

atoms to be coplanar, and the iron is 0.110 Å out of this plane. The two phenyl substituents are on opposite sides of this plane with the C<sub>11</sub>-C<sub>16</sub> ring on the same side as the iron atom. The negative charge and the double bonds do not appear to be localized as in III; there is instead extensive delocalization of the ligand  $\pi$  system. This delocalization is not typical of iron(III)-imine complexes as there are usually<sup>9-13</sup> distinct carbon-nitrogen single bonds and carbon-nitrogen double bonds. This type of delocalization is postulated for the intermediate in transamination and other reactions of metal complexes of the imines of pyridoxal and  $\alpha$ -amino acids.<sup>14</sup> The delocalization in the iron compound may be enhanced by the phenyl substituents since the phenyl rings are aligned with the chelate rings.

The phenyl groups have the expected parameters. The carbon-carbon bond distances vary from 1.33 to 1.42 Å with an average of 1.38 (3) Å; the angles vary from 118 to 123° with an average of 120 (1)°.

The mechanism of formation of the tridentate ligand is of considerable interest. The dependence on metal ion and molecular oxygen suggests an oxidative deamination process, as observed with vitamin B<sub>6</sub> complexes<sup>14</sup> followed by condensation with a second molecule of  $\alpha$ -aminoacetophenone.

In the absence of a metal ion, the  $\alpha$ -aminoacetophenone hydrochloride seems stable in solution. However upon neutralization of the hydrochloride salt self-condensation takes place to yield a cyclic dimer, C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>. With iron(II) chloride in the absence of oxygen, the  $\alpha$ -aminoacetophenone hydrochloride reacts to form a salt, (C<sub>8</sub>H<sub>10</sub>NO)<sub>2</sub>FeCl<sub>4</sub>. An orange

solution of this salt in ethanol upon exposure to air gives a red solution from which green crystals of the iron(III) compound separate. With an excess of  $\alpha$ -aminoacetophenone hydrochloride in the absence of molecular oxygen, the color of the solution changes to yellow and the iron is apparently reduced. Addition of oxygen restores the red color of the iron(III) compound.

**Registry No.** FeLCl<sub>2</sub>(EtOH), 68070-71-3; I·HCl, 5468-37-1; (C<sub>8</sub>H<sub>10</sub>NO)<sub>2</sub>FeCl<sub>4</sub>, 68036-76-0.

**Supplementary Material Available:** Table of observed and calculated structure factors for FeLCl<sub>2</sub>(EtOH) (9 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) B. N. Figgis and J. Lewis, *Mod. Coord. Chem.*, 403 (1960).
- (2) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digit(s).
- (3) "International Tables for X-Ray Crystallography", Vol. 1, Kynoch Press, Birmingham, England, 1952.
- (4) Programs utilized were Zalkin's FORDP Fourier summation program, Iber's NUCLS modification of the Busing-Martin-Levy least-squares program, Doeden's RBANG rigid-group orientation program, and Johnson's ORTEP program.
- (5) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
- (6) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- (7) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
- (8) Supplementary material.
- (9) M. Gerlach and F. E. Mabbs, *J. Chem. Soc. A*, 1598 (1967).
- (10) M. Gerlach and F. E. Mabbs, *J. Chem. Soc. A*, 1900 (1967).
- (11) J. A. Bertrand and J. L. Breece, *Inorg. Chim. Acta*, **8**, 267 (1974).
- (12) J. A. Bertrand, J. L. Breece, and P. G. Eller, *Inorg. Chem.*, **13**, 125 (1974).
- (13) J. A. Bertrand and P. G. Eller, *Inorg. Chem.*, **13**, 927 (1974).
- (14) R. H. Holm, *Inorg. Biochem.*, 1150 (1973).

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202

## Structural Chemistry of Molybdenum Complexes of Cyclic Polythia Ethers. Crystal and Molecular Structure of (Hydrosulfido)(oxo)(1,5,9,13-tetrathiacyclohexadecane)molybdenum(IV) Trifluoromethanesulfonate

RICHARD E. DESIMONE\* and MILTON D. GLICK

Received July 7, 1978

The crystal and molecular structures of (hydrosulfido)(oxo)(1,5,9,13-tetrathiacyclohexadecane)molybdenum(IV) trifluoromethanesulfonate are reported. The complex crystallizes in the monoclinic space group  $P2_1/c$  with four molecules per unit cell of dimensions  $a = 7.494$  (3) Å,  $b = 20.500$  (6) Å,  $c = 14.902$  (5) Å,  $\beta = 101.09$  (3)°, and  $V = 2248$  (1) Å<sup>3</sup>. Full-matrix least-squares refinement gave final discrepancy factors of  $R_1 = 0.035$  and  $R_2 = 0.047$  for 2509 data for which  $F^2 > 2.5\sigma(F^2)$ . The macrocyclic ring is coordinated to molybdenum in the conventional planar tetradentate manner, with oxo and hydrosulfido groups occupying trans positions along the symmetry axis of the monomeric cation. A comparison of bonding parameters in the title complex with those in the sulfur-bridged dimeric precursor complex is given.

### Introduction

In our investigation of molybdenum complexes of cyclic polythia ethers, we have studied in detail the reaction of the binuclear quadruply bonded dimolybdenum trifluoromethanesulfonate [Mo<sup>II</sup><sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> with the 16-membered macrocyclic polythia ether 1,5,9,13-tetrathiacyclohexadecane.<sup>1</sup> The reaction yields several products, three of which have been structurally characterized. This is the last of three reports on those complexes.<sup>1,2</sup>

Previous structural work on complexes of cyclic polythia ethers has revealed interesting features, dictated in part by the constraints imposed by the macrocycle. These have included the exo or "inside out" conformation found in the complex (NbCl<sub>5</sub>)<sub>2</sub>(14-ane[S<sub>4</sub>])<sup>3,4</sup> and the unique bridging nature of tetradentate 16-ane[S<sub>4</sub>] in the complex [Mo<sub>2</sub>(SH)<sub>2</sub>(16-ane[S<sub>4</sub>])](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O from which the title

compound is derived.<sup>1</sup> This is the first mononuclear molybdenum complex of a cyclic polythia ether for which the structure has been determined. The most notable feature is the terminal SH group in the lower axial coordination site. Bridging SH groups or SR groups are not uncommon in Mo chemistry, but terminal sulfur ligands are usually the doubly bonded sulfide.

### Experimental Section

The synthesis of the title compound has been reported previously.<sup>1</sup> Crystals were isolated from the reaction vessel with only a wash of warm hexane to remove surface organic contaminants. The crystals were found to be air stable but were nonetheless sealed in thin-walled capillaries as a precaution.

A suitable crystal measuring approximately 0.38 × 0.19 × 0.11 mm<sup>3</sup> was mounted on a Syntex P<sub>2</sub> four-circle diffractometer. Oscillation photographs, together with a small set of counter data,

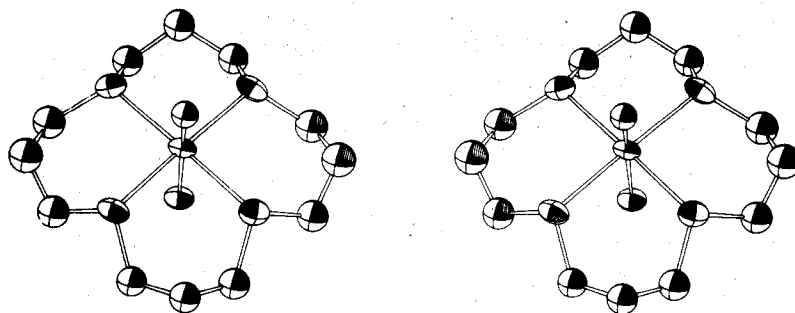


Figure 1. Stereoscopic projection of the cation  $[\text{MoO}(\text{SH})(16\text{-ane}[\text{S}_4])]^+$ .

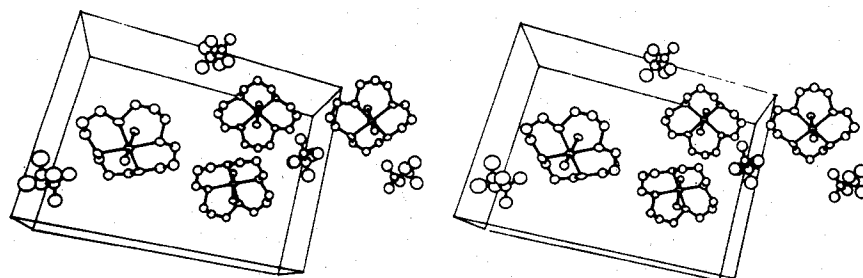


Figure 2. Unit cell contents in stereoscopic projection.

established that the crystal was monoclinic. Fifteen reflections with  $2\theta$  between 25 and  $32^\circ$  were centered using a programmed centering routine. Lattice constants and errors were determined by least-squares refinement of the angles defining these 15 reflections, yielding the following values:  $a = 23.116(11) \text{ \AA}$ ,  $b = 20.508(7) \text{ \AA}$ ,  $c = 7.497(3) \text{ \AA}$ ,  $\beta = 140.78(2)^\circ$ ,  $V = 22.47(11) \text{ \AA}^3$ . Intensity data were collected in the  $\pm h, k, l$  quadrants to a value of  $2\theta = 45^\circ$  using Mo  $K\alpha$  radiation ( $\lambda 0.71069 \text{ \AA}$ ). The monochromator consisted of a highly oriented graphite crystal in the parallel mode. The  $\theta$ - $2\theta$  scan technique was used with a scan rate of  $2.02^\circ/\text{min}$  and a scan range of  $1^\circ$  below Mo  $K\alpha_1$  to  $1^\circ$  above Mo  $K\alpha_2$  in  $2\theta$ . Backgrounds were measured at each end of the scan for a total time equal to half of the scan time. During data collection, the intensities of three standard reflections were measured every 50 reflections with no indication of decomposition or crystal movement. The data were reduced to  $F^2$  and  $\sigma(F^2)$  by procedures previously described.<sup>5</sup> Standard deviations were assigned as

$$\sigma(I) = [(\sigma_{\text{counter}}(I))^2 + (0.04I)^2]^{1/2}$$

where  $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$ ,  $I$  = net intensity,  $B$  = background counts, and  $K$  = ratio of scan time to background time. Corrections were made for Lorentz and polarization effects but not for extinction or absorption. The linear absorption coefficient for Mo  $K\alpha$  radiation is  $10.6 \text{ cm}^{-1}$ . Data with  $F^2 > 2.5\sigma(F^2)$  were separated from the entire data set of 3354 reflections yielding a total of 2509 observed reflections. The systematic absences indicated the space group was  $P2_1/a$ .

In light of the nonstandard setting and the large value of  $\beta$ , which would lead to extensive correlation of variables, the data were transformed to a cell with symmetry  $P2_1/c$ . The required direct cell transformation is

$$\begin{bmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 2 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}_{\text{old}} = \begin{bmatrix} a \\ b \\ c \end{bmatrix}_{\text{new}}$$

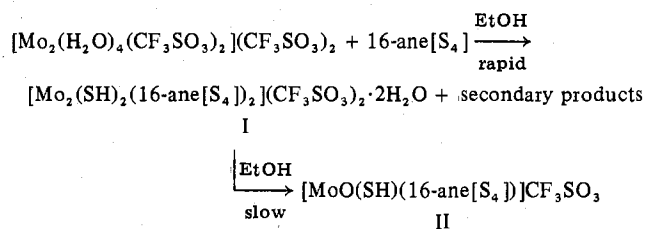
and the new parameters are  $a = 7.494(3) \text{ \AA}$ ,  $b = 20.500(6) \text{ \AA}$ ,  $c = 14.902(5) \text{ \AA}$ ,  $\beta = 101.09(3)^\circ$ , and  $V = 2248(1) \text{ \AA}^3$ . The solution and refinement were carried out in the latter cell. The calculated density based on 4 molecules/unit cell is  $1.745 \text{ g/cm}^3$ ; the experimental density is  $1.75_5 \text{ g/cm}^3$ .

The structure was solved by Patterson-Fourier techniques. The position of the molybdenum atom was clearly revealed by the Patterson synthesis, and a structure factor calculation based on this atom produced a standard unweighted residual  $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$  of 0.503 and a weighted residual  $R_2 = [(\sum w(|F_o| - |F_c|)^2) / \sum wF_o^2]^{1/2}$  of 0.568. The six sulfur atoms were clearly revealed in a Fourier map phased by the single Mo atom. A structure factor calculation incorporating these seven atoms gave  $R_1 = 0.309$  and  $R_2 = 0.384$ .

Addition of all of the remaining nonhydrogen atoms resulted in  $R_1 = 0.181$  and  $R_2 = 0.230$ . Refinement of positional and isotropic thermal parameters produced  $R_1 = 0.108$  and  $R_2 = 0.137$ . The use of anisotropic thermal parameters for Mo and S gave  $R_1 = 0.062$  and  $R_2 = 0.088$ . At this point hydrogen atom positions for the 24 macrocycle hydrogens were calculated and their contribution incorporated in a fixed manner into the least-squares refinement yielding  $R_1 = 0.058$  and  $R_2 = 0.079$ . Final refinement with anisotropic thermal parameters on all nonhydrogen atoms (244 variables) gave final values of  $R_1 = 0.035$  and  $R_2 = 0.047$ . A final difference Fourier map showed that the five largest residual peaks (0.67–0.95 e) reside within the anion. The highest residual peak in the cation is 0.61 e at a point  $\sim 0.55 \text{ \AA}$  from S(5), the terminal sulfur atom.

## Results and Discussion

Our understanding of the reactions of cyclic polythia ethers with dimolybdenum trifluoromethanesulfonate suggests that the title compound (II) is formed in the sequence of reactions



from the cleavage product of the sulfur-bridged dimer via slow oxidative addition of solvent and/or free water. As such the coordination about the Mo in II differs from that in I only by the addition of the oxo ligand. The structure of the cation is shown in Figure 1. Table I lists atomic coordinates and thermal parameters with standard deviations for nonhydrogen atoms in the asymmetric unit. Figure 2 shows the unit cell contents in stereoscopic projection, and Table II lists bond lengths and angles. As an aid to visualizing ring conformation, a schematic drawing of the cation is presented in Figure 3. A tabulation of dihedral angles and displacements from the plane of the four sulfur atoms of the macrocycle is available along with a listing of calculated and observed structure factors.<sup>6</sup>

The metal coordination sphere features an endodentate tetradentate macrocyclic ring with four coplanar sulfur atoms at distances from the molybdenum atom of 2.476–2.484  $\text{\AA}$ . Out of the plane of the ring, the Mo atom is bonded to an oxygen at 1.667  $\text{\AA}$  and to the terminal SH at 2.486  $\text{\AA}$ . The

Table I. Atomic Coordinates and Thermal Parameters<sup>a,b</sup>

atom	x	y	z	atom	x	y	z
Mo	0.43811 (6)	-0.23398 (3)	0.01810 (3)	C(1)	0.3405 (9)	-0.0685 (3)	-0.0563 (4)
S(1)	0.5248 (2)	-0.1276 (1)	-0.0411 (1)	C(2)	0.2701 (10)	-0.0555 (3)	0.0315 (5)
S(2)	0.6263 (2)	-0.2897 (1)	-0.0774 (1)	C(3)	0.1333 (9)	-0.1049 (3)	0.0516 (5)
S(3)	0.3353 (2)	-0.3402 (1)	0.0699 (1)	C(4)	0.0221 (8)	-0.2210 (3)	0.1061 (4)
S(4)	0.2336 (2)	-0.1781 (1)	0.1058 (1)	C(5)	0.0447 (8)	-0.2909 (4)	0.1391 (4)
S(5)	0.1788 (2)	-0.2394 (1)	-0.1137 (1)	C(6)	0.0945 (8)	-0.3391 (3)	0.0712 (4)
S(6)	-0.1128 (3)	-0.4856 (1)	0.2357 (1)	C(7)	0.3275 (10)	-0.4047 (3)	-0.0141 (4)
F(1)	-0.1748 (8)	-0.0587 (3)	0.2163 (4)	C(8)	0.5062 (11)	-0.3664 (3)	-0.1224 (4)
F(2)	0.2217 (7)	-0.4762 (3)	0.2154 (4)	C(9)	0.5300 (9)	-0.2496 (3)	-0.1862 (4)
F(3)	-0.0756 (8)	-0.4523 (3)	-0.1352 (4)	C(10)	0.6231 (9)	-0.2496 (3)	-0.1862 (4)
O(1)	0.2261 (8)	-0.0414 (3)	0.2624 (4)	C(11)	0.6850 (9)	-0.1796 (3)	-0.1790 (4)
O(2)	-0.1713 (8)	-0.4462 (3)	0.1610 (4)	C(12)	0.5467 (9)	-0.1315 (3)	-0.1607 (4)
O(3)	-0.0618 (8)	-0.0415 (3)	-0.1747 (4)	C(13)	-0.0918 (11)	-0.4776 (4)	-0.2168 (6)
O(4)	0.6116 (5)	-0.2299 (2)	0.1067 (2)				

atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Mo	0.00963 (9)	0.00224 (2)	0.00225 (2)	-0.00013 (3)	0.00098 (3)	-0.00003 (1)
S(1)	0.0156 (3)	0.0027 (0)	0.0041 (1)	-0.0012 (1)	0.0021 (1)	-0.0000 (0)
S(2)	0.0134 (3)	0.0033 (1)	0.0031 (1)	-0.0010 (1)	0.0018 (1)	-0.0001 (0)
S(3)	0.0165 (3)	0.0028 (0)	0.0036 (1)	0.0004 (1)	0.0017 (1)	0.0008 (0)
S(4)	0.0126 (3)	0.0032 (1)	0.0037 (1)	-0.0006 (1)	0.0026 (1)	-0.0009 (0)
S(5)	0.0119 (3)	0.0028 (0)	0.0026 (1)	-0.0009 (1)	-0.0004 (1)	0.0002 (0)
S(6)	0.0260 (4)	0.0031 (1)	0.0061 (1)	-0.0005 (1)	0.0037 (1)	-0.0003 (1)
F(1)	0.0470 (16)	0.0067 (2)	0.0165 (5)	-0.0086 (5)	0.0073 (8)	-0.0029 (3)
F(2)	0.0296 (12)	0.0108 (3)	0.0123 (4)	-0.0040 (6)	0.0046 (6)	0.0010 (3)
F(3)	0.0417 (17)	0.0125 (3)	0.0141 (4)	0.0012 (6)	0.0063 (7)	-0.0084 (3)
O(1)	0.0408 (16)	0.0063 (2)	0.0104 (4)	0.0078 (5)	0.0068 (7)	0.0001 (2)
O(2)	0.0344 (16)	0.0071 (3)	0.0118 (4)	0.0020 (5)	0.0035 (7)	0.0048 (3)
O(3)	0.0321 (15)	0.0061 (2)	0.0102 (4)	-0.0009 (5)	0.0030 (6)	0.0039 (3)
O(4)	0.0115 (7)	0.0041 (1)	0.0029 (2)	-0.0001 (3)	0.0011 (3)	0.0001 (1)
C(1)	0.0224 (15)	0.0026 (2)	0.0066 (4)	0.0065 (5)	0.0037 (7)	0.0003 (2)
C(2)	0.0276 (18)	0.0025 (2)	0.0089 (5)	-0.0006 (5)	0.0059 (8)	-0.0010 (2)
C(3)	0.0203 (15)	0.0031 (2)	0.0075 (4)	0.0031 (5)	0.0054 (7)	-0.0011 (2)
C(4)	0.0130 (11)	0.0035 (2)	0.0065 (4)	-0.0008 (4)	0.0046 (6)	-0.0007 (2)
C(5)	0.0168 (13)	0.0042 (2)	0.0048 (3)	-0.0011 (5)	0.0039 (6)	0.0006 (2)
C(6)	0.0177 (13)	0.0028 (2)	0.0053 (3)	-0.0013 (4)	0.0020 (6)	-0.0006 (2)
C(7)	0.0288 (18)	0.0023 (2)	0.0076 (5)	-0.0007 (5)	0.0049 (8)	-0.0002 (2)
C(8)	0.0354 (21)	0.0026 (2)	0.0067 (4)	0.0029 (5)	0.0048 (8)	0.0001 (2)
C(9)	0.0272 (17)	0.0029 (2)	0.0055 (4)	0.0015 (5)	0.0031 (7)	-0.0006 (2)
C(10)	0.0255 (16)	0.0037 (2)	0.0031 (3)	0.0006 (5)	0.0040 (6)	0.0001 (2)
C(11)	0.0207 (15)	0.0042 (2)	0.0042 (3)	-0.0013 (5)	0.0045 (6)	0.0003 (2)
C(12)	0.0220 (15)	0.0041 (2)	0.0039 (3)	-0.0004 (5)	0.0035 (6)	0.0009 (2)
C(13)	0.0292 (19)	0.0042 (3)	0.0082 (6)	0.0007 (6)	0.0044 (9)	-0.0015 (3)

<sup>a</sup> Standard deviations from the full variance-covariance matrix are given in parentheses for the least significant digits. <sup>b</sup> The form of the anisotropic temperature factor is  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{13} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

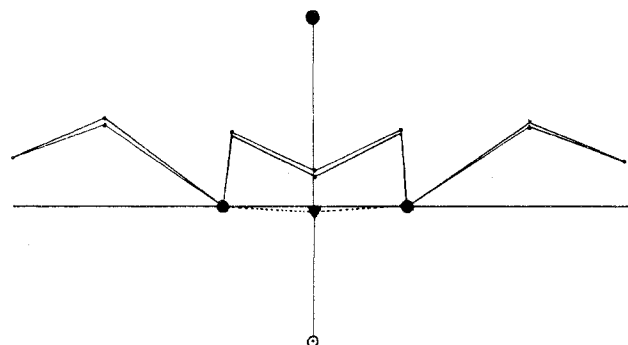


Figure 3. Schematic drawing of the cation, showing ring conformation and location of metal ion relative to the ring: ●, S; ▲, Mo; ○, O.

Mo=O distance is very typical of Mo<sup>IV</sup>=O distances but is about 0.1 Å shorter than found in the oxo-bridged Mo<sup>IV</sup> dimer which we have recently characterized as a third product of this same reaction.<sup>2</sup> A survey of several oxomolybdenum complexes in several oxidation states indicates that within a range of ~0.1 Å, Mo<sup>IV</sup>=O bond lengths depend somewhat on the trans ligand. The stronger the trans ligand, the longer the Mo<sup>IV</sup>=O bond length seems to be. All of the Mo-S bond lengths are very similar to those found in the dimeric precursor molecule I which is a Mo<sup>II</sup> species, i.e., 2.46–2.48 Å. This may

at first appear somewhat surprising, but the cavity of the macrocycle limits the variability in bond length considerably. Since both Mo<sup>II</sup> and Mo<sup>IV</sup> evidently fit into roughly the same sized cavity (allowing for slight differences in ring conformation and out-of-plane location of the metal), one could reasonably conclude that Mo<sup>IV</sup> fits the cavity with room to spare, although it is unlikely that the cavity is so large as to allow the ion to “rattle around”. Were it not for the strongly bonded oxo ligand trans to the SH, this ligand would be expected to exhibit a shorter Mo-S bond length than is observed. As it is, the Mo<sup>IV</sup>-SH distance is 0.015 Å longer than the Mo<sup>II</sup>-SH distance. All of this points up the difficulty in assigning “typical” bond lengths without consideration of the overall bonding picture.

We have not unambiguously found the hydrogen on the terminal sulfur. As with the precursor complex I however, we find a small amount of electron density ~0.6 Å from the sulfur atom which may be the best we can expect to do in the way of finding this hydrogen atom. There is no doubt, however, that we are *not* dealing with a doubly bonded sulfide as a sixth ligand. Recent structural studies on completely sulfur-coordinated Mo<sup>V</sup> complexes find the Mo<sup>V</sup>=S distances to be as short as 1.93 Å,<sup>7</sup> but more typically in the range 2.08–2.13 Å.<sup>8,9</sup>

Apparently because of the ample cavity size, the Mo ion sits close to the plane defined by the four sulfur atoms of the

Table II.<sup>a</sup> Interatomic Distances (Å) and Angles (deg)

Distances			
Mo-S(1)	2.484 (2)	C(1)-C(2)	1.526 (9)
Mo-S(2)	2.469 (1)	C(2)-C(3)	1.511 (9)
Mo-S(3)	2.483 (2)	C(4)-C(5)	1.514 (9)
Mo-S(4)	2.476 (1)	C(5)-C(6)	1.512 (9)
Mo-S(5)	2.486 (1)	C(7)-C(8)	1.536 (9)
Mo-O(4)	1.667 (3)	C(8)-C(9)	1.517 (9)
S(1)-C(1)	1.818 (7)	C(10)-C(11)	1.504 (9)
S(1)-C(12)	1.822 (6)	C(11)-C(12)	1.494 (9)
S(2)-C(3)	1.800 (7)	S(6)-C(13)	1.778 (8)
S(2)-C(4)	1.813 (6)	S(6)-O(1)	1.429 (5)
S(3)-C(6)	1.814 (7)	S(6)-O(2)	1.376 (5)
S(3)-C(7)	1.809 (6)	S(6)-O(3)	1.429 (5)
S(4)-C(9)	1.804 (7)	C(13)-F(1)	1.302 (9)
S(4)-C(10)	1.813 (6)	C(13)-F(2)	1.361 (9)
		C(13)-F(3)	1.306 (8)
Angles			
S(5)-Mo-S(1)	88.69 (5)	S(2)-C(4)-C(5)	114.6 (4)
S(5)-Mo-S(2)	88.26 (6)	C(4)-C(5)-C(6)	115.2 (5)
S(5)-Mo-S(3)	87.91 (6)	C(5)-C(6)-S(3)	113.0 (4)
S(5)-Mo-S(4)	88.21 (6)	S(3)-C(7)-C(8)	114.3 (5)
O(4)-Mo-S(1)	91.31 (5)	C(7)-C(8)-C(9)	112.9 (6)
O(4)-Mo-S(2)	91.74 (5)	C(8)-C(9)-S(4)	113.1 (5)
O(4)-Mo-S(3)	92.09 (5)	S(4)-C(10)-C(11)	114.7 (4)
O(4)-Mo-S(4)	91.79 (5)	C(10)-C(11)-C(12)	115.3 (5)
S(1)-Mo-S(2)	89.10 (5)	C(11)-C(12)-S(1)	113.9 (4)
S(1)-Mo-S(3)	176.59 (5)	O(1)-S(6)-O(2)	112.8 (4)
S(2)-Mo-S(3)	91.05 (5)	O(1)-S(6)-O(3)	110.2 (4)
S(2)-Mo-S(4)	176.47 (9)	O(2)-S(6)-O(3)	121.0 (4)
S(3)-Mo-S(4)	88.87 (5)	O(1)-S(6)-C(13)	101.3 (4)
S(4)-Mo-S(1)	90.77 (5)	O(2)-S(6)-C(13)	105.7 (4)
C(12)-S(1)-C(1)	96.7 (3)	O(3)-S(6)-C(13)	103.2 (4)
C(3)-S(2)-C(4)	97.3 (3)	F(1)-C(13)-F(2)	99.8 (7)
C(6)-S(3)-C(7)	96.7 (3)	F(1)-C(13)-F(3)	115.5 (7)
C(9)-S(4)-C(10)	96.7 (3)	F(2)-C(13)-F(3)	101.6 (7)
S(1)-C(1)-C(2)	112.9 (5)	F(1)-C(13)-S(6)	114.9 (6)
C(1)-C(2)-C(3)	114.3 (5)	F(2)-C(13)-S(6)	110.4 (6)
C(2)-C(3)-S(2)	114.0 (5)	F(3)-C(13)-S(6)	112.8 (6)

<sup>a</sup> Number in parentheses represents the estimated standard deviation of the least significant digit(s).

macrocycle, displaced only 0.07 Å toward the oxo group. The O-Mo-S angles range from 91.3 to 92.1°. The structural parameters defining the macrocyclic ring are quite regular. Carbon-sulfur distances average 1.812 Å (range of 0.018 Å). Carbon-carbon distances average 1.514 Å (range of 0.042 Å). C-S-C angles average 96.9° (range of 0.5°), and S-C-C angles average 114.0° (range of 2-4°). Dihedral angles are consistent with a relatively strain-free conformation, although as we have previously pointed out, the usual criteria for strain

in cyclic hydrocarbons do not seem particularly applicable here.<sup>1</sup>

As with other structures in this series, the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> anion is the least satisfactory aspect. S-O distances average 1.411 Å (range of 0.053 Å), and C-F distances average 1.323 Å (range of 0.059 Å). O-S-O angles average 114.7° (range of 10.8°), and F-C-F angles average 105.6° (range of 15.7°). Thermal parameters on F and O atoms are substantially higher than for other atoms in the molecule, indicating high thermal and/or rotational motion.

There are no intermolecular contacts or evidence of extended structure.

In summary, this structure substantiates our notion that the molecule is derived from its precursor I by cleavage of the sulfur bridge and reaction with solvent. It provides another example of a Mo<sup>IV</sup> complex containing a terminal Mo-S bond and serves as a prototype for a planar-coordinated monomeric Mo<sup>IV</sup> complex of a cyclic polythia ether.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. M.D.G. also acknowledges support of the National Science Foundation.

**Registry No.** II, 67351-10-4.

**Supplementary Material Available:** A listing of calculated and observed structure factors and a diagram giving dihedral angles and mean displacements from the plane of the four sulfurs of the macrocycle (11 pages). Ordering information is given on any current masthead page.

#### References and Notes

- J. Cragel, Jr., V. B. Pett, M. D. Glick, and R. E. DeSimone, *Inorg. Chem.*, **17**, 2885 (1978).
- R. E. DeSimone, J. Cragel, Jr., and M. D. Glick, *J. Coord. Chem.*, in press.
- R. E. DeSimone and M. D. Glick, *J. Am. Chem. Soc.*, **97**, 942 (1975).
- R. E. DeSimone and M. D. Glick, *J. Coord. Chem.*, **5**, 181 (1976).
- (a) Local versions of the following programs were used: (i) TRACER II, S. L. Lawton's cell reduction program; (ii) SYNCOR, W. Schmonsees' program for data reduction; (iii) FORDAP, A. Zalkin's Fourier program; (iv) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program, respectively; (v) ORTEP, C. K. Johnson's program for drawing crystal models. (b) Scattering factors for Mo, S, F, O, C and H were taken from "The International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Eds., Kynoch Press, Birmingham, England, 1974.
- Supplementary material.
- B. Spivak, Z. Don, and E. I. Steifel, *Inorg. Nucl. Chem. Lett.*, **11**, 501 (1975).
- G. Bunzey and J. H. Enemark, *Inorg. Chem.*, **17**, 682 (1978).
- J. T. Huneke and J. H. Enemark, *Inorg. Chem.*, in press.