\theta \leq 37^\circ$ ), 20% ( $3^\circ \leq 2\theta \leq 40^\circ$ ), and 25% ( $3^\circ \leq 2\theta \leq 43^\circ$ ) decreases upon completion of the indicated data collections. For the third of these, it was confirmed that the orientation matrix and unit cell parameters were the same at the beginning and end of data collection. Data were processed with the program XTAPE of the SHELXTL program package (Nicolet XRD Corp., Madison, WI). Empirical absorption corrections were applied with the program XEMP. Maximum and minimum transmission factors were 0.92 and 0.84, respectively. A decay correlation of the data was effected by applying

- (23) (a) Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Liu, R.-S. *J. Am. Chem. Soc.* **1979**, *101*, 491. (b) Day, V. W.; Thompson, M. R.; Day, C. S.; Klemperer, W. G.; Liu, R.-S. *Ibid.* **1980**, *102*, 5973.  
 (24) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93.

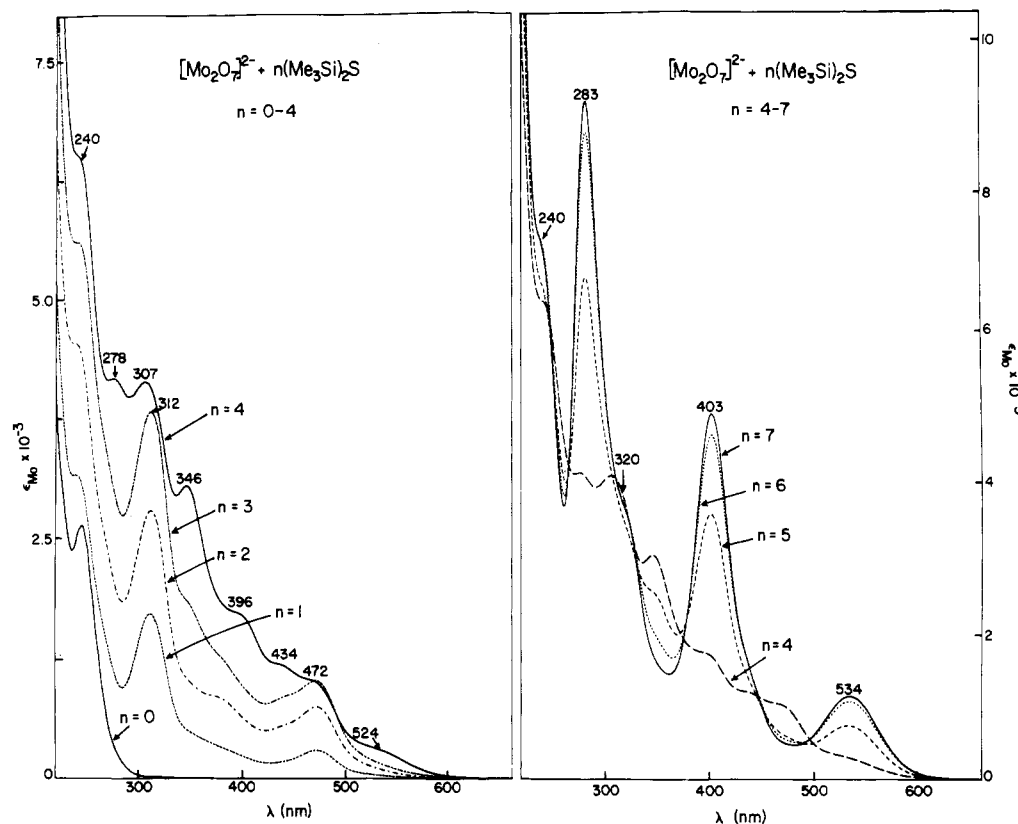


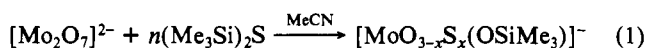
Figure 1. UV-visible absorption spectra of the reaction systems  $[\text{Mo}_2\text{O}_7]^{2-}/n(\text{Me}_3\text{Si})_2\text{S}$  ( $n = 0-7$ ) in acetonitrile solution.

batch scale factors derived from common check reflections and the linear least-squares method of Rae and Blake.<sup>25</sup> After equivalent reflections were merged,  $R_{\text{merge}}$  was 1.2%. The systematic absences  $h0l$  ( $h + l = 2n + 1$ ) and  $0k0$  ( $k = 2n + 1$ ) indicated the space group to be  $P2_1/n$  ( $C_{2h}$ , No. 14<sup>26</sup> in a nonstandard setting). This choice was confirmed by successful solution and refinement of the structure.

**Structure Solution and Refinement.** The direct methods program SOLV located the Mo atom. The remaining non-hydrogen atoms of the anion and cation were found by successive difference Fourier maps and blocked-cascade least-squares refinements. Atom scattering factors were taken from a standard source.<sup>27</sup> With use of 1883 unique data convergence was reached at  $R = 7.7\%$  for isotropic, and at  $R = 5.6\%$  for anisotropic, refinement of all non-hydrogen atoms. Phenyl rings were treated as rigid hexagons ( $\text{C}-\text{C} = 1.395 \text{ \AA}$ ). In the final stages of refinement, hydrogen atoms were included in the cation and anion at  $0.96 \text{ \AA}$  from, and with isotropic thermal parameters  $1.2\times$  that of, the bonded carbon atom. A final difference Fourier map revealed one peak ( $0.39 \text{ e/\AA}^3$ ) near the Mo atom and several random features ( $\leq 0.37 \text{ e/\AA}^3$ ). Final  $R$  factors and other data are included in Table I; atom coordinates are listed in Table II.<sup>28</sup>

## Results and Discussion

**Preparation of Reaction Systems.** The compound  $(n\text{-Bu}_4\text{N})_2[\text{Mo}_2\text{O}_7]^{19,24}$  provides a convenient source of the simplest isopoly oxomolybdate. It is soluble in acetonitrile, in which medium reaction system 1 can be examined free from potential



complications of hydrolysis. These systems are most effectively monitored by NMR owing to the presence of  $^1\text{H}$ ,  $^{17}\text{O}$  (by enrichment),  $^{29}\text{Si}$ , and  $^{95}\text{Mo}$  nuclei. Reproducible spectroscopic results were obtained from reactions conducted at  $\sim 0.01 \text{ M}$   $[\text{Mo}_2\text{O}_7]^{2-}$  with  $n = 0.5-7$  equiv of  $(\text{Me}_3\text{Si})_2\text{S}$ . After a 24-h reaction period at ambient temperature, all volatile components

were removed and the residues, which were completely soluble, were dissolved in acetonitrile at the concentrations appropriate to a particular spectroscopic measurement. For a system with a given  $n$  value, the same sample (at different concentrations, as required) was used for all measurements. Monitoring of systems in situ with  $n > 2$  equiv of  $(\text{Me}_3\text{Si})_2\text{S}$  and  $> 0.3 \text{ M}$   $[\text{Mo}_2\text{O}_7]^{2-}$ , a concentration range suitable for economical  $^{17}\text{O}$  or  $^{95}\text{Mo}$  NMR data acquisition times, revealed complicated reaction mixtures. In particular,  $^{17}\text{O}$  spectra exhibited signals whose intensities tended to decrease over 24-h periods. This behavior, which became more pronounced as  $n$  was increased, is suggestive of the formation of paramagnetic or otherwise NMR-undetectable products. Systems with  $n \leq 2$  equiv gave NMR spectra in situ that were identical with those prepared by the first procedure. While partial reduction of Mo(VI) appears to occur in both the concentrated and more dilute systems (vide infra), the latter proved far more amenable to NMR detection of reaction products. Consequently, the results described here refer to these systems unless noted otherwise.

**UV-Visible Spectra.** Spectra of systems with  $n = 1-7$  equiv of  $(\text{Me}_3\text{Si})_2\text{S}$ , displayed in Figure 1, show removal of colorless  $[\text{Mo}_2\text{O}_7]^{2-}$  ( $n = 0$ ) and progressive development of visible chromophores. Spectral changes culminate with formation of a species at  $n = 6-7$  having  $\lambda_{\text{max}} = 283, 403, \text{ and } 534 \text{ nm}$ . On the basis of spectra of the series  $[\text{MoO}_{4-x}\text{S}_x]^{2-}$ ,<sup>2,12</sup> some or all of the new bands at 300–600 nm arise from  $\text{S}_i \rightarrow \text{Mo}$  charge transfer. For example, in acetonitrile  $[\text{MoOS}_3]^{2-}$  exhibits a similar spectral pattern with  $\lambda_{\text{max}} = 310, 400, \text{ and } 459 \text{ nm}$ .<sup>12</sup> The final species, at least, contains tetrahedral Mo(VI) with  $\text{Mo}=\text{S}$  bonds similar to those in  $[\text{MoOS}_3]^{2-}$ <sup>29</sup> and  $[\text{MoS}_4]^{2-}$ ,<sup>30</sup> whose mean bond lengths are 2.17–2.18 Å.

**NMR Spectra.** The course of reactions in system 1 was examined by multinuclear NMR methods. Klemperer and co-workers<sup>19,21,24,31,32</sup> have pioneered  $^{17}\text{O}$  spectroscopy as a structural

(25) Rae, A. D.; Blake, A. B. *Acta Crystallogr.* 1966, 20, 586.

(26) "International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1973; Vol. I, p 99.

(27) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(28) See paragraph at the end of this article concerning supplementary material available.

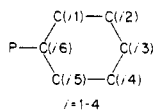
(29) Krebs, B.; Müller, A.; Kindler, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* 1970, 25B, 222.

(30) (a) Lapasset, J.; Chezeau, N.; Beloungue, P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1976, B32, 3087. (b) Kanatzidis, M.; Coucouvanis, D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 1983, C39, 835.

**Table II.** Atom Coordinates ( $\times 10^4$ ) for  $(\text{Ph}_4\text{P})[\text{MoS}_3(\text{OSiMe}_3)]$ 

atom	x	y	z
Mo	230 (1) <sup>a</sup>	2196 (1)	3016 (1)
S(1)	306 (2)	2137 (3)	4280 (2)
S(2)	-1175 (2)	1798 (2)	2258 (2)
S(3)	584 (2)	3838 (2)	2725 (2)
O	1055 (5)	1155 (5)	2820 (4)
Si	2138 (2)	829 (3)	2954 (2)
C(1)	2332 (11)	-623 (13)	3270 (14)
C(2)	2404 (10)	1044 (16)	2022 (8)
C(3)	2865 (12)	1720 (22)	3741 (12)
P <sup>b</sup>	1316 (2)	2322 (2)	8646 (1)
C(11)	2373 (4)	633 (6)	9566 (4)
C(12)	3061 (4)	-185 (6)	9741 (4)
C(13)	3557 (4)	-373 (6)	9202 (4)
C(14)	3366 (4)	255 (6)	8487 (4)
C(15)	2678 (4)	1073 (6)	8313 (4)
C(16)	2182 (4)	1261 (6)	8852 (4)
C(21)	-114 (5)	1358 (6)	9063 (4)
C(22)	-632 (5)	1144 (6)	9582 (4)
C(23)	-410 (5)	1681 (6)	10337 (4)
C(24)	328 (5)	2433 (6)	10573 (4)
C(25)	845 (5)	2647 (6)	10054 (4)
C(26)	624 (5)	2110 (6)	9299 (4)
C(31)	173 (4)	3203 (5)	7197 (4)
C(32)	-430 (4)	3153 (5)	6390 (4)
C(33)	-617 (4)	2138 (5)	5982 (4)
C(34)	-202 (4)	1172 (5)	6381 (4)
C(35)	401 (4)	1222 (5)	7188 (4)
C(36)	588 (4)	2237 (5)	7596 (4)
C(41)	2774 (4)	3797 (5)	8910 (4)
C(42)	3168 (4)	4854 (5)	9019 (4)
C(43)	2630 (4)	5771 (5)	9070 (4)
C(44)	1698 (4)	5630 (5)	9011 (4)
C(45)	1304 (4)	4573 (5)	8901 (4)
C(46)	1842 (4)	3656 (5)	8851 (4)

<sup>a</sup> Estimated standard deviations in parentheses in this and following tables. <sup>b</sup> Labeling scheme for cation:



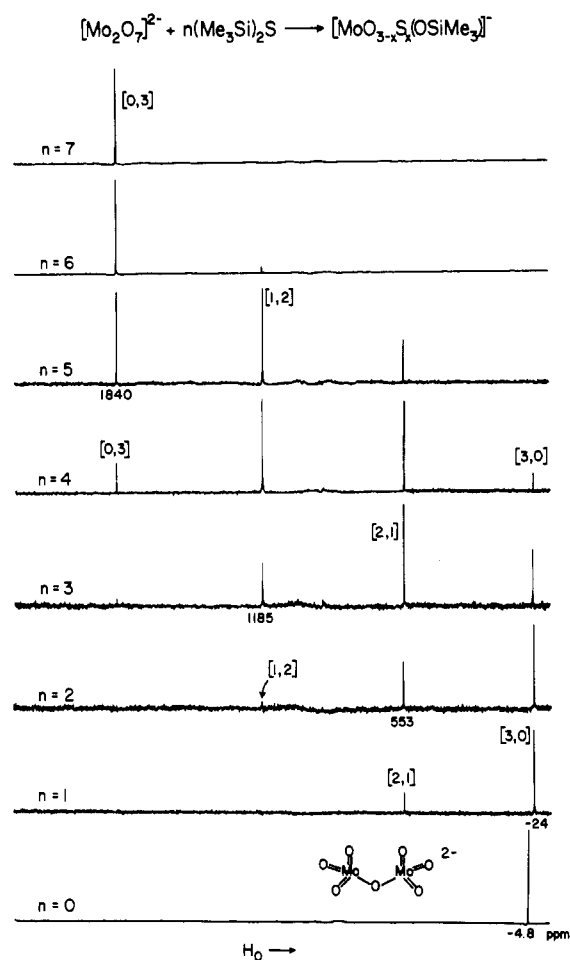
probe of polyoxoanions. The value of <sup>95</sup>Mo spectroscopy in structural studies is now well documented,<sup>33</sup> some leading aspects have been summarized.<sup>34</sup>

(a)  $[\text{MoO}_{4-x}\text{S}_x]^{2-}$ . The utility of <sup>95</sup>Mo spectra in the examination of the reactions 1 derives from the  $\sim 500$ – $600$  ppm downfield shift increment in aqueous solution for each unit increase in  $x$  in the series  $[\text{MoO}_{4-x}\text{S}_x]^{2-}$ .<sup>35</sup> Given the possible occurrence of these species as reaction products and the sensitivity of the  $[\text{MoS}_4]^{2-}$  shift to solvent,<sup>36,37</sup> precise shifts in acetonitrile were desired. These were obtained by preparing  $(\text{Et}_4\text{N})_2[\text{MoO}_2\text{S}_2]$  by the procedure of McDonald et al.<sup>12</sup> Correlation of the <sup>95</sup>Mo spectrum of this product in acetonitrile with the aqueous solution results<sup>35</sup> showed that the major species was  $[\text{MoO}_2\text{S}_2]^{2-}$ , but with significant quantities of  $[\text{MoO}_3\text{S}]^{2-}$  and  $[\text{MoOS}_3]^{2-}$ . Chemical shifts are listed in Table III. Addition of <sup>17</sup>O-enriched water to an acetonitrile

**Table III.** <sup>95</sup>Mo and <sup>17</sup>O Chemical Shifts in Acetonitrile Solutions at 297 K

species	shift, ppm	
	<sup>95</sup> Mo	<sup>17</sup> O <sup>c</sup>
$[\text{MoO}_4]^{2-}$	0 <sup>b</sup> (8)	544 (148)
$[\text{MoO}_3\text{S}]^{2-}$	451 (14)	624 <sup>d</sup> (45)
$[\text{MoO}_2\text{S}_2]^{2-}$	997 (12)	696 <sup>d</sup> (45)
$[\text{MoOS}_3]^{2-}$	1586 (10)	759 <sup>d</sup> (44)
$[\text{MoS}_4]^{2-}$	2209 <sup>e</sup> (15)	
$[\text{Mo}_2\text{O}_7]^{2-}$	-4.8 (17)	715 (t, 70), 247 (b, 200)
$[\text{Mo}_2\text{O}_6\text{S}]^{2-}$	570 (25)	779 (70), 724 (t, 78); 0.3 (50) 272 (b, 160)
$[\text{MoO}_3(\text{OSiMe}_3)]^-$	-24 (12)	714 (70), 131 (140, OSi)
$[\text{MoO}_2\text{S}(\text{OSiMe}_3)]^-$	553 (14)	779 (70), 156 (130, OSi)
$[\text{MoOS}_2(\text{OSiMe}_3)]^-$	1185 (15)	829 (70), 174 (130, OSi)
$[\text{MoS}_3(\text{OSiMe}_3)]^-$	1840 (12)	190 (130, OSi)

<sup>a</sup> Line width (Hz) in parentheses. <sup>b</sup> Shift reference. <sup>c</sup> Vs. <sup>17</sup>OH<sub>2</sub> in CD<sub>3</sub>CN. <sup>d</sup> <sup>17</sup>O enrichment: 0.22 g of  $(\text{Et}_4\text{N})_2[\text{MoO}_2\text{S}_2]$  with impurities (see text) in 3 mL of acetonitrile + 20  $\mu\text{L}$  of 50% <sup>17</sup>OH<sub>2</sub>. <sup>e</sup>  $(\text{Et}_4\text{N})_2[\text{MoS}_4]$ .

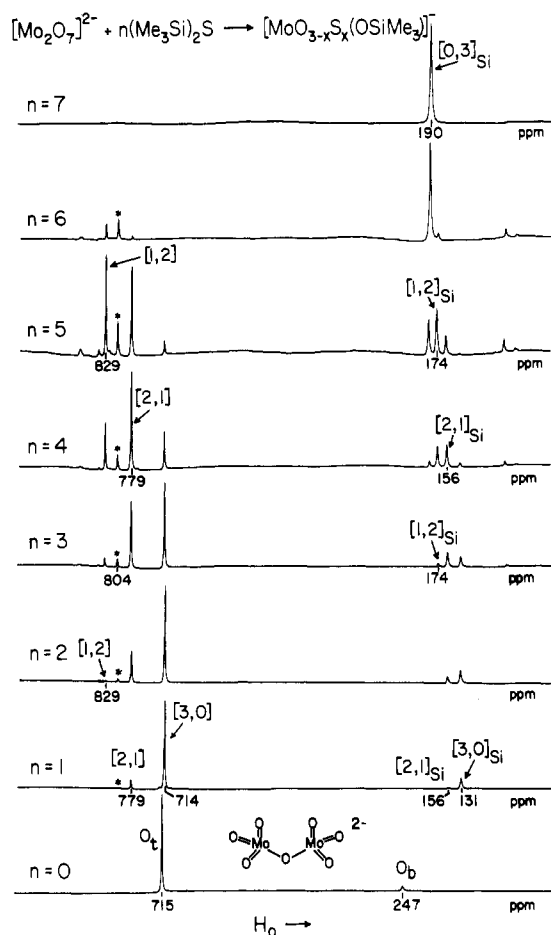


**Figure 2.** <sup>95</sup>Mo NMR spectra of the reaction systems  $[\text{Mo}_2\text{O}_7]^{2-}/n-(\text{Me}_3\text{Si})_2\text{S}$  ( $n = 0$ – $7$ ) in acetonitrile solution. Species are designated in this and following figures as  $[3-x, x]$  (see text).

solution of this preparation of  $(\text{Et}_4\text{N})_2[\text{MoO}_2\text{S}_2]$  afforded well-resolved spectra of the three ions. The integrated <sup>17</sup>O resonances gave the concentration ratio  $[\text{MoOS}_3]^{2-}:[\text{MoO}_3\text{S}]^{2-}:[\text{MoO}_2\text{S}_2]^{2-} = 1:1.2:5.9$  for this preparation. A very weak resonance was detected at 544 ppm. This was assigned to  $[\text{MoO}_4]^{2-}$  on the basis of very similar shifts of this ion in aqueous solution vs. <sup>17</sup>OH<sub>2</sub> external reference (532,<sup>31,38</sup> 540<sup>39</sup> ppm). Both the <sup>95</sup>Mo and <sup>17</sup>O shifts vary linearly with  $x$  in the series  $[\text{MoO}_{4-x}\text{S}_x]^{2-}$ .

- (31) Filowitz, M.; Klemperer, W. G. *J. Chem. Soc., Chem. Commun.* **1976**, 233.  
 (32) Klemperer, W. G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 246.  
 (33) For an extensive list of references, cf.: Minelli, M.; Hubbard, J. L.; Enemark, J. H. *Inorg. Chem.* **1984**, *23*, 970.  
 (34) Enemark, J. H. In "Nitrogen Fixation: The Chemical-Biochemical-Genetic Interface"; Newton, W. E., Müller, A., Eds.; Plenum Press: New York, 1983; pp 329–339.  
 (35) Lutz, O.; Nölle, A.; Kroneck, P. Z. *Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1977**, *32A*, 505.  
 (36) Gheller, S. F.; Gazzana, P. A.; Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G.; Rodgers, J. R.; Snow, M. R. *Inorg. Chim. Acta* **1981**, *54*, L131.  
 (37) Gheller, S. F.; Hambley, T. W.; Rodgers, J. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Inorg. Chem.* **1984**, *23*, 2519. This paper, which reports <sup>95</sup>Mo shifts of  $[\text{MoO}_{4-x}\text{S}_x]^{2-}$  in acetonitrile, appeared after the completion of our research. Their shift data and those in Table III are in good agreement.

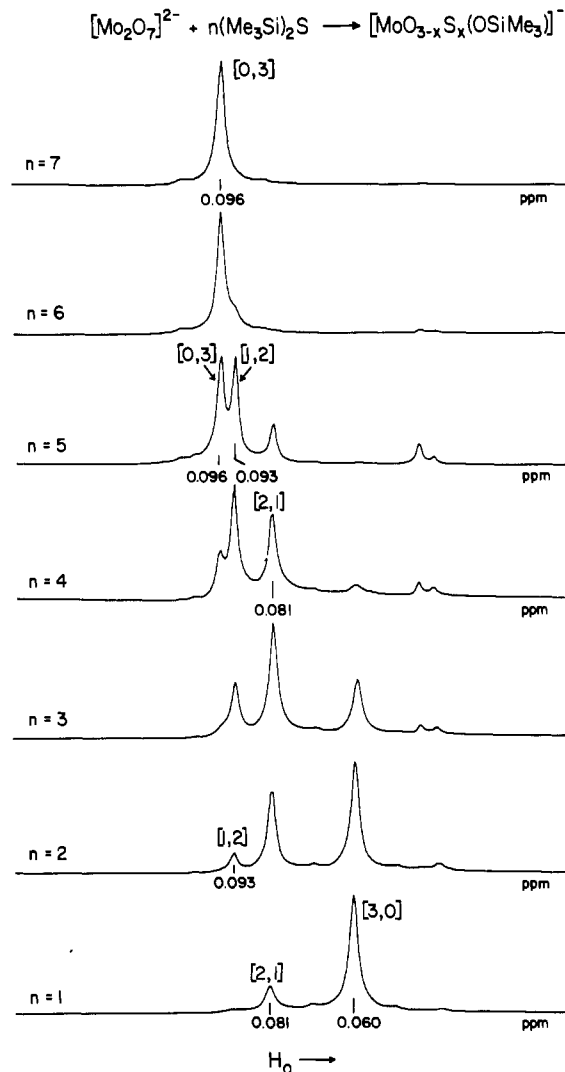
- (38) Müller, K. F.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 984.  
 (39) Figgis, B. N.; Kidd, R. G.; Nyholm, R. S. *Proc. R. Soc. London, A* **1962**, *269*, 469.



**Figure 3.**  $^{17}\text{O}$  NMR spectra of the reaction systems  $[\text{Mo}_2\text{O}_7]^{2-}/n(\text{Me}_3\text{Si})_2\text{S}$  ( $n = 0-7$ ) in acetonitrile solution. The subscript Si refers to an O atom in the  $\text{Me}_3\text{SiO}$  group of the designated species; the signal marked with an asterisk has the same chemical shift as  $[\text{Mo}_2\text{O}_7\text{S}_6]^{2-}$ .

**(b)  $[\text{Mo}_2\text{O}_7]^{2-}/n(\text{Me}_3\text{Si})_2\text{S}$  Systems.**  $^{95}\text{Mo}$ ,  $^{17}\text{O}$ , and  $^1\text{H}$  NMR spectra for  $n = 0-7$  systems are presented in Figures 2, 3, and 4, respectively. The  $^{95}\text{Mo}$  spectrum of  $[\text{Mo}_2\text{O}_7]^{2-}$  shows a single line at  $-4.8$  ppm, slightly shielded compared to the aqueous  $[\text{MoO}_4]^{2-}$  external reference. The  $^{17}\text{O}$  spectrum of this ion exhibits bridging and terminal signals at 247 and 715 ppm, in good agreement with previous results.<sup>19,24</sup> The intensity ratio  $\text{O}_t:\text{O}_b \approx 7:1$  is presumably due mainly to greater enrichment per site in the terminal positions. As will be shown, the identifiable reaction products are  $[\text{MoO}_{3-x}\text{S}_x(\text{OSiMe}_3)]^-$ , designated as  $[3-x,x]$  ( $x = 0-3$ ). These products, from each equivalent  $n$  of  $(\text{Me}_3\text{Si})_2\text{S}$ , are schematically summarized in Figure 5.

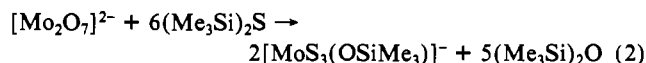
In the  $n = 1$  system the  $^{95}\text{Mo}$  and  $^{17}\text{O}$  signals of  $[\text{Mo}_2\text{O}_7]^{2-}$  are eliminated. Two signals of unequal intensity at  $-24$  and  $553$  ppm are observed in the  $^{95}\text{Mo}$  spectrum. This is inconsistent with retention of a binuclear structure in the observable products, and the  $577$  ppm shift difference accords with the introduction of a  $\text{S}_t$  atom at one Mo atom. The other Mo atom is fully O-ligated. Similarly, in the  $^{17}\text{O}$  spectrum two resonances of very different intensities are found in the  $\text{O}_t$  region at  $714$  and  $779$  ppm. Two additional signals, upfield at  $131$  and  $156$  ppm, also occur. Further, two resonances of unequal intensity with shifts expected for the  $\text{Me}_3\text{Si}$  group are found in the  $^1\text{H}$  spectrum. Neither these signals nor those in the upfield region of the  $^{17}\text{O}$  spectrum are due to  $(\text{Me}_3\text{Si})_2\text{O}$  or unreacted  $(\text{Me}_3\text{Si})_2\text{S}$ ,<sup>40</sup> which have been removed in the preparation of samples. These results are interpreted in terms of cleavage of  $[\text{Mo}_2\text{O}_7]^{2-}$  to form  $[3,0]$  and  $[2,1]$ , with the latter being the minority product. Chemical shifts of these and other products are collected in Table III. Relative



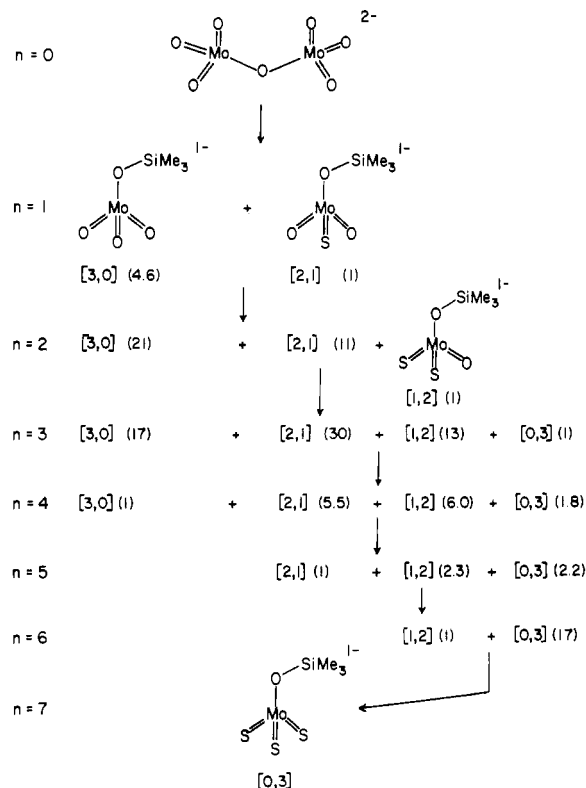
**Figure 4.**  $^1\text{H}$  NMR spectra of the reaction systems  $[\text{Mo}_2\text{O}_7]^{2-}/n(\text{Me}_3\text{Si})_2\text{S}$  ( $n = 1-7$ ) in acetonitrile solution. Signals upfield of  $0.06$  ppm are unidentified.

amounts of products formed in this and succeeding  $n$ -equiv systems, estimated from integrated  $^{95}\text{Mo}$  signal intensities, are given in Figure 5. The same order of product distribution in each system was found in the  $^{17}\text{O}$  spectra.

Upon increasing  $n$  values a clear spectral pattern, associated with progressive growth and decay of  $[3-x,x]$  species, emerges. Thus, in the  $n = 2$  system the ratio  $[3,0]:[2,1]$  decreases to  $1.9:1$ , and resonances from a new species are just observable. At  $n = 3$  these resonances are more evident. The  $1185$  ppm  $^{95}\text{Mo}$  signal,  $632$  ppm more deshielded than that of  $[2,1]$ , indicates introduction of a second  $\text{S}_t$  atom. This is accompanied by the emergence of new signals at  $829$  ( $\text{O}_t$ ) and  $174$  ( $\text{OSiMe}_3$ ) ppm in the  $^{17}\text{O}$  spectrum, and a new feature at  $0.093$  ppm in the  $^1\text{H}$  spectrum. All of these resonances are assigned to  $[1,2]$  and become more intense relative to those of  $[3,0]$  and  $[2,1]$  at  $n = 4$ . In the  $n = 4, 5$  systems new features appear at  $1840$  ( $^{95}\text{Mo}$ ),  $190$  ( $^{17}\text{O}$ ), and  $0.096$  ( $^1\text{H}$ ) ppm. The  $^{95}\text{Mo}$  signal is deshielded by  $655$  ppm compared to that of  $[1,2]$ , indicating introduction of another  $\text{S}_t$  atom. At  $n = 6$  all other resonances are very weak or absent, and at  $n = 7$  no other resonances are observable. Clearly the final product lacks  $\text{O}_t$  atoms and retains the  $\text{Me}_3\text{SiO}$  ligand, leading to its formulation as  $[0,3]$ ,  $[\text{MoS}_3(\text{OSiMe}_3)]^-$ . In a separate experiment, this anion was prepared by means of reaction 2 with an excess ( $7.6$  equiv) of the sulfide reagent and was obtained in  $31\%$  purified yield as its  $\text{Ph}_4\text{P}^+$  salt.



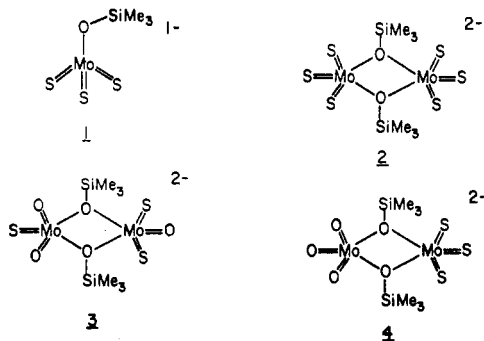
(40) Chemical shifts in acetonitrile solution:  $(\text{Me}_3\text{Si})_2\text{O}$ ,  $0.056$  ( $^1\text{H}$ ),  $39.9$  ( $^{17}\text{O}$ ) ppm;  $(\text{Me}_3\text{Si})_2\text{S}$ ,  $0.32$  ( $^1\text{H}$ ) ppm.



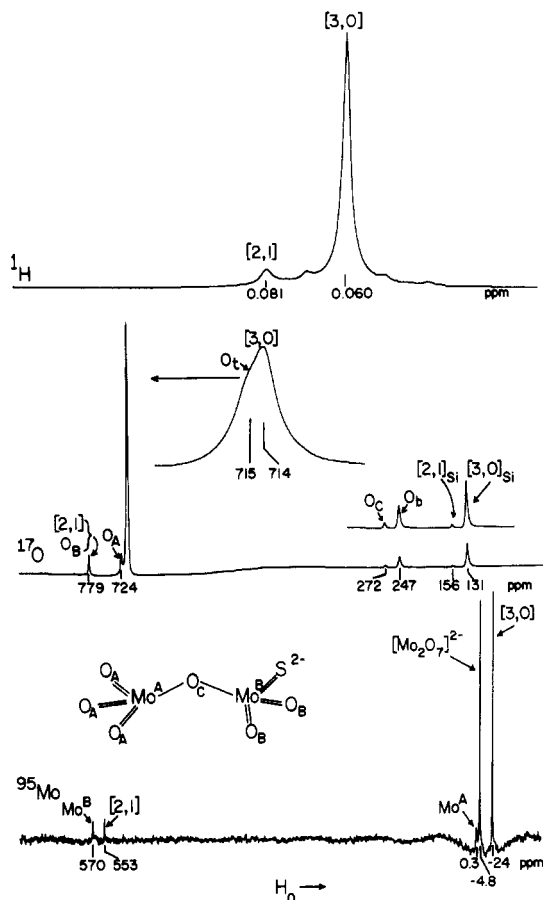
**Figure 5.** Schematic depiction of the reaction products  $[\text{MoO}_{3-x}\text{S}_x(\text{OSiMe}_3)]^- = [3-x, x]$  from  $[\text{Mo}_2\text{O}_7]^{2-} + n$  equiv of  $(\text{Me}_3\text{Si})_2\text{S}$  in acetonitrile solutions. For each  $n$  value relative amounts of products estimated from  $^{95}\text{Mo}$  signal intensities are given in parentheses.

Identification of the detectable products in reaction system 1 (Figure 5) would not have been possible without complementary use of  $^{95}\text{Mo}$ ,  $^{17}\text{O}$ , and  $^1\text{H}$  NMR spectroscopy. Species identification is strongly supported by internal consistency in the three types of spectra, viz., that stepwise substitution of  $\text{O}_t$  by  $\text{S}_t$  results in monotonic low-field shifts, as found for  $[\text{MoO}_{4-x}\text{S}_x]^{2-}$  (Table III). None of these species were found among the reaction products. Similarly deshielded  $^{95}\text{Mo}$  resonances have also been observed in the products of the reaction of  $\text{MoO}_2(\text{R}_2\text{NO})_2$  and  $(\text{Me}_3\text{Si})_2\text{S}$ .<sup>41</sup>

**Nuclearity of Reaction Products.** The NMR results are sufficient to establish the product stoichiometries  $[\text{MoO}_{3-x}\text{S}_x(\text{OSiMe}_3)]^-$ . They and the analytical data of the product of reaction 2 do not necessarily distinguish the mononuclear species depicted in the scheme of Figure 5 from certain polynuclear forms. The situation is illustrated for one binuclear possibility where the forms 1 and 2 are not distinguishable. Any dimeric species



$[\text{Mo}_2\text{O}_{6-x}\text{S}_x(\mu\text{-OSiMe}_3)_2]^{2-}$  must have inequivalent sites when  $x$  is odd,<sup>42</sup> as for the isomers 3 and 4 of the  $x = 3$  species. Dimers



**Figure 6.**  $^1\text{H}$ ,  $^{17}\text{O}$ , and  $^{95}\text{Mo}$  NMR spectra of the reaction system  $[\text{Mo}_2\text{O}_7]^{2-}/0.5 (\text{Me}_3\text{Si})_2\text{S}$  in acetonitrile solution. Signal assignments are indicated; the  $\text{O}_t$  and  $\text{O}_b$  signals are due to  $[\text{Mo}_2\text{O}_7]^{2-}$ .

or higher species containing  $\mu\text{-O}$  and  $\mu\text{-S}$  ligands are also easily conceived. Some support for binuclear forms follows from structurally preceded, discrete trioxomolybdenum(VI) compounds with more than four ligands.<sup>43-45</sup>

The following evidence strongly favors mononuclear structures. (i) X-ray structural analysis of [0,3] as its  $\text{Ph}_4\text{P}^+$  salt shows it to have the mononuclear form 1 (vide infra). (ii) The relatively narrow  $^{95}\text{Mo}$  line widths (Table III) are generally associated with (approximately) cubic environments.<sup>34,37</sup> (iii) No pairs of equally intense  $^{95}\text{Mo}$  resonances, indicative of dimeric species with 1-5  $\text{S}_t$  atoms, were observed (Figure 2). (iv) For  $\text{Ph}_4\text{P}^+$  and  $n\text{-Bu}_4\text{N}^+$  salts of [0,3] in the equivalent concentration ( $c$ ) range 0.2-30 mM in acetonitrile, plots of the conductivity difference  $\lambda_o - \lambda_c$  vs.  $c^{1/2}$ <sup>46</sup> were linear with a slope of 310. In this solvent ( $n\text{-Bu}_4\text{N}$ )<sub>2</sub>[Mo<sub>2</sub>O<sub>7</sub>] and ( $n\text{-Bu}_4\text{N}$ )(ClO<sub>4</sub>) gave slopes of 661 and 405 (lit.<sup>47</sup> 353), respectively. Comparison with these and other<sup>48</sup> data satisfactorily establishes that compounds of [0,3] are 1:1 electrolytes. Further, deviations of conductivities from linearity above ~30 mM are indicative of ion pairing rather than dimerization to a 2:1 electrolyte containing anion 2. These results suggest that other [3-x, x] species in Figure 5 may also be mononuclear in acetonitrile. Lastly, the possibility that the solution species formed in the  $n = 7$  system is  $[\text{Mo}_2\text{S}_6(\mu\text{-OSiMe}_3)(\mu\text{-SSiMe}_3)]^{2-}$  was discounted by the presence of a single  $^{29}\text{Si}\{^1\text{H}\}$  signal (at 18.9 ppm).

**Other Reaction Products.** In a scheme of attractive simplicity, overall reaction 3 would occur in the  $n = 1$  system, followed by

(41) Minelli, M.; Enemark, J. H.; Wiegardt, K.; Hahn, M. *Inorg. Chem.* **1983**, *22*, 3952.

(42) When  $x$  is even, isomers based on unequal numbers of  $\text{S}_t$  atoms at the two Mo sites or, when equal, of (any) inequivalent ligand site occupation are possible as well.

(43) Cotton, F. A.; Elder, R. C. *Inorg. Chem.* **1964**, *3*, 397.

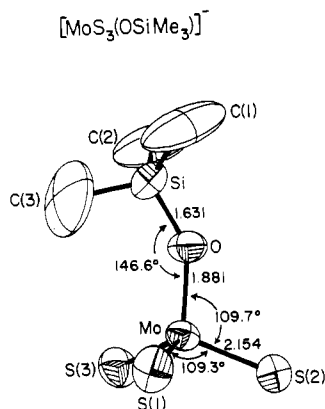
(44) Park, J. J.; Glick, M. D.; Hoard, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 301.

(45) Butcher, R. J.; Penfold, B. R. *J. Cryst. Mol. Struct.* **1976**, *6*, 13.

(46) Feltham, R. D.; Hayter, R. G. *J. Chem. Soc.* **1964**, 4587.

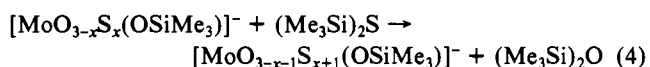
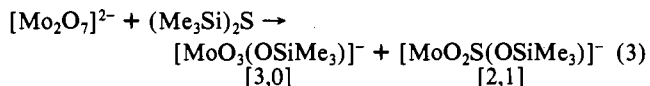
(47) Coetzee, J. F.; Cunningham, G. P. *J. Am. Chem. Soc.* **1965**, *87*, 2529.

(48) Davison, A.; Howe, D. V.; Shawl, E. T. *Inorg. Chem.* **1967**, *6*, 458. Balch, A. L.; Dance, I. G.; Holm, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 1139.



**Figure 7.** Structure of  $[\text{MoS}_3(\text{OSiMe}_3)]^-$ , showing the atom-numbering scheme, 50% probability ellipsoids, and selected distances and angles.

the sequential O/S substitution of the product ions at higher  $n$  values in reaction 4. Although reaction 3 is consistent with the

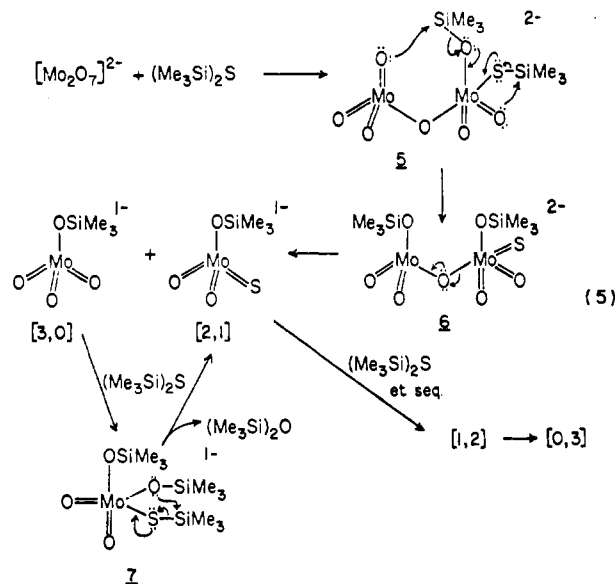


observation that no  $(\text{Me}_3\text{Si})_2\text{O}$  is detectable until  $n > 1$ , it cannot represent the total situation because [3,0] is the predominant product. Further, product distribution is not affected by the reaction of any  $(\text{Me}_3\text{Si})_2\text{O}$  formed with  $[\text{Mo}_2\text{O}_7]^{2-}$ . NMR spectra of an acetonitrile solution 0.16 M in both compounds proved no reaction after 22 h at ambient temperature. This matter was further examined in a case with excess  $[\text{Mo}_2\text{O}_7]^{2-}$ . NMR spectra of the  $n = 0.5$  system in Figure 6 reveal a complicated situation. Present are unreacted  $[\text{Mo}_2\text{O}_7]^{2-}$  and both [3,0] and [2,1], which are formed in unequal amounts. Intensities of  $^{95}\text{Mo}$  signals give the mole ratio [3,0]: $[\text{Mo}_2\text{O}_7]^{2-}$ : [2,1] = 8.6:4:1. Two previously unobserved  $^{95}\text{Mo}$  (A, B) and three such  $^{17}\text{O}$  (A–C) resonances occur. (On the basis of relative intensities, the [2,1] and  $\text{O}_B$  signals are concluded to be coincident in the  $^{17}\text{O}$  spectrum.) The  $^{17}\text{O}$  and  $^{95}\text{Mo}$  chemical shifts (Table III) and the equally intense  $^{95}\text{Mo}$  resonances are sensibly consistent with  $[\text{Mo}_2\text{O}_6\text{S}]^{2-}$ , whose structure is shown in Figure 6. This species and [2,1] are formed in equal amounts. When the  $^{17}\text{O}$  spectrum of an in situ system was examined at 3–90 min after mixing of reactants, no signals other than those in Figure 6 were observed. Examination of the  $n = 0.5$ –2 systems in situ showed no unreacted  $(\text{Me}_3\text{Si})_2\text{S}$ .

The preponderance of (observable) sulfur-free products in the  $n = 0.5$ –2 systems and the detection of [3,0] up to  $n = 5$  (Figure 3) indicate diversion of some Mo/S content to a form not detectable by at least  $^{95}\text{Mo}$  NMR under the conditions used. This situation is most likely to occur by reduction to Mo(IV, V), perhaps via a Mo–SSiMe<sub>3</sub> intermediate. Evidence in favor of this proposal is found in the occurrence of a  $^{17}\text{O}$  signal at 804 ppm in the  $n = 1$ –6 systems (Figure 3). This signal is coincident with that obtained by enriching the  $\text{O}_t$  ligands of the diamagnetic Mo(V) dimer salt  $(\text{Me}_4\text{N})_2[\text{Mo}_2\text{O}_2\text{S}_2(\text{S}_2)_2]^{13}$  with  $^{17}\text{OH}_2$  in a ~0.1 M solution in 1:1 v/v DMF/ $\text{CD}_3\text{CN}$ . No  $^{95}\text{Mo}$  signal could be detected under conditions employed for the Mo(VI) spectra of Figure 2. Signals of other Mo(V) dimers are 1–2 orders of magnitude broader than those of tetrahedral Mo(VI) species and are best observed at elevated temperatures where the effects of correlation broadening are diminished.<sup>49</sup> Others have found that reaction of certain dioxomolybdenum(VI) complexes with  $(\text{Me}_3\text{Si})_2\text{S}$  afforded paramagnetic species and no new  $^{95}\text{Mo}$  signals.<sup>50</sup> Apparent reduction is also found in the  $n = 7$  system. Here spectropho-

tomeric yields of [0,3], measured at 403 and 534 nm and based on the extinction coefficients of the isolated  $\text{Ph}_4\text{P}^+$  salt, are 82–89%. No attempts were made with any reaction system to characterize species that were not detectable in  $^{95}\text{Mo}$  NMR spectra.

**Mechanistic Aspects.** The preceding results are presented to support the likely reduction of some Mo(VI) reactant and product(s) to Mo(V) species. The evidence at hand does not permit identification or quantitation of these species in the form of stoichiometric reactions. The most important aspect of the present work is the reaction chemistry of the Mo(VI) species, commencing with  $[\text{Mo}_2\text{O}_7]^{2-}$ . Equation 5 provides a mechanistic interpretation



of the main products (but not their relative amounts) summarized for different equivalents  $n$  of  $(\text{Me}_3\text{Si})_2\text{S}$  in Figure 5. Cleavage of the reactant occurs by means of addition across a Mo=O bond, forming the intermediate **5** with a  $\text{Me}_3\text{SiO}$  group and one five-coordinate Mo(VI) atom. Two nucleophilic attacks on the relatively electropositive Si centers by  $\text{O}_t$  atoms generate **6**, which cleaves in the direction of the less saturated Mo(VI) center to give [3,0] and [2,1], the only detectable products in the  $n = 1$  system. Reaction of [3,0] with  $(\text{Me}_3\text{Si})_2\text{S}$  then forms the related intermediate **7**, which upon elimination of siloxane (observed at  $n > 1$ ) produces [2,1]. Repetitions of the steps give the remaining products [2,1] and [0,3]. The reactions derive driving force from the nucleophilicity of  $\text{O}_t$  ligands (as in, e.g., protonation<sup>51</sup>) and the ~35 kcal/mol larger homolytic bond energy of Si–O vs. that of Si–S.<sup>52</sup> In the  $n = 7$  system [0,3] does not react with a further equivalent of  $(\text{Me}_3\text{Si})_2\text{S}$ , presumably because the elimination of  $(\text{Me}_3\text{Si})_2\text{O}$  is not favored at the expense of forming a Mo–SSiMe<sub>3</sub> bond. Throughout the reaction systems there was no evidence for the formation of  $[\text{MoS}_4]^{2-}$  or the conceivable species  $[\text{Mo}_2\text{S}_7]^{2-}$ , which would be expected to be analogous to  $[\text{Ga}_2\text{S}_7]^{8-}$ , known in the form of its  $\text{Ba}^{2+}$  salt.<sup>53</sup>

**Structure of  $[\text{MoS}_3(\text{OSiMe}_3)]^-$ .** The crystal structure of  $(\text{Ph}_4\text{P})[\text{MoS}_3(\text{OSiMe}_3)]$  consists of well-separated cations and mononuclear anions **1**. The cation structure is unexceptional and is not further considered. In Figure 7 the structure of  $[\text{MoS}_3(\text{OSiMe}_3)]^-$  is displayed; dimensional data are collected in Table IV. Metric features of the  $\text{Me}_3\text{SiO}$  group are normal. The anion is configured with a Mo–O–Si angle of 146.6 (4)°, and an attendant dihedral angle of 34.2° between  $\text{C}_3$  and  $\text{S}_3$  planes. The  $\text{Mo}^\text{VI}\text{S}_3\text{O}$  unit has trigonally distorted tetrahedral stereochemistry. The mean Mo–S distance of 2.154 (6) Å is slightly shorter than mean distances in  $[\text{MoO}_2\text{S}_2]^{2-}$ –<sup>54</sup> (2.188 (1) Å),  $[\text{MoOS}_3]^{2-}$ –<sup>29</sup>

(49) Gheller, S. F.; Hambley, T. W.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *J. Am. Chem. Soc.* **1983**, *105*, 1527.

(50) Minelli, M.; Yamanouchi, K.; Enemark, J. H.; Subramanian, P.; Kaul, B. B.; Spence, J. T. *Inorg. Chem.* **1984**, *23*, 2554.

(51) Harmer, M. A.; Sykes, A. G. *Inorg. Chem.* **1980**, *19*, 2881.

(52) Tacke, R.; Wannagat, U. *Top. Curr. Chem.* **1979**, *84*, 5.

(53) Eisenmann, B.; Jakowski, M.; Schafer, H. *Rev. Chim. Miner.* **1984**, *21*, 12.

**Table IV.** Selected Interatomic Distances (Å) and Angles (deg) for  $(\text{Ph}_4\text{P})[\text{MoS}_3(\text{OSiMe}_3)]$ 

Mo-S(1)	2.148 (3)	Mo-S(3)	2.155 (3)
Mo-S(2)	2.159 (3)	mean	2.154 (6)
Mo-O	1.881 (7)	Mo...Si	3.364 (3)
Si-O	1.631 (8)		
Si-C(1)	1.831 (17)	Si-C(3)	1.799 (21)
Si-C(2)	1.801 (17)	mean	1.811 (25)
P-C(16)	1.785 (7)	P-C(46)	1.780 (7)
P-C(26)	1.794 (8)	mean	1.787 (6)
P-C(36)	1.790 (6)		
S(1)-Mo-S(2)	108.8 (1)	C(1)-Si-C(2)	110.0 (10)
S(1)-Mo-S(3)	109.4 (1)	C(1)-Si-C(3)	110.3 (10)
S(2)-Mo-S(3)	109.6 (1)	C(2)-Si-C(3)	109.1 (9)
S(1)-Mo-O	110.1 (2)	C(16)-P-C(26)	108.4 (3)
S(2)-Mo-O	109.1 (2)	C(16)-P-C(36)	109.3 (3)
S(3)-Mo-O	109.9 (2)	C(16)-P-C(46)	110.8 (3)
Mo-O-Si	146.6 (4)	C(26)-P-C(36)	109.5 (3)
C(1)-Si-O	109.2 (6)	C(26)-P-C(46)	110.8 (2)
C(2)-Si-O	110.4 (5)	C(36)-P-C(46)	110.0 (3)
C(3)-Si-O	107.7 (8)		

(2.178 (2) Å), and  $[\text{MoS}_4]^{2-}$  (2.178 (6),<sup>30a</sup> 2.177 (6)<sup>30b</sup> Å). This is doubtless a consequence of the presence of a two-electron  $(\text{Me}_3\text{SiO}^-)$  instead of a four-electron donor  $(\text{O}^{2-}, \text{S}^{2-})$ , with the shortened distances representing a slightly greater contribution of Si atoms to charge neutralization. As would be expected, the Mo-O bond distance of 1.881 (7) Å is much longer than that in  $[\text{MoOS}_3]^{2-}$  (1.785 (10) Å). In addition, it is shorter than the Mo-O single bonds in the six-coordinate Mo(VI) complex  $\text{Mo}(\text{NC}_{10}\text{H}_{15})_2(\text{OSiMe}_2)_4$ <sup>55</sup> (1.905 Å) and much shorter than these bonds in the Mo(IV) and Mo(III) complexes  $\text{Mo}(\text{OSiMe}_3)_4$ - $(\text{NHMe}_2)_2$ <sup>56</sup> and  $[\text{Mo}(\text{OSiMe}_3)_3(\text{NHMe}_2)_2]$ <sup>57</sup> (1.95 Å in both), respectively. Metal(VI, VII) compounds of the type  $[\text{MY}_3\text{X}]^{0-}$ , in which Y is a double- and X is a single-bonded ligand, are not uncommon. Familiar examples include the oxyhalides  $[\text{CrO}_3\text{X}]^-$  and  $\text{MO}_3\text{X}$  (X = F, Cl, Br; M = Mn, Te, Re). Related compounds are  $\text{ReO}_3(\text{OSiMe}_3)$ ,<sup>58</sup>  $\text{Re}(\text{N}-t\text{-Bu})_3(\text{OSiMe}_3)$ ,<sup>59</sup>  $\text{ReO}_3\text{C}-\text{H}_3$ ,<sup>60</sup> and polymeric  $\text{MoO}_4\text{SnMe}_2$ .<sup>61</sup> With molybdenum, salts of  $[\text{MoO}_3\text{Cl}]^-$  have been isolated<sup>62</sup> and generation of the alkylmolybdates  $[\text{MoO}_3\text{R}]^-$  has been claimed.<sup>63</sup> These species have not been well characterized.

Of the previously known four-coordinate Mo(VI) species,  $[\text{MoS}_3(\text{OSiMe}_3)]^-$  is expected to resemble  $[\text{MoOS}_3]^{2-}$  most closely. Under  $C_{3v}$  symmetry mean values of S-Mo-S and O-Mo-S angles of the two anions are within 1°. The  $\nu_{\text{MoS}}$  bands of  $[\text{MoS}_3(\text{OSiMe}_3)]^-$ , at 512 and 503 (sh)  $\text{cm}^{-1}$ , are  $\sim 40 \text{ cm}^{-1}$  higher than those of  $[\text{MoOS}_3]^{2-}$ ,<sup>64</sup> consistent with the marginally longer Mo-S bonds (2.179 (5) Å<sup>29</sup>) of the latter. Extended Hückel calculations of  $[\text{MoS}_3(\text{OSiMe}_3)]^-$  afford an orbital order in the HOMO and LUMO regions that accords closely with the proposed MO scheme for  $[\text{MoOS}_3]^{2-}$ .<sup>65</sup> This result conforms to the previously noted similarity in the intense LMCT spectra of the two ions. The lowest energy band can be securely assigned as  $^1\text{A}_1 \rightarrow ^1\text{E}$ ; proposed assignments for other bands of  $[\text{MoOS}_3]^{2-}$  are given elsewhere.<sup>65</sup>

**Summary.** Reaction of  $[\text{Mo}_2\text{O}_7]^{2-}$  with  $n = 1-7$  equiv of  $(\text{Me}_3\text{Si})_2\text{S}$  in acetonitrile solution generates the series  $[\text{MoO}_{3-x}\text{S}_x(\text{OSiMe}_3)]^-$  ( $x = 0-3$ ). Detection and identification of these species provide an instructive example of the utility of multinuclear NMR spectroscopy. Identification was aided by monotonic deshielding of  $^{17}\text{O}$  and  $^{95}\text{Mo}$  resonances as  $x$  increases, a behavior previously found in the series  $[\text{MoO}_{4-x}\text{S}_x]^{2-}$  ( $x = 0-4$ ). A plausible mechanistic interpretation of principal product formation involves addition of  $(\text{Me}_3\text{Si})_2\text{S}$  across Mo=O bonds followed by elimination of  $(\text{Me}_3\text{Si})_2\text{O}$  from intermediates 5-7 to generate Mo=S groups. The  $\text{Me}_3\text{Si}$  group migration in the process 5  $\rightarrow$  6 is proposed to account for the mononuclear products. The terminal series member,  $[\text{MoS}_3(\text{OSiMe}_3)]^-$ , has been isolated as its  $\text{Ph}_4\text{P}^+$  salt, which is a 1:1 electrolyte in acetonitrile. This species is structurally and spectroscopically related to  $[\text{MoOS}_3]^{2-}$ . Product distribution implies some reduction of Mo(VI) by the sulfide reagent; reduction products have not been detected by  $^{95}\text{Mo}$  NMR spectroscopy and are unidentified. This result, together with the formation of mononuclear species as the principal products, suggests that the cage structures of polyoxomolybdates(VI) of higher nuclearity may not be sustainable upon O/S substitution. This has proven to be the case in the reaction of  $[\text{Mo}_8\text{O}_{26}]^{4-}$  with  $(\text{Me}_3\text{Si})_2\text{S}$ , from which trinuclear species containing reduced Mo have been isolated.<sup>66</sup> Lastly,  $[\text{MoS}_3(\text{OSiMe}_3)]^-$  may prove to be a useful precursor to new mono- and polynuclear Mo-S species. This matter is under investigation.

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**Registry No.**  $(\text{Ph}_4\text{P})[\text{MoS}_3(\text{OSiMe}_3)]$ , 96211-55-1;  $(n\text{-Bu}_4\text{N})_2[\text{Mo}_2\text{O}_7]$ , 64444-05-9;  $(\text{Me}_3\text{Si})_2\text{S}$ , 3385-94-2;  $[\text{MoO}_3(\text{OSiMe}_3)]^-$ , 96211-58-4;  $[\text{MoO}_2\text{S}(\text{OSiMe}_3)]^-$ , 96211-59-5;  $[\text{MoOS}_2(\text{OSiMe}_3)]^-$ , 96211-60-8.

**Supplementary Material Available:** X-ray structural data for  $(\text{Ph}_4\text{P})[\text{MoS}_3(\text{OSiMe}_3)]$ , including listings of observed and calculated structure factors, anisotropic thermal parameters of non-hydrogen atoms, and positional and thermal parameters of hydrogen atoms (13 pages). Ordering information is given on any current masthead page.

- (54) Kutzler, F. W.; Scott, R. A.; Berg, J. M.; Hodgson, K. O.; Doniach, S.; Cramer, S. P.; Chang, C. H. *J. Am. Chem. Soc.* **1981**, *103*, 6083.  
 (55) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1980**, *19*, 777.  
 (56) Chisholm, M. H.; Reichert, W. W.; Thornton, P. *J. Am. Chem. Soc.* **1978**, *100*, 2744.  
 (57) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 153.  
 (58) Schmidt, M.; Schmidbaur, H. *Chem. Ber.* **1959**, *92*, 2667; *Inorg. Synth.* **1967**, *9*, 149.  
 (59) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1105.  
 (60) Beattie, I. R.; Jones, P. J. *Inorg. Chem.* **1979**, *18*, 2318.  
 (61) Sasaki, Y.; Imoto, H.; Nagano, O. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1417.  
 (62) Königer-Ahlborn, E.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 574.  
 (63) Schrauzer, G. N.; Hughes, L. A.; Strampach, N. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 380.

- (64) Müller, A.; Diemann, E.; Heidborn, U. *Z. Anorg. Allg. Chem.* **1969**, *371*, 136.  
 (65) Diemann, E.; Müller, A. *Spectrochim. Acta, Part A* **1970**, *26A*, 215. Müller, A.; Diemann, E.; Neumann, F.; Menge, R. *Chem. Phys. Lett.* **1972**, *16*, 521.  
 (66) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.*, in press.