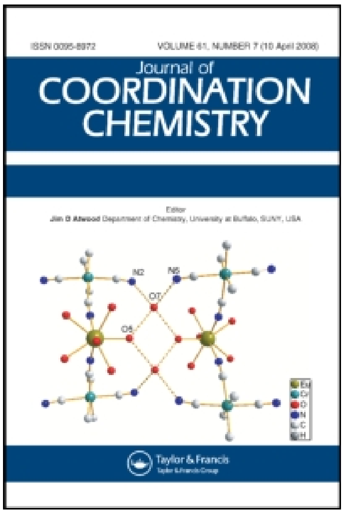

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STRUCTURAL CHEMISTRY OF MOLYBDENUM COMPLEXES OF CYCLIC POLYTHIAETHERS: THE CRYSTAL AND MOLECULAR STRUCTURE OF ETHOXIDO-OXO-BIS(1,5,9,13-TETRATHIACYCLOHEXADECANE)-μ-OXODIMOLYB-DENUM(IV) TRIFLUOROMETHANESULFONATE HYDRATE

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STRUCTURAL CHEMISTRY OF MOLYBDENUM COMPLEXES OF CYCLIC POLYTHIAETHERS: THE CRYSTAL AND MOLECULAR STRUCTURE OF ETHOXIDO-OXO-BIS(1,5,9,13-TETRATHIACYCLOHEXADECANE)-μ-OXODIMOLYBDENUM(IV) TRIFLUOROMETHANESULFONATE HYDRATE

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The crystal and molecular structures of ethoxido-oxo-bis(1,5,9,13-tetrathiacyclohexadecane)-μ-oxodimolybdenum-(IV) trifluoromethanesulfonate hydrate are reported. The complex crystallizes in the orthohombic space group $Pn2_1a$ with four molecules per unit cell of dimensions a = 16.149(2)Å, b = 20.477(4)Å, c = 15.217(2)Å and V = 5381(2)Å^3. Full matrix least squares refinement gave final discrepancy factors of R_1 = .076 and R_2 = .094 for 3147 data having $F^2 > 2.5\sigma(F^2)$. The molecular structure is highlighted by a linear O–Mo=O—Mo=O unit. The two macrocycles coordinate each Mo atom in a "planar" tetradentate mode, and are staggered ∿43° relative to one another.

INTRODUCTION

In our investigation of molybdenum complexes of cyclic polythiaethers we have studied in detail the reaction of the binuclear quadruply bonded 'dimolybdenum trifluoromethanesulfonate', $[Mo_2^{II}(H_2O)_4(CF_3SO_3)_2](CF_3SO_3)_2$ with the 16-membered macrocyclic polythiaether 1,5,9,13-tetrathiacyclohexadecane. The reaction yields several products, three of which have been structurally characterized.[1,2]

$$\text{`}Mo_2(CF_3SO_3)_4\text{'} + 16\text{-ane}[S_4] \xrightarrow[EtOH]{}$$

$$[Mo_2^{II}(SH)_2(16\text{-ane}[S_4])_2](CF_3SO_3)_2 \cdot 2H_2O \qquad (i)$$

$$+[Mo_2^{IV}O_2(16\text{-ane}[S_4])_2OC_2H_5](CF_3SO_3)_3 \cdot H_2O \qquad (ii)$$

$$+[Mo^{IV}O(SH)(16\text{-ane}[S_4])]CF_3SO_3 \qquad (iii)$$

This report deals with (ii), the second of these complexes.

Previous structural work on complexes of cyclic polythiaethers has revealed several interesting and unique features, dictated in part by the constraints imposed by the macrocycle. This has been especially true of complexes with metals of the second transition series which have been studied in this laboratory.[3,4] In the title compound we find the macrocycle behaving typically,[5] as a tetradentate ligand, in planar coordination about the metal ions. The most significant feature of the molecule appears to be the linear –O–Mo=O---Mo=O unit holding the two halves of the molecule together.

EXPERIMENTAL

The synthesis of the title compound was carried out as previously described.[1] Crystals isolated from the reaction mixture were washed with cold ethanol to remove traces of surface contaminants, and used directly. Although the compound in the solid state proved to be relatively air stable, the crystals were none-the-less sealed in thin walled capillaries as a precaution against deterioration.

Collection of Data

A suitable crystal measuring approximately .5 mm x .4 mm x .6 mm was mounted on a Syntex $P2_1$ four-circle diffractometer. Oscillation photographs, together with a small set of counter data, established that the crystal was orthorhombic. Fifteen reflections with 2θ between 23° and 30° were centered using a programmed centering routine. Lattice constants and errors were determined by least squares refinement of the angles defining these

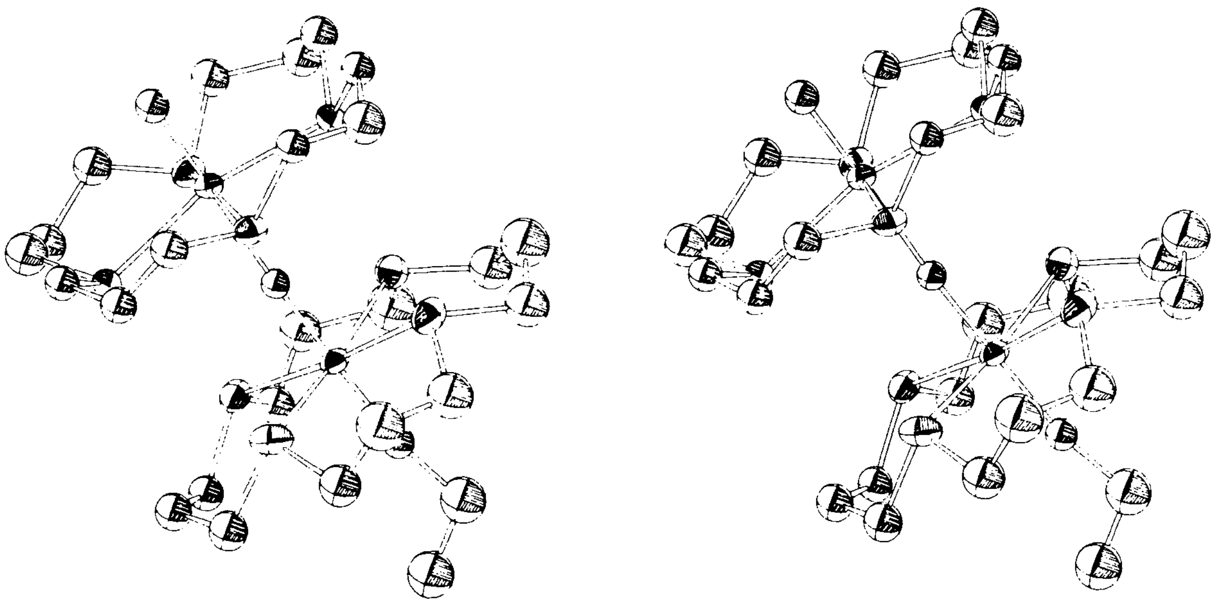

FIGURE 1 Stereoscopic view of the cation $[Mo_2^{IV}O_2(16\text{-ane}[S_4])_2OC_2H_5]^{+3}$.

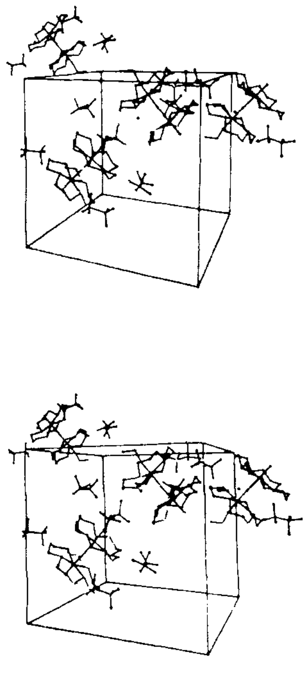

FIGURE 2 Unit cell contents in stereoscopic projection.

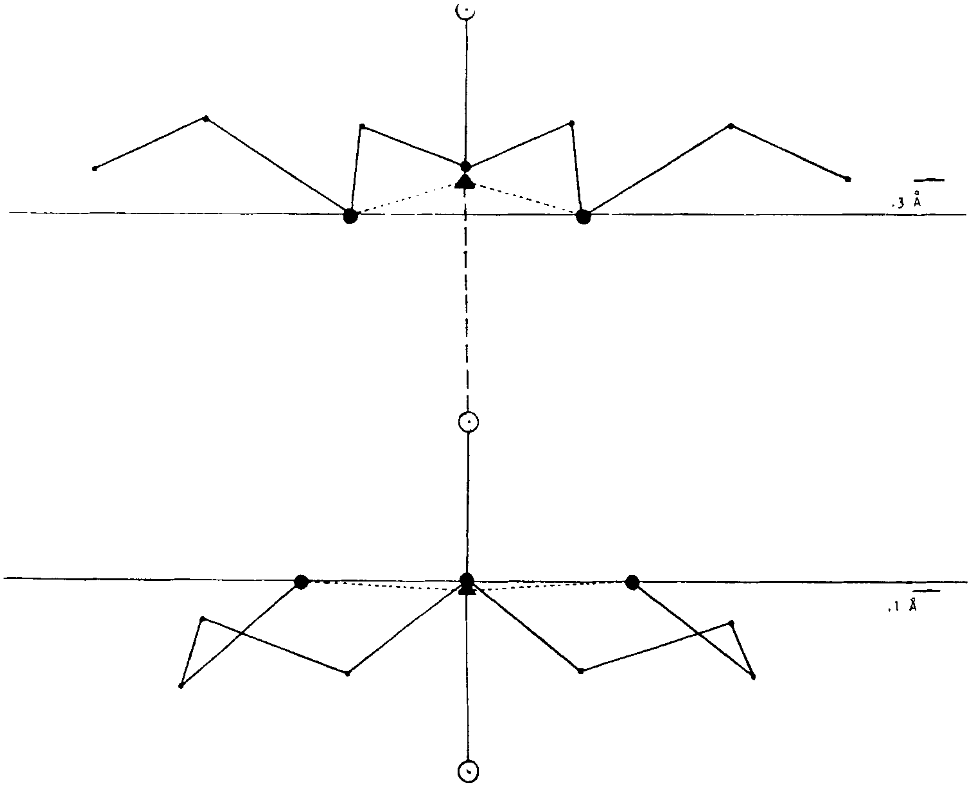

FIGURE 3 Schematic drawing of the cation, showing ring conformation and location of metal ions relative to the rings. ● = S, ▲ = Mo, ○ = O.

15 reflections, yielding the following values: a = 16.149 ± .002Å, b = 20.477 ± .004Å, c = 16.271 ± .002Å, with a unit cell volume of 5381.0 ± 1.5Å. Using this calculated volume, with 4 molecules per unit cell, the calculated density is 1.64 gm/cm^3; the experimental density is 1.67 g/cm^3. Data collection proceeded with these cell parameters. Intensity data were collected to a value of $2\theta = 45°$ in the (+h, +k, +l) octant using MoK$_\alpha$ radiation, $\lambda = .71069$Å. The monochromator consisted of a highly oriented graphite crystal in the parallel mode. The ω-scan technique was used with a scan rate of 2.02°/min. Backgrounds were measured at each end of the scan for a total time equal to one-half 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.[6] Standard deviations were assigned as follows:

$$\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (0.41)^2]^{1/2}$$

where $\sigma_{\text{counter}} = (1 + K^2 B)^{1/2}$, I = net intensity, B = total background counts and K = ratio of scan time to background time. Data were corrected for Lorentz and polarization effects, but extinction and absorption corrections were not applied. The linear absorption coefficient for MoK$_\alpha$ radiation is $\mu = 9.4$ cm^{-1}. Of the 5229 data examined, 3147 data for which $F^2 > 2.5\sigma(F^2)$ were used throughout the solution and refinement process. Systematic absences indicated that the space group was either Pnma or Pn2$_1$a.

Solution of the structure via Patterson-Fourier techniques proceeded initially in the group Pnma. The molybdenum atoms were readily located from the Patterson map, at which point it became clear that the quadruple bond in the starting material was no longer present. A structure-factor calculation with two Mo atoms led to a conventional unweighted residual,

$$R_1 = \frac{\Sigma||Fo|-|Fc||}{\Sigma|Fo|}$$

of .42 and a weighted

$$R_2 = \left[\frac{\Sigma w(|Fo|-|Fc|)^2}{\Sigma wFo^2}\right]^{1/2}$$

of .50. The phasing of the molybdenum atoms was sufficient to reveal the oxygen atoms along the Mo-Mo axis and two sets of coordinated sulfurs from the macrocycle. After breaking the pseudo-symmetry, it became clear that the apparent mirror at y = ¾ was not real, and that the correct space group is Pn2$_1$a. Subsequent cycles of least squares refinement and Fourier synthesis in the group Pn2$_1$a revealed the coordinated ethoxide, the carbon atoms of the macrocycles, and the rather poorly defined anions. Refinement of positional and isotropic thermal parameters reduced R$_1$ to .136 and R$_2$ to .177. At this point, a difference map revealed a small isolated peak which was interpreted as an oxygen atom of a lattice water molecule. Residual peaks about the molybdenum atoms and several small peaks within the anions remained at this point. Anisotropic refinement of thermal parameters of Mo and S reduced R$_1$ to .088 and R$_2$ to .115. Hydrogen atom positions were then calculated, and their structure factors incorporated in a fixed manner into the refinement. Two further cycles of least squares refinement with 321 variables reduced R$_1$ to .076 and R$_2$ to .094, their final values. Inclusion of anisotropic thermal parameters on the remaining non-anion atoms reduced R$_1$ to .072 and R$_2$ to .090, but this was not considered significant in view of the large number (145) of additional parameters introduced.

RESULTS AND DISCUSSION

The structure of the cation is shown in Figure 1, where it can be seen that the quadruple bond present in the starting material has been replaced by a weakly oxo-bridged structure. This is the apparent result of an oxidative addition process involving solvent ethanol and/or water bound to the trifluoromethanesulfonate salt. The coordination at the sixth site of the two molybdenum atoms differs--this site contains a weak bridging oxo bond in the case of Mo (1) and a strong bond to ethoxide in the case of Mo (2). This makes precise assignment of oxidation states a non-trivial problem as is discussed below. Table I lists atomic coordinates and thermal parameters with standard deviations for non-hydrogen atoms. Figure 2 shows the unit cell contents in stereoscopic projection, and Tables II and III list significant bond lengths and angles. As an aid to visualizing ring conformations, a schematic drawing of the cation is presented in Figure 3. Dihedral angles and displacements from the plane of the four sulfur atoms of the macrocycle are indicated on the schematic drawing of Figure 4.

As indicated above, the essential features of the metal coordination sphere are the oxo-bridged dimeric structure and the normal tetradentate

TABLE I
Atomic coordinates and thermal parameters[a,b]

Atom	x	y	z	β_{11} (B)	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Mo(1)	0.3236(1)	0.7500(0)	0.6289(1)	0.0031(1)	0.0024(1)	0.0028(1)	−0.0001(1)	−0.0004(1)	−0.0002(1)
Mo(2)	0.1442(1)	0.7642(1)	0.4693(1)	0.0028(1)	0.0027(1)	0.0025(1)	−0.0003(1)	−0.0006(1)	0.0002(1)
S(1)	0.3932(4)	0.6907(4)	0.5185(4)	0.0039(3)	0.0035(2)	0.0033(3)	0.0006(2)	−0.0003(2)	−0.0008(2)
S(2)	0.3677(4)	0.8540(3)	0.5643(4)	0.0036(3)	0.0031(2)	0.0039(3)	−0.0009(2)	−0.0001(2)	0.0003(2)
S(3)	0.2232(4)	0.8128(3)	0.7112(3)	0.0036(3)	0.0034(2)	0.0029(2)	0.0003(2)	0.0002(2)	−0.0004(2)
S(4)	0.2495(4)	0.6494(4)	0.6656(4)	0.0045(3)	0.0031(2)	0.0031(2)	−0.0007(2)	−0.0005(2)	0.0004(2)
S(5)	0.2462(4)	0.7998(4)	0.3646(4)	0.0035(3)	0.0046(2)	0.0030(2)	−0.0001(2)	0.0005(2)	0.0007(2)
S(6)	0.1295(4)	0.8805(3)	0.5148(4)	0.0048(3)	0.0032(2)	0.0045(3)	0.0008(2)	−0.0006(3)	−0.0004(2)
S(7)	0.0513(4)	0.7313(4)	0.5830(4)	0.0039(3)	0.0055(3)	0.0040(3)	−0.0010(2)	0.0002(2)	0.0010(2)
S(8)	0.1680(5)	0.6495(3)	0.4339(4)	0.0074(4)	0.0030(2)	0.0042(3)	−0.0002(3)	−0.0016(3)	−0.0001(2)
S(9)	0.4042(4)	0.4920(4)	0.3440(5)	0.0036(3)	0.0046(3)	0.0058(4)	−0.0000(2)	−0.0000(3)	−0.0005(3)
S(10)	0.0605(7)	0.4991(5)	0.7314(6)	0.0080(6)	0.0051(4)	0.0067(5)	−0.0007(4)	−0.0007(4)	0.0008(3)
S(11)	0.2515(7)	0.6839(6)	0.0429(6)	0.0085(6)	0.0072(5)	0.0055(4)	−0.0021(4)	−0.0018(4)	0.0015(4)
C(1)	0.4913(20)	0.7261(16)	0.4949(20)	7.0(7)					
C(2)	0.4884(20)	0.7969(16)	0.4646(20)	7.4(8)					
C(3)	0.4717(16)	0.8494(14)	0.5351(17)	6.0(6)					
C(4)	0.3805(17)	0.9175(14)	0.6371(17)	6.1(6)					
C(5)	0.2918(17)	0.9289(14)	0.6908(17)	5.9(6)					
C(6)	0.2726(17)	0.8824(14)	0.7539(17)	6.2(6)					
C(7)	0.2015(14)	0.7730(12)	0.8080(14)	4.8(5)					
C(8)	0.1676(19)	0.7039(16)	0.7959(19)	7.6(8)					
C(9)	0.2278(14)	0.6505(12)	0.7778(14)	4.7(5)					
C(10)	0.3167(16)	0.5776(14)	0.6620(17)	5.7(6)					
C(11)	0.3525(16)	0.5682(14)	0.5829(17)	5.7(6)					
C(12)	0.4261(15)	0.6105(13)	0.5578(14)	5.0(5)					
C(13)	0.2158(17)	0.8785(14)	0.3145(17)	5.8(6)					
C(14)	0.2180(19)	0.9308(15)	0.3742(18)	6.9(7)					
C(15)	0.1280(25)	0.9364(21)	0.4347(25)	11.0(10)					
C(16)	0.0294(20)	0.9036(16)	0.5461(19)	7.4(8)					
C(17)	−0.0053(24)	0.8594(22)	0.6147(25)	10.7(11)					
C(18)	−0.0395(20)	0.7888(16)	0.5984(21)	8.5(8)					

TABLE I, cont.
Atomic coordinates and thermal parameters[a,b]

Atom	x	y	z	β_{11} (B)	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
C(19)	−0.0083(21)	0.6552(18)	0.5506(20)	9.4(10)					
C(20)	0.0488(22)	0.6025(20)	0.5242(25)	9.4(10)					
C(21)	0.0729(19)	0.6026(16)	0.4401(19)	6.9(7)					
C(22)	0.1861(16)	0.6394(13)	0.3214(16)	5.8(6)					
C(23)	0.2554(16)	0.6776(13)	0.2943(16)	5.6(6)					
C(24)	0.2411(13)	0.7499(13)	0.2763(13)	4.9(5)					
C(25)	−0.0273(21)	0.7782(18)	0.3539(22)	8.8(9)					
C(26)	−0.0162(20)	0.7593(21)	0.2685(22)	9.3(8)					
C(27)	0.4437(32)	0.5330(26)	0.2533(33)	13.4(14)					
C(28)	0.0453(31)	0.4483(27)	0.8142(31)	11.8(13)					
C(29)	0.2434(30)	0.5977(25)	0.0227(32)	14.9(13)					
O(1)	0.4046(8)	0.7447(8)	0.7014(9)	4.6(3)					
O(2)	0.2271(7)	0.7579(8)	0.5392(7)	3.6(3)					
O(3)	0.0555(8)	0.7713(7)	0.3963(8)	4.1(3)					
O(4)	0.3219(14)	0.5201(11)	0.3478(14)	9.0(6)					
O(5)	0.4149(13)	0.4293(11)	0.3126(14)	7.6(5)					
O(6)	0.4519(16)	0.5082(12)	0.4035(16)	9.2(6)					
O(7)	0.1456(18)	0.5020(13)	0.7275(17)	10.6(7)					
O(8)	0.0209(18)	0.5550(16)	0.7345(18)	14.1(8)					
O(9)	0.0418(18)	0.4548(15)	0.6717(19)	11.6(8)					
O(10)	0.3101(14)	0.6867(12)	0.0891(15)	8.4(6)					
O(11)	0.2621(17)	0.7029(15)	−0.0248(20)	15.3(8)					
O(12)	0.1878(18)	0.7091(15)	0.0891(20)	16.9(8)					
O(13)	0.2400(25)	0.3958(25)	0.5393(25)	23.4(7)					
F(1)	0.4026(16)	0.5295(12)	0.1904(16)	14.4(7)					
F(2)	0.4393(15)	0.5937(13)	0.2550(15)	16.3(7)					
F(3)	0.5271(16)	0.5192(12)	0.2360(15)	12.7(6)					
F(4)	0.0751(13)	0.3952(12)	0.8236(14)	11.0(6)					
F(5)	−0.0430(15)	0.4429(12)	0.8153(14)	15.0(7)					
F(6)	0.0559(15)	0.4886(12)	0.8870(16)	13.2(7)					
F(7)	0.1565(14)	0.5917(12)	−0.0112(14)	15.0(6)					
F(8)	0.2888(15)	0.5988(13)	−0.0439(15)	19.6(6)					
F(9)	0.2154(14)	0.5768(12)	0.0975(16)	19.8(6)					

[a] Standard deviations from the full variance-covariance matrix are given in parentheses for the least significant digit(s).

[b] The form of the anisotropic temperature factor is:
$\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

planar coordination of the macrocycle. The single nearly linear (O–Mo–O angles are 177–179°) oxo-bridge may be viewed as a somewhat unusual structural feature for oxo-molybdenum complexes. Double bridging, associated with a *cis* arrangement of oxo-ligands and which presumably leads to a "tighter", more stable complex is found far more often. From our knowledge of the conformational versatility[4] of these macrocyclic ligands it is doubtful that such a bridging mode is dictated by the macrocycle. Most likely the ethoxide-containing fragment (Mo(2)), being already six coordinate, is the controlling factor. Alternate bridging modes to other oxomolybdenum fragments than that found, would require less than tetradentate macrocyclic coordination. Energetics would seem to favor the tetradentate over a tridentate macrocycle. This does not explain however, why we do not find monomeric ethoxido-oxo species and dimeric *cis* oxo species. We have indeed found no evidence for either.

The relative weakness of the single oxo bridge is reflected in both structural and chemical observations. The Mo(1)---O(2) distance of 2.14Å is rather long, especially when compared to the Mo(2)–O(3) bond of 1.86Å to the ethoxide. This long bond length is reflected in the relative instability of the complex. Although crystals are stable indefinitely in a well-stoppered vial, aqueous solutions decompose rapidly to a pale, almost colorless solution. Bright blue acetonitrile solutions are stable for 2 or 3 days, before turning a pale violet. When subjected to electrochemical reduction, the complex is irreversibly reduced.[1] All of these observations are consistent with a relatively weak bridge which is readily cleaved by solvent or a decrease in the acidity of the metal centers upon reduction.

The two Mo=O bond lengths are almost identical at 1.764Å and 1.761Å. While one might expect a significantly longer distance in the bridging oxo bond, the situation is complicated by an inability to precisely define the oxidation states of the two metal centers. The presence of two oxo groups, an ethoxide ion and three $CF_3SO_3^-$ anions require a total positive charge of +8. The compound is diamagnetic in the solid state. We can arbitrarily assign the +4 oxidation state to each Mo. Alternatively the complex can be viewed as a strongly coupled Mo^{III}–Mo^{V} system. (Evidence for a fairly strongly coupled unit exists in the IR spectra,[1] but this does not imply coupling of electronic origin.) In weighing these alternatives it is unlikely that two such strongly coupled metal atoms would differ by 2 in formal charge; the strong coupling would effectively equalize the charges. Good evidence for this comes from examination of the Mo–S bond distances which average to 2.461Å on Mo(1) and 2.476Å on Mo(2). A significant difference in charge on the Mo atoms would certainly lead to a greater difference in these values.

One final point concerning the bridging structure deserving of mention, is why the structure does not extend beyond a dimer. Without knowing the precise mechanism by which the complex is formed, one can probably infer from the absence of other species that one-half of the Mo species contain coordinated ethoxide. The combinatorial possibilities are thus severely limited, as extended chains may only be formed of 5-coordinate moieties, which as we have already pointed out could just as well dimerize to a bridging *cis* dioxo structure. Since neither of these apparently occur, the structure found here must be a significantly more stable species than might appear at first glance, relative to the other possibilities.

The tetradentate macrocylic coordination in this complex is quite normal. No significant distortion or strain appears in either ring. The two rings are puckered away from each other and, interestingly, the two Mo atoms are also displaced away from each other. (See Figure 3.) Mo(1) is .33Å above the plane of the 4 sulfur atoms of its ring while Mo(2) is .10Å below a similar plane defined for the other ring. The near planarity of Mo(2) reflects strong axial ligands in both axial sites, whereas the greater displacement of Mo(1) reflects one strong and one weak axial ligand. Cavity size appears adequate for a Mo(IV) ion, consistent with our previous observation that Mo(II) will nearly fit the same cavity.[1] The two macrocycles are staggered relative to one another, one being rotated 42.7° from the orientation of the other. The rings are almost parallel, the two planes defined by the sets of 4 sulfur atoms are canted 3.3° to one another.

The cation and all distances and angles associated with it are satisfactorily defined. This is not the case with the anions, however. The CF_3 and SO_3 groups seem to be undergoing a considerable amount of thermal motion, possibly rotational in nature, and many of their structural parameters are clearly unsatisfactory. In spite of a variety of attempts, no reasonable model has been found to accomodate the observed behavior. The thermal parameters on some of the fluorine atoms lead one to suspect partial occupancy, but this is not borne out by the thermal parameters of the sulfur. In the case of the one molecule of lattice water, partial occupancy remains a distinct possibility.

TABLE II[a]
Interatomic distances

Atom	Distances (Å)	Atoms	Distances (A)
Mo(1)–S(1)	2.442(6)	C(19)–C(20)	1.48(5)
Mo(1)–S(2)	2.479(6)	C(20)–C(21)	1.42(4)
Mo(1)–S(3)	2.464(6)	C(22)–C(23)	1.43(3)
Mo(1)–S(4)	2.457(7)	C(23)–C(24)	1.52(4)
Mo(2)–S(5)	2.479(6)	C(25)–O(3)	1.51(3)
Mo(2)–S(6)	2.501(7)	C(25)–C(26)	1.45(4)
Mo(2)–S(7)	2.475(6)	C(27)–S(9)	1.81(5)
Mo(2)–S(8)	2.449(8)	C(28)–S(10)	1.72(5)
Mo(1)–O(1)	1.764(14)	C(29)–S(11)	1.80(5)
Mo(1)–O(2)	2.142(12)	C(27)–F(1)	1.22(5)
Mo(1)–O(3)	1.866(14)	C(27)–F(2)	1.25(5)
Mo(2)–O(2)	1.761(12)	C(27)–F(3)	1.41(5)
S(1)–C(1)	1.78(3)	C(28)–F(4)	1.20(5)
S(1)–C(12)	1.84(3)	C(28)–F(5)	1.43(5)
S(2)–C(3)	1.75(3)	C(28)–F(6)	1.45(5)
S(2)–C(4)	1.77(3)	C(29)–F(7)	1.31(5)
S(3)–C(6)	1.77(3)	C(29)–F(8)	1.37(5)
S(3)–C(7)	1.81(2)	C(29)–F(9)	1.51(5)
S(4)–C(9)	1.83(3)	S(9)–O(4)	1.45(2)
S(4)–C(10)	1.86(2)	S(9)–O(5)	1.39(3)
S(5)–C(13)	1.76(2)	S(9)–O(6)	1.28(3)
S(5)–C(24)	1.87(3)	S(10)–O(7)	1.38(3)
S(6)–C(15)	1.73(4)	S(10)–O(8)	1.31(3)
S(6)–C(16)	1.76(3)	S(10)–O(9)	1.36(3)
S(7)–C(18)	1.90(3)	S(11)–O(10)	1.20(3)
S(7)–C(19)	1.91(3)	S(11)–O(11)	1.18(3)
S(8)–C(21)	1.81(3)	S(11)–O(12)	1.37(3)
S(8)–C(22)	1.87(3)		
C(1)–C(2)	1.53(4)		
C(2)–C(3)	1.59(4)		
C(4)–C(5)	1.70(4)		
C(5)–C(6)	1.43(4)		
C(7)–C(8)	1.53(4)		
C(8)–C(9)	1.49(4)		
C(10)–C(11)	1.42(4)		
C(11)–C(12)	1.53(4)		
C(13)–C(14)	1.45(4)		
C(14)–C(15)	1.76(5)		
C(16)–C(17)	1.54(5)		
C(17)–C(18)	1.57(5)		

[a] Standard deviations from the full variance-covariance matrix are given in parentheses for the least significant digit(s).

TABLE III[a]
Interatomic angles

Atoms	Angle (°)	Atoms	Angle (°)
O(1)–Mo(1)–S(1)	96.9(5)	S(6)–C(16)–C(17)	113(2)
O(1)–Mo(1)–S(2)	97.0(5)	C(16)–C(17)–C(18)	123(3)
O(1)–Mo(1)–S(3)	99.0(5)	C(17)–C(18)–S(7)	108(2)
O(1)–Mo(1)–S(4)	98.5(5)	S(7)–C(19)–C(20)	111(2)
O(2)–Mo(2)–S(5)	87.8(4)	C(19)–C(20)–C(21)	117(3)
O(2)–Mo(2)–S(6)	87.2(6)	C(20)–C(21)–S(8)	107(2)
O(2)–Mo(2)–S(7)	87.6(4)	S(8)–C(22)–C(23)	111(2)
O(2)–Mo(2)–S(8)	87.9(6)	C(22)–C(23)–C(24)	118(2)
O(1)–Mo(1)–O(2)	178.6(8)	C(23)–C(24)–S(5)	114(2)
O(2)–Mo(2)–O(3)	179.2(6)	O(3)–C(25)–C(26)	108(3)
Mo(1)–O(2)–Mo(2)	177.3(7)	O(4)–S(9)–O(5)	120(1)
S(1)–Mo(1)–S(2)	89.0(2)	O(4)–S(9)–O(6)	115(1)
S(1)–Mo(1)–S(4)	89.2(2)	O(5)–S(9)–O(6)	116(1)
S(1)–Mo(1)–S(3)	164.1(2)	O(4)–S(9)–C(27)	100(2)
S(2)–Mo(1)–S(4)	164.4(2)	O(5)–S(9)–C(27)	95(2)
S(2)–Mo(1)–S(3)	88.4(2)	O(6)–S(9)–C(27)	106(2)
S(3)–Mo(1)–S(4)	89.1(2)	O(7)–S(10)–O(8)	117(2)
S(5)–Mo(2)–S(6)	89.2(2)	O(7)–S(10)–O(9)	103(2)
S(5)–Mo(2)–S(8)	91.0(3)	O(8)–S(10)–O(9)	120(2)
S(5)–Mo(2)–S(7)	175.0(3)	O(7)–S(10)–C(28)	102(2)
S(6)–Mo(2)–S(8)	175.0(3)	O(8)–S(10)–C(28)	115(2)
S(6)–Mo(2)–S(7)	88.9(3)	O(9)–S(10)–C(28)	97(2)
S(7)–Mo(2)–S(8)	90.4(3)	O(10)–S(11)–O(11)	117(2)
C(12)–S(1)–C(1)	100(1)	O(10)–S(11)–O(12)	103(2)
C(3)–S(2)–C(4)	96(1)	O(11)–S(11)–O(12)	120(3)
C(6)–S(3)–C(7)	96(1)	O(10)–S(11)–C(29)	102(2)
C(9)–S(4)–C(10)	99(1)	O(11)–S(11)–C(29)	99(3)
C(24)–S(5)–C(13)	98(1)	O(12)–S(11)–C(29)	114(3)
C(15)–S(6)–C(16)	92(2)	F(1)–C(27)–F(2)	93(4)
C(18)–S(7)–C(19)	99(1)	F(1)–C(27)–F(3)	110(5)
C(21)–S(8)–C(22)	97(1)	F(2)–C(27)–F(3)	105(4)
S(1)–C(1)–C(2)	115(2)	F(1)–C(27)–S(9)	118(5)
C(1)–C(2)–C(3)	114(2)	F(2)–C(27)–S(9)	115(4)
C(2)–C(3)–S(2)	113(2)	F(3)–C(27)–S(9)	114(4)
S(2)–C(4)–C(5)	110(2)	F(4)–C(28)–F(5)	109(4)
C(4)–C(5)–C(6)	117(2)	F(4)–C(28)–F(6)	111(4)
C(5)–C(6)–S(3)	110(2)	F(5)–C(28)–F(6)	99(4)
S(3)–C(7)–C(8)	112(2)	F(4)–C(28)–S(10)	126(4)
C(7)–C(8)–C(9)	118(2)	F(5)–C(28)–S(10)	101(3)
C(8)–C(9)–S(4)	109(2)	F(6)–C(28)–S(10)	106(3)
S(4)–C(10)–C(11)	112(2)	F(7)–C(29)–F(8)	102(4)
C(10)–C(11)–C(12)	119(2)	F(7)–C(29)–F(9)	90(3)
C(11)–C(12)–S(1)	112(2)	F(8)–C(29)–F(9)	158(5)
S(5)–C(13)–C(14)	110(2)	F(7)–C(29)–S(11)	102(3)
C(13)–C(14)–C(15)	114(3)	F(8)–C(29)–S(11)	95(3)
C(14)–C(15)–S(6)	111(2)	F(9)–C(29)–S(11)	100(3)

[a] Standard deviations from the full variance-covariance matrix are given in parentheses for the least significant digit(s).

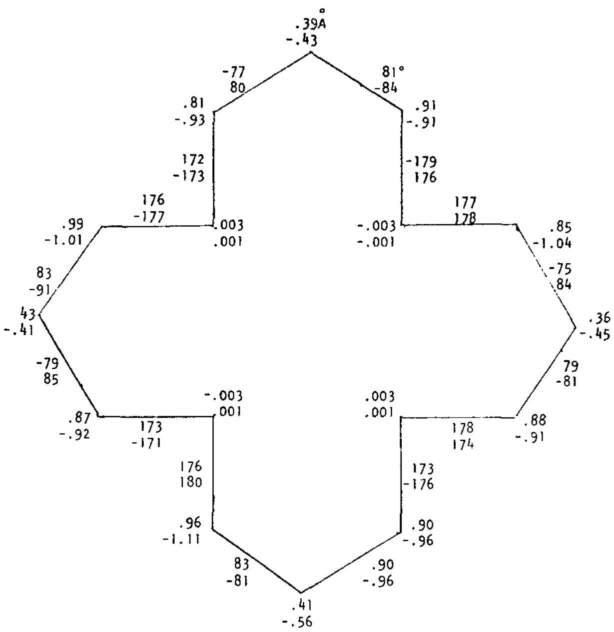

FIGURE 4 Schematic drawing of the ring 16-ane[S_4] showing dihedral angles and displacement of atoms from the plane of the 4 sulfur atoms. Upper set of figures refer to ring about Mo(1), lower set to ring about Mo(2).

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6. Local versions of the following programs were used: (1) TRACER II, S. L. Lawton's cell reduction program; (2) SYNCOR, W. Schmonsees' program for data reduction; (3) FORDAP, A. Zalkin's Fourier program; (4) ORFLS and ORFFE, W. Busing, K. Martin and H. Levy's full matrix least-squares program and function and error program, respectively; (5) ORTEP, C. K. Johnson's program for drawing crystal models.