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Triply Bridged Binuclear Complexes of Oxomolybdenum(V) with Thiolate Ligands

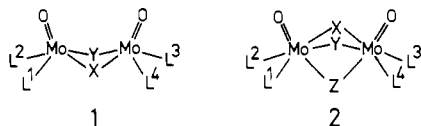
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Reaction of $[\text{MoOCl}_3(\text{thf})_2]$ with aromatic thiols HSAr ($\text{Ar} = \text{Ph}$ or $4\text{-MeC}_6\text{H}_4$) and sodium methoxide/methanol yields the complex ions $[\text{Mo}_2\text{O}_2(\text{SAr})_6(\text{OMe})]^-$, which have been obtained as crystalline $[\text{Et}_4\text{N}]^+$ salts. The structure of $[\text{Et}_4\text{N}][\text{Mo}_2\text{O}_2(4\text{-MeC}_6\text{H}_4\text{S})_6(\text{OMe})]$ has been determined by single-crystal X-ray diffraction. Crystals are orthorhombic, space group $P2_12_12_1$, with $a = 26.416(4) \text{ \AA}$, $b = 41.380(6) \text{ \AA}$, $c = 15.237(2) \text{ \AA}$, and $Z = 12$. Refinement, based on 7034 diffractometer data, gave $R = 0.110$. There are three crystallographically independent anions, each with two terminal oxo groups, four terminal and two bridging thiolate ligands, and a bridging methoxy ligand, arranged around a Mo_2 center with $\text{Mo-Mo} = 2.919(5) \text{ \AA}$.

Introduction

Although many doubly bridged binuclear oxomolybdenum(V) complexes (1) are known,² fewer triply bridged species



(2) have been studied. Of these, crystal structures have been reported almost exclusively for complexes in which some of the ligands coordinate through more than one atom.³⁻⁹ Only very recently has a structure been determined in which every ligand coordinates through a single donor atom.⁹ $[\text{Mo}_2\text{O}_2(\text{SAr})_6\text{Z}]^-$, with $\text{Ar} = \text{Ph}$ or $4\text{-MeC}_6\text{H}_4$ and $\text{Z} = \text{OMe}$ or NH_2 , have been prepared by treating the $[\text{MoO}(\text{SAr})_4]^-$ salts with a source of the methoxy or amido ligand Z ,⁸ and for these, structure 2 has been proposed. We report here the syntheses of such complexes by an alternative route and the crystal structure of $[\text{Et}_4\text{N}][\text{Mo}_2\text{O}_2(4\text{-MeC}_6\text{H}_4\text{S})_6(\text{OMe})]$.

Experimental Section

Preparation of Binuclear Complexes. Solvents were dried and deoxygenated before use. Reactions were carried out in an atmosphere of purified dinitrogen.

4-Methylbenzenethiol (2.00 g, 16.1 mmol) was dissolved in methanolic sodium methoxide (17 cm^3 , 1 M). The solution was added to a stirred solution of $[\text{MoOCl}_3(\text{thf})_2]$ (1.43 g, 3.93 mmol) in MeOH (25 cm^3). The reaction mixture developed a clear, deep orange color. After 1 h, NaCl was removed by filtration, and $[\text{Et}_4\text{N}]\text{Br}$ (1.38 g, 6.55 mmol) in MeOH (25 cm^3) was added to the filtrate. The solution was cooled to ca. -10°C overnight. The resulting dark red solid was collected by filtration, washed with methanol ($3 \times 15 \text{ cm}^3$), and dried over P_2O_5 in vacuo. Yield 0.91 g, 0.81 mmol, ca. 40%. The product was recrystallized by cooling from acetonitrile/methanol, giving red blocks. Anal. Calcd for $\text{C}_{51}\text{H}_{65}\text{NMo}_2\text{O}_3\text{S}_6$: C, 54.5; H, 5.8; N, 1.2; Mo, 17.1; S, 17.1. Found: C, 54.2; H, 6.1; N, 1.1; Mo, 17.3; S, 17.1.

The SPh complex was prepared in the same way. Anal. Calcd for $\text{C}_{45}\text{H}_{53}\text{NMo}_2\text{O}_3\text{S}_6$: C, 51.9; H, 5.1; N, 1.3; Mo, 18.4; S, 18.5. Found: C, 51.6; H, 4.7; N, 0.9; Mo, 19.1; S, 18.3.

Spectroscopic Measurements. Spectra were recorded on the following instruments: for IR, Perkin-Elmer 577 (Nujol mull); for Raman, Spex (powdered solids, 100-mW excitation at 514.5 nm); for UV-visible, Perkin-Elmer 402 (CH_3CN solution); for ^1H NMR,

Varian SC300 (300 MHz, $\text{Me}_2\text{SO}-d_6$ solution at 24°C); for ^{95}Mo NMR, Bruker WM250 with 10-mm probe (0.12 M solution in DMF under N_2 at ca. 300 K).

Crystal Structure Determination. A crystal of $[\text{Et}_4\text{N}][\text{Mo}_2\text{O}_2(4\text{-MeC}_6\text{H}_4\text{S})_6(\text{OMe})]$, of dimensions ca. $0.45 \times 0.45 \times 0.30 \text{ mm}$, sealed in a capillary tube, was examined on a Stoe-Siemens AED four-circle diffractometer, with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$).¹⁰ All measurements were made at room temperature. Unit cell dimensions were refined by least-squares methods from 2 θ values of 42 centered reflections ($20 < 2\theta < 25^\circ$, 2θ determined as the difference in ω measurements on the positive and negative sides of the direct beam). The space group is $P2_12_12_1$, with $a = 26.416(4) \text{ \AA}$, $b = 41.380(6) \text{ \AA}$, $c = 15.237(2) \text{ \AA}$, $V = 16655 \text{ \AA}^3$, and $Z = 12$.

Because of the large size of the problem (three independent cation-anion pairs in the asymmetric unit) and because the crystals appeared to be somewhat X-ray sensitive, a high-speed data collection was carried out. Intensity data were collected to a maximum 2θ of 45° , with θ/ω scans and a profile-fitting procedure.¹¹ In 4 days, 13 350 reflections were measured. By the end of the data collection, the intensities of three standard reflections, monitored approximately once per hour each, had not significantly changed, but the reflection profile form had deteriorated somewhat and now appeared slightly split.

No absorption corrections were applied: $\mu = 6.95 \text{ cm}^{-1}$, and azimuthal scans of selected strong reflections indicated no significant variation of intensity with azimuthal angle. Averaging of equivalent reflections gave 11 794 unique data (merging $R = 0.039$), 6818 with $F > 4\sigma(F)$.

Application of multisolution tangent refinement with random values for all starting phases yielded coordinates for six Mo atoms.¹² The other non-hydrogen atoms were located in subsequent difference syntheses. With Mo and S atoms only and individual isotropic thermal parameters, $R (= \sum|\Delta|/\sum|F_o|)$ converged to 0.28. At this stage it was clear from projections of the unit cell contents and from the reluctance with which atoms emerged from the difference syntheses that the structure was subject to pseudosymmetry, as well as to high thermal motion. The arrangement of Mo and S atoms is close to hexagonal in projection along the b axis (vide infra); a cell reduction and vector generation program¹³ indicated that the lattice vectors $[101]$ and $[\bar{1}01]$ were 30.495 \AA long, enclosed an angle of 120.04° , and formed with the c axis ($2c = 30.474 \text{ \AA}$) angles of 119.98° . A further check was made on the true symmetry by remounting the original crystal, and subsequently a second crystal of similar size, on the diffractometer. The lengths of the three orthorhombic axes and of the lattice vectors $[101]$ and $[\bar{1}01]$ were confirmed both by oscillation photographs taken about these vectors and by an exhaustive and unsuccessful search for significant intensity at positions corresponding to half-integral values for one or more indices simultaneously. This search was accomplished by collecting a restricted set of data from the second crystal with both a and c doubled in length, and with even shorter counting times: 18 815 data were measured in 4 days. The orthorhombic Laue symmetry was confirmed by examination of sets of reflections that would be equivalent for each of the various or-

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Table I. Refined Atomic Coordinates ($\times 10^4$)

atom	x	y	z	atom	x	y	z
Mo(1A)	2898 (1)	949 (1)	600 (2)	C(11B)	-579 (5)	8177 (4)	3520 (11)
Mo(2A)	2119 (1)	548 (1)	-209 (1)	C(21B)	-550 (5)	7030 (4)	1766 (12)
Mo(1B)	152 (1)	7781 (1)	1895 (1)	C(31B)	476 (7)	8603 (3)	2322 (11)
Mo(2B)	112 (1)	7417 (1)	3539 (1)	C(41B)	522 (7)	7286 (4)	163 (12)
Mo(1C)	1954 (1)	4223 (1)	5294 (2)	C(51B)	331 (8)	7923 (4)	5397 (13)
Mo(2C)	2805 (1)	3888 (1)	4483 (2)	C(61B)	462 (7)	6608 (4)	3177 (12)
S(1A)	2171 (3)	1146 (2)	-236 (5)	C(3C)	1779 (14)	3978 (9)	3204 (29)
S(2A)	2919 (3)	349 (2)	404 (5)	C(11C)	3111 (6)	4642 (4)	5456 (11)
S(3A)	2824 (4)	1456 (3)	1442 (7)	C(21C)	2347 (7)	3506 (4)	6396 (10)
S(4A)	3367 (4)	866 (3)	1973 (6)	C(31C)	1886 (6)	5020 (4)	4494 (14)
S(5A)	1204 (2)	606 (2)	-222 (7)	C(41C)	944 (7)	3687 (4)	5852 (15)
S(6A)	1767 (3)	21 (2)	239 (7)	C(51C)	3501 (8)	4394 (4)	3121 (15)
S(1B)	35 (2)	8009 (2)	3363 (4)	C(61C)	2491 (8)	3068 (4)	4170 (13)
S(2B)	73 (2)	7188 (2)	2047 (4)	N(1D)	4269 (8)	4154 (5)	414 (16)
S(3B)	597 (3)	8289 (2)	1552 (6)	C(1D)	4475 (14)	3824 (9)	823 (27)
S(4B)	637 (3)	7676 (2)	556 (5)	C(2D)	4286 (12)	4439 (8)	1055 (22)
S(5B)	530 (3)	7541 (3)	4934 (6)	C(3D)	3699 (21)	4129 (14)	418 (46)
S(6B)	525 (3)	6916 (2)	3975 (6)	C(4D)	4572 (19)	4233 (13)	-388 (41)
S(1C)	2721 (3)	4476 (2)	4647 (5)	C(5D)	4313 (20)	3753 (12)	1771 (38)
S(2C)	2128 (2)	3640 (2)	5356 (5)	C(6D)	4907 (19)	4509 (12)	1284 (33)
S(3C)	1488 (3)	4703 (2)	4834 (7)	C(7D)	3561 (29)	3966 (19)	-644 (66)
S(4C)	1058 (3)	4057 (3)	5302 (7)	C(8D)	4588 (23)	4675 (16)	-612 (48)
S(5C)	3238 (4)	4005 (3)	3099 (6)	N(1E)	3612 (10)	2466 (6)	2435 (17)
S(6C)	2841 (4)	3374 (2)	3682 (6)	C(1E)	3299 (22)	2342 (13)	3291 (45)
O(1A)	3335 (7)	1014 (5)	-175 (14)	C(2E)	3885 (17)	2115 (10)	2305 (31)
O(2A)	2303 (6)	505 (4)	-1254 (11)	C(3E)	3454 (17)	2526 (11)	1448 (34)
O(3A)	2225 (6)	744 (4)	1066 (12)	C(4E)	3957 (12)	2729 (8)	2698 (22)
O(1B)	-448 (6)	7828 (4)	1595 (12)	C(5E)	2661 (30)	2305 (17)	2794 (50)
O(2B)	-482 (6)	7377 (4)	3774 (11)	C(6E)	4230 (18)	2030 (12)	3195 (36)
O(3B)	706 (6)	7592 (4)	2758 (11)	C(7E)	3177 (27)	2848 (17)	1409 (53)
O(1C)	2104 (7)	4291 (4)	6347 (13)	C(8E)	4341 (18)	2813 (11)	1997 (33)
O(2C)	3244 (6)	3857 (4)	5251 (12)	N(1F)	4289 (8)	839 (5)	4652 (16)
O(3C)	2093 (6)	4043 (4)	4021 (11)	C(1F)	4629 (13)	1117 (9)	4244 (26)
C(3A)	1994 (16)	700 (10)	1861 (33)	C(2F)	4327 (14)	515 (9)	4165 (26)
C(11A)	2344 (7)	1310 (5)	-1268 (11)	C(3F)	3735 (14)	868 (9)	4396 (28)
C(21A)	3336 (6)	201 (5)	-414 (12)	C(4F)	4571 (18)	790 (13)	5550 (38)
C(31A)	2472 (8)	1761 (4)	881 (14)	C(5F)	4632 (14)	1105 (10)	3257 (29)
C(41A)	3640 (12)	503 (6)	1969 (22)	C(6F)	4979 (28)	432 (18)	4003 (50)
C(51A)	1026 (5)	997 (3)	-520 (13)	C(7F)	3654 (29)	1172 (18)	4949 (65)
C(61A)	2210 (6)	-275 (4)	422 (15)	C(8F)	4679 (27)	402 (19)	5620 (56)
C(3B)	1268 (13)	7634 (8)	2840 (24)				

thorhombic, trigonal, and hexagonal Laue groups. Similar intensities were always obtained for groups of 8 reflections, consistent with orthorhombic symmetry, with large discrepancies often being observed between intensities of reflections that should be equivalent for the other symmetries. Data reduction with the assumption, in turn, of Laue group symmetries $6/mmm$, $6/m$, $\bar{3}m1$, and $\bar{3}1m$ gave merging R values of 0.313, 0.290, 0.310, and 0.278, respectively. Results for Laue group $\bar{3}$ are less clear-cut, as only an octant of data was collected and "equivalent" reflections are restricted to the section with $l = 0$; here, the merging R was 0.244, based on ca. 250 reflections.

The second data set, purged of the insignificant "super-cell" reflections, was merged with the original set, to give 7034 unique reflections with $F > 4\sigma(F)$; the merging R was 0.062. Refined unit cell parameters for the second crystal (also from 42 reflections) were insignificantly different from those of the first: $a = 26.424$ (4) Å, $b = 41.380$ (5) Å, and $c = 15.238$ (2) Å.

Structure refinement was made difficult by the pseudosymmetry, by the size of the problem (189 unique non-hydrogen atoms), and by the relatively imprecise data (caused by weak scattering, itself a consequence of high thermal motion, and by the fast counting times). Mo and S atoms were assigned anisotropic thermal parameters, and O, N, and C atoms, isotropic thermal parameters. The thiolate substituents were constrained as rigid regular hexagons with C-C = 1.395 Å and with C-CH₃ = 1.500 Å on the external bisectors of the appropriate ring C-C-C angles. No attempt was made to locate H atoms or to include them in the refinement, although they represent about 12% of the electrons. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0016F^2$, and $\sum w\Delta^2$ was minimized ($\Delta = |F_o| - |F_c|$). Final values for R and for R_g [$= (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$] were 0.110 and 0.120, respectively. Parameter shifts in the final cycles were all less than the corresponding esd values, and the mean shift/esd was < 0.1 . A difference synthesis after the last cycle contained no significant features. An analysis of the variance showed no unusual trends with indices,

Table II. Selected Bond Lengths (Å)

bond	anion A	anion B	anion C
Mo(1)-Mo(2)	2.916 (4)	2.925 (4)	2.916 (4)
Mo(1)-S(1)	2.446 (8)	2.447 (7)	2.485 (8)
Mo(1)-S(2)	2.501 (8)	2.474 (8)	2.457 (9)
Mo(1)-S(3)	2.469 (11)	2.464 (9)	2.438 (11)
Mo(1)-S(4)	2.455 (10)	2.447 (8)	2.462 (9)
Mo(1)-O(1)	1.673 (20)	1.662 (17)	1.677 (19)
Mo(1)-O(3)	2.093 (17)	2.117 (16)	2.110 (16)
Mo(2)-S(1)	2.480 (7)	2.470 (8)	2.455 (8)
Mo(2)-S(2)	2.452 (7)	2.466 (7)	2.454 (8)
Mo(2)-S(5)	2.430 (7)	2.449 (10)	2.447 (9)
Mo(2)-S(6)	2.466 (9)	2.437 (10)	2.456 (10)
Mo(2)-O(2)	1.674 (17)	1.620 (16)	1.652 (17)
Mo(2)-O(3)	2.126 (18)	2.096 (16)	2.107 (16)

$\sin \theta$, or F_o ; neglect of H atoms produced an increase in $V = (\sum w\Delta^2 / \sum w)^{1/2}$ at low $\sin \theta$. The value of V (the rms deviation of a reflection of unit weight on an absolute scale of $|F_o|$) for the whole data set was 9.1 electrons.

Refined atomic coordinates together with bond lengths involving Mo atoms are presented in Tables I and II. Tables of structure factors, together with thermal parameters and other details of the molecular geometry, are available as supplementary material.

Results and Discussion

Crystal Structure. The structure of $[\text{Et}_4\text{N}][\text{Mo}_2\text{O}_2(4\text{-MeC}_6\text{H}_4\text{S})_6(\text{OMe})]$ contains three independent cations and three independent anions. Differences in the geometry of the three anions are slight, and all have the same arrangement of ligands with virtually the same aromatic ring orientations, as shown for one anion in Figure 1. The pseudohexagonal

Table III. Comparison of Triply Bridged Binuclear Oxomolybdenum(V) Complexes^a

	complex ^b										
	1	2	3	4	5	6	7	8	9	10	11
Mo-Mo	2.725 (1)	2.628 (1)	2.676 (1)	2.739 (1)	2.731 (1)	2.728 (1)	2.677 (5)	2.822 (2)	2.649 (1)	2.915 (1)	2.919 (5)
Mo-O	1.686 (7)	1.693 (6)	1.699 (7)	1.692 (5)	1.687 (10)	1.676 (7)	1.673 (5)	1.656 (6)	1.686 (7)	1.658 (9)	1.66 (2)
Mo-X	2.489 (3)	2.484 (2)	2.506 (16)	2.483 (18)	2.480 (21)	2.480 (12)	2.491 (7)	2.455 (4)	1.957 (7)	2.445 (3)	2.47 (2)
Mo-Y	2.334 (1)	1.937 (12)	1.957 (6)	2.055 (5)	2.024 (12)	2.014 (17)	2.045 (31)	2.460 (8)	2.474 (4)	2.449 (3)	2.47 (2)
Mo-Z	2.202 (14)	2.190 (17)	2.215 (15)	2.194 (30)	2.176 (27)	2.176 (39)	2.688 (11)	2.613 (12)	2.644 (3)	2.651 (3)	2.11 (2)
Δ(Mo)	0.389 (3)	0.392 (6)	0.40 ^c	0.36 ^c	0.34 ^c	0.32 ^c	0.392 (40)	0.396 (6)	0.38 ^c	0.40 ^c	0.42 (1)
O-Mo-X	89.4 (2)	90.2 (2)	89.4 (12)	91.0 (9)	89.2 (18)	89.1 (4)	93.0 (26)	95.7 (10)	103.3 (3)	95.0 (3)	95 (1)
O-Mo-Y	102.7 (2)	103.6 (4)	101.9 (13)	97.0 (14)	98.0 (23)	97.4 (20)	102.5 (12)	95.6 (13)	92.7 (3)	93.7 (3)	95 (1)
O-Mo-Z	155.5 (4)	158.9 (3)	156.5 (17)	153.0 (11)	153.6 (4)	153.3 (6)	160.6 (19)	158.2 (2)	160.8 (3)	155.1 (3)	152 (1)
Mo-X-Mo	66.4 (4)	63.9 (6)	64.5 (1)	67.0 (1)	66.8 (1)	66.7 (1)	65.0 (5)	70.2 (1)	85.4 (4)	73.2 (1)	72.6 (5)
Mo-Y-Mo	71.4 (4)	85.5 (2)	86.3 (2)	83.6 (1)	84.9 (3)	85.2 (1)	81.8 (16)	70.7 (1)	64.7 (1)	73.0 (1)	72.6 (5)
Mo-Z-Mo	76.5 (9)	73.8 (2)	74.3 (2)	77.2 (1)	77.7 (3)	77.6 (1)	59.7 (9)	63.4 (1)	59.6 (1)	66.7 (1)	87.6 (6)
X-Mo-Y	110.4 (5)	104.5 (2)	104.0 (8)	104.3 (8)	103.2 (7)	103.0 (2)	106.6 (9)	109.9 (1)	109.9 (1)	106.9 (1)	106.6 (5)
X-Mo-Z	68.0 (1)	70.4 (2)		69.2 (9)	69.6 (3)	69.5 (9)	70.8 (2)	73.1 (3)	70.7 (2)	72.2 (1)	69.5 (8)
Y-Mo-Z	77.9 (2)	74.6 (4)		71.6 (7)	73.0 (8)	73.3 (6)	73.6 (3)	71.9 (1)	72.1 (1)	70.8 (1)	69.5 (8)
ref	3	4	5	8	8	8	6	7	9	9	this work

^a Bond lengths in Å; angles in deg; estimated standard deviations in parentheses. Quoted values are averages for equivalent dimensions within each structure. ^b (1) $L^1L^2 = L^3L^4 = (Et_2NCS_2)_2$; $XZ = (SCH_2CH_2O)$; $Y = S$. (2) $L^1L^2 = L^3L^4 = oxinato$; $XZ = (SCH_2CH_2O)$; $Y = O$. (3) $L^1L^2 = L^3L^4 = XZ = (SCH_2CH_2O)$; $Y = O$. (4) $L^1L^2 = L^4Y = XZ = (SCH_2CH_2O)$; $L^3 = (SCH_2CH_2OH)$. (5) $L^1L^2 = L^4Y = XZ = (SCH_2CH_2O)$; $L^3 = Cl$. (6) $L^1 = L^2 = L^3 = Cl$; $L^4Y = XZ = (SCH_2CH_2O)$. (7) $L^1L^2 = L^3L^4 = (Et_2NCS_2)_2$; $X = Z = SPh$; $Y = O$. (8) $L^1L^2 = L^3L^4 = (Et_2NCS_2)_2$; $X = Y = SPh$; $Z = Cl$. (9) $L^1L^2 = L^3L^4 = (Me_2NCS_2)_2$; $X = O$; $Y = Z = SPh$. (10) $L^1 = L^2 = L^3 = L^4 = Z = Cl$; $X = Y = SPh$. (11) $L^1 = L^2 = L^3 = L^4 = X = Y = 4-MeC_6H_4S$; $Z = OMe$. ^c No esd quoted.

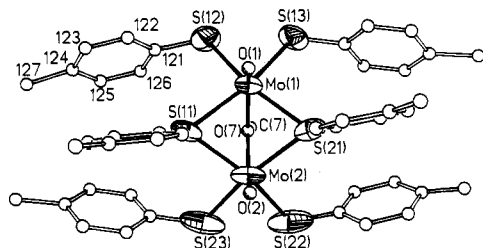


Figure 1. Structure of one of the three crystallographically independent $[Mo_2O_2(4-MeC_6H_4S)_6(OMe)]^-$ anions. All aromatic groups follow the same numbering scheme. Thermal motion of Mo and S atoms are depicted as 40% probability ellipsoids; O and C atoms are assigned the arbitrary radius of 0.2 Å for clarity. The A anion is shown; B and C anions are numbered in the same way.

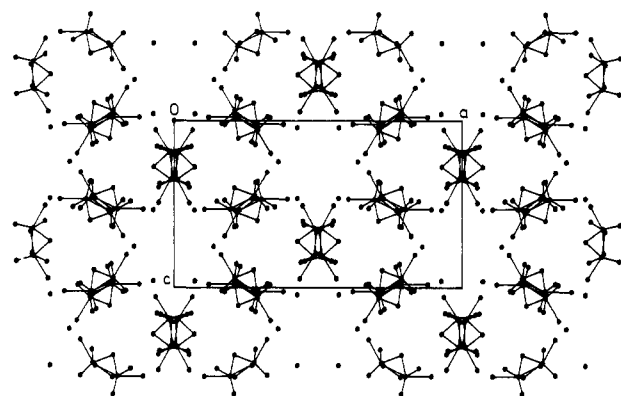


Figure 2. Projection down the *b* axis, showing the pseudo-hexagonal arrangement. C atoms are omitted.

projection along the *b* axis is shown in Figure 2. The packing arrangement approximates to the symmetry elements of space group $P6_322$, the pseudo-hexagonal cell having half the volume of the true orthorhombic cell ($a = 15.237$ and $c = 41.380$ Å): this corresponds to a *B*-centered lattice on the orthorhombic axes. Deviations from this pseudo-*B*-centered arrangement are not large but are clearly sufficient to prevent a true hexagonal packing: we note that the mean intensity of reflections with $h + l$ odd is less than half that for the reflections with $h + l$ even, in accordance with the pseudo-*B*-centering. The oscillation photographs for the vectors $[001]$, $[101]$, and $[\bar{1}01]$ are very similar if the weaker odd-numbered layers of reflections on the second and third of these photographs are ignored. Indeed, all three show mirror symmetry for the strong reflections; such symmetry would be a requirement for Laue group $6/mmm$, to which the space group $P6_322$ belongs. This symmetry, however, is not observed for the reflections with $h + l$ odd, as is demonstrated not only by the appearance of the photographs but also by the attempt to perform data reduction in hexagonal and trigonal Laue groups (vide supra).

In each anion, four $4-MeC_6H_4S$ ligands are bonded terminally, and two, together with the OMe ligand, bridge the pair of Mo atoms. This appears to be only the second structurally characterised triply bridged binuclear Mo(V) complex in which all of the ligands are coordinated through a single donor atom. The coordination of each Mo atom may be described as distorted octahedral; the two octahedra share a common face defined by two bridging $4-MeC_6H_4S$ ligands and a bridging OMe ligand. The OMe ligand is trans to the

terminal oxo ligand on each Mo atom. The Mo atom is displaced 0.42 (2) Å on average out of the mean plane of the four coordinated S atoms, the displacement being towards the oxo ligand. Mean dimensions of the coordination are summarized in Table III, together with corresponding values for other triply bridged oxomolybdenum(V) complexes. The angle between the two MoS_2 planes in the central bridging region is 164.1 (5)°.

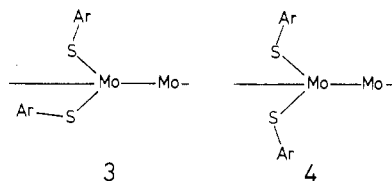
The Mo-O bond length for the six-coordinate Mo atoms in this complex (1.66 (2) Å) is not significantly greater than those observed in $[Ph_4As][MoO(SPh)_4]$ (1.669 (9) Å)¹⁴ or $[Me_4N]_2[Mo_2O_4(SPh)_4]$ (1.677 (17) Å),¹⁵ in both of which the coordination position trans to oxygen is vacant. The distance lies well within the range of values (1.65–1.70 Å) for the triply bridged oxomolybdenum(V) dimers listed in Table III. The out-of-plane displacement of the Mo atoms is, however, greater than in any of the other triply bridged complexes, although by no means as great as in the $[MoO(SPh)_4]^-$ and $[Mo_2O_4(SPh)_4]^{2-}$ anions (0.82 and 0.71 Å, respectively). The Mo-Mo separation in the $4-MeC_6H_4S$ complex is among the largest for these binuclear complexes but substantially less than those observed in triply bridged iron-molybdenum-sulfur "cube cluster dimers" (e.g., ca. 3.7 Å in $[Fe_6Mo_2S_8(SR)_9]^{3-}$;^{16,17}

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ca. 3.3 Å in $[\text{Fe}_6\text{Mo}_2\text{S}_9(\text{SR})_8]^{3-}$,¹⁷ and 3.142 (3) Å in $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SPh})_6(\text{OMe})_3]^{3-}$, which has three bridging methoxy groups¹⁸.

Bond angles defined by the various thiolate ligands around Mo are of interest, in comparison with those observed in $[\text{Me}_4\text{N}]_2[\text{Mo}_2\text{O}_4(\text{SPh})_4]$.¹⁵ In this latter compound, the two crystallographically independent anions differ in the orientations of the ligands relative to the $\text{Mo}_2\text{O}_4^{2+}$ core. For each molybdenum atom within one of the anions, one of the benzenethiolate ligands has its S-C bond approximately parallel to the Mo-Mo vector, whereas the other such ligand has its S-C bond aligned more nearly perpendicular to this vector. With this rearrangement, a direct S-S bonding interaction is impossible (3). The S-Mo-S angles in this



$[\text{Mo}_2\text{O}_4(\text{SPh})_4]^{2-}$ anion are 81.8 (5) Å, close to those observed in $[\text{MoO}(\text{SPh})_4]^-$ (mean 83 (2)°), and similar to the $\text{S}_b\text{-Mo-S}_t$ angles (mean 86 (1)°) between bridging and terminal ligands in the 4-MeC₆H₄S complex reported here. In the second $[\text{Mo}_2\text{O}_4(\text{SPh})_4]^{2-}$ anion, however, all S-C bonds are roughly perpendicular to the Mo-Mo vector (4), and the S-Mo-S angle is as low as 73.8 (4)°. A similar situation exists for the terminal ligands in $[\text{Mo}_2\text{O}_2(4\text{-MeC}_6\text{H}_4\text{S})_6(\text{OMe})]^-$, for which $\text{S}_t\text{-Mo-S}_t$ averages 74 (1)°. Thus, there is a relatively close approach between adjacent sulfur atoms in this arrangement: S...S is 2.94 (3) Å for the second $[\text{Mo}_2\text{O}_4(\text{SPh})_4]^{2-}$ anion and 2.95 (5) Å for the terminal 4-MeC₆H₄S ligands. These distances are less than the 3.07 Å separation observed in some tris(dithiolene) complexes, where S-S interactions are considered to be present,¹⁹ and have led to suggestions of some direct S-S bonding interaction.¹⁶ A partial disulfide bond has also been proposed in the complex $[\text{MoO}_2(\text{SC}(\text{CH}_2)_2\text{CH}_2\text{N}(\text{H})(\text{CH}_3)_2)]_2$,²⁰ where the S...S distance is 2.764 (5) Å and S-Mo-S is 70 (2)°.

Spectroscopic Properties. The IR spectra of $[\text{Et}_4\text{N}][\text{Mo}_2\text{O}_2(\text{SAr})_6(\text{OMe})]$ (Ar = 4-MeC₆H₄ or Ph) are similar to those of the corresponding $[\text{Et}_4\text{N}][\text{MoO}(\text{SAr})_4]$ salts. Important differences between these spectra include the shift of $\nu(\text{Mo-O})$ to higher frequency (943 and 939 cm⁻¹ for the dinuclear complexes with Ar = Ph or 4-MeC₆H₄, respectively, as compared with 935 cm⁻¹ for both of the mononuclear complexes) and the appearance of $\nu(\text{C-O})$ for the coordinated methoxide group at 1050 and 1048 cm⁻¹, respectively, for the two dinuclear systems. Each of several ligand vibrations observed for the mononuclear complexes is split into two bands for the binuclear species, due to the presence of both bridging and terminal thiolate ligands. Also, a large number of bands in the 200–450-cm⁻¹ region, observed only for the binuclear complexes, are presumably due to the $\text{Mo}(\mu\text{-SAR})_2(\mu\text{-OMe})\text{Mo}$ bridge.

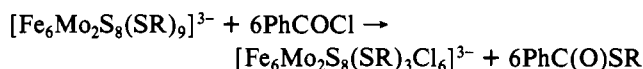
In addition to the $\nu(\text{Mo-O})$ vibration at 943 cm⁻¹, the Raman spectrum of $[\text{Et}_4\text{N}][\text{Mo}_2\text{O}_2(4\text{-MeC}_6\text{H}_4\text{S})_6(\text{OMe})]$ contains three strong features at 425, 358, and 290 cm⁻¹, and there are corresponding IR absorptions at 425, 353, and 280 cm⁻¹. These are assigned to $\nu(\text{Mo-S})$ vibrations, partly be-

cause such modes generally appear to be strong in the Raman spectrum.²¹ The 358-cm⁻¹ Raman shift is attributed to the $\nu(\text{Mo-S})$ vibrations of the terminal thiolate ligands, since a band is observed at a similar frequency (350 cm⁻¹) in the IR spectrum of $[\text{Et}_4\text{N}][\text{MoO}(4\text{-MeC}_6\text{H}_4\text{S})_4]$. The two Raman shifts at 425 and 285 cm⁻¹ are assigned to Mo-S stretching vibrations of the $\text{Mo}(\mu\text{-4-MeC}_6\text{H}_4\text{S})_2\text{Mo}$ moiety, presumably involving significant coupling with the Mo-O modes of the $\text{Mo}(\mu\text{-OMe})\text{Mo}$ arrangement.

The electronic absorption spectra of $[\text{Et}_4\text{N}][\text{Mo}_2\text{O}_2(\text{SAr})_6(\text{OMe})]$ (Ar = Ph or 4-MeC₆H₄), recorded in MeCN, are in good agreement with those reported previously.⁸ However, the ¹H NMR spectra of these complexes were not detected by previous workers,⁸ and this failure was ascribed to residual paramagnetism, possibly arising from dissociation of the complex into monomeric species in solution. These workers always found EPR resonances due to $[\text{MoO}(\text{SAr})_4]^-$ in solution. No trace of these latter signals was identified in the present study, and good quality NMR spectra were obtained. The ¹H NMR spectrum of the 4-MeC₆H₄S complex shows signals at δ 1.15 (triplet) and 3.19 (quartet) due to the cation, at 6.9 and 7.1 (multiplets, relative intensities 16:8) due to the aromatic protons of the terminal and bridging thiolate ligands, respectively, and at 2.21, 2.29, and 2.76 (singlets, relative intensities 6:12:3) due to the 4-methyl substituents of the bridging and terminal thiolates and to the methoxy ligand, respectively. For the SPh complex, the corresponding figures are δ 1.15 (triplet), 3.19 (quartet), 7.0 and 7.2 (multiplets), and 2.81 (singlet).

The ⁹⁵Mo NMR spectrum of $[\text{Et}_4\text{N}][\text{Mo}_2\text{O}_2(4\text{-MeC}_6\text{H}_4\text{S})_6(\text{OMe})]$ shows a single resonance at 718 ppm (line width 157 Hz), relative to 2 M Na₂MoO₄ at pH 11 as external standard. Values between 450 and 650 ppm have been observed for *cis*-dioxomolybdenum(VI) complexes with S-donor ligands.²²

Reaction with Benzoyl Chloride. The triply bridged structure of the $[\text{Mo}_2\text{O}_2(4\text{-MeC}_6\text{H}_4\text{S})_6(\text{OMe})]^-$ ion is similar to the bridging moiety in the iron-molybdenum-sulfur "cube cluster dimers" such as $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SR})_9]^{3-}$, which contains a $\text{Mo}(\mu\text{-SR})_3\text{Mo}$ bridging unit.^{16,17} These complexes react with excess benzoyl chloride²² to form thiobenzoate esters, according to the equation



In this reaction, only the terminal (iron-bound) thiols are displaced and excess benzoyl chloride is unable to attack the bridging $\text{Mo}(\mu\text{-SR})_3\text{Mo}$ moiety. It was therefore of interest to investigate the behavior of $[\text{Et}_4\text{N}][\text{Mo}_2\text{O}_2(4\text{-MeC}_6\text{H}_4\text{S})_6(\text{OMe})]$ under such conditions.

Over 2 days, the $[\text{Mo}_2\text{O}_2(4\text{-MeC}_6\text{H}_4\text{S})_6(\text{OMe})]^-$ was gradually converted completely into $[\text{MoOCl}_4]^-$ by an excess of benzoyl chloride. Use of only 4 (or fewer) molar equiv of benzoyl chloride/atom of Mo gave a slow reaction, producing a mixture of $[\text{MoOCl}_4]^-$ and unchanged starting material. Similar results were obtained with $[\text{Et}_4\text{N}][\text{Mo}_2\text{O}_2(\text{SPh})_6(\text{OMe})]$. Thus, it appears that benzoyl chloride is capable of displacing all of the coordinated thiolate (and methoxy) groups in these complex ions. Unlike the "cube cluster dimers", the bridging positions here do not appear to be inert with respect to substitution. The presence of terminal oxo ligands trans to the bridging methoxide ligand may facilitate its displace-

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ment, and it may be that, once the first bridging ligand is displaced, subsequent attack on the remaining positions is more rapid.

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Registry No. $[\text{Et}_4\text{N}]_2[\text{Mo}_2\text{O}_7(4\text{-MeC}_6\text{H}_4\text{S})_6(\text{OMe})]$, 69532-73-6; $[\text{Et}_4\text{N}]_2[\text{Mo}_2\text{O}_7(\text{SPh})_6(\text{OMe})]$, 69609-04-7; $\text{MoOCl}_3(\text{thf})_2$, 20529-42-4; benzoyl chloride, 98-88-4.

Supplementary Material Available: Listings of calculated atomic coordinates, anisotropic thermal parameters, isotropic thermal parameters, bond lengths, bond angles, and observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

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Ring Size Effects on the Structure of Macrocyclic Ligand Complexes: Copper(II) Complexes with 12–16-Membered Cyclic Tetrathia Ethers

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Crystal structures have been resolved at room temperature for a series of Cu(II) complexes with cyclic tetrathia ether ligands having the general formulation $\text{Cu}^{\text{II}}([\text{n}] \text{aneS}_4)(\text{ClO}_4)_2(\text{H}_2\text{O})_x$, where n represents the total number of carbon and sulfur atoms in the macrocyclic ligand ring ($n = 12, 13, 15, 16$) and $x = 1$ for $n = 12$ or 13 and zero for the other compounds. The respective space groups, lattice constants, and final R factors for these four compounds are as follows: for orthorhombic $\text{Cu}^{\text{II}}([\text{12}] \text{aneS}_4)(\text{ClO}_4)_2(\text{H}_2\text{O})$ space group $Pbc2_1$, $a = 9.010$ (2) Å, $b = 15.775$ (3) Å, $c = 13.380$ (2) Å, $Z = 4$, $R = 0.127$, $R_w = 0.162$; for monoclinic $\text{Cu}^{\text{II}}([\text{13}] \text{aneS}_4)(\text{ClO}_4)_2(\text{H}_2\text{O})$ space group $P2_1/c$, $a = 18.073$ (3) Å, $b = 13.607$ (3) Å, $c = 18.167$ (3) Å, $\beta = 119.759$ (1)°, $Z = 8$, $R = 0.081$, $R_w = 0.116$; for monoclinic $\text{Cu}^{\text{II}}([\text{15}] \text{aneS}_4)(\text{ClO}_4)_2$ space group $P2_1/n$, $a = 7.994$ (1) Å, $b = 9.167$ (3) Å, $c = 13.978$ (3) Å, $\beta = 99.29$ (3)°, $Z = 2$, $R = 0.066$, $R_w = 0.085$; for monoclinic $\text{Cu}^{\text{II}}([\text{16}] \text{aneS}_4)(\text{ClO}_4)_2$ space group $P2_1/c$, $a = 7.931$ (3) Å, $b = 9.613$ (5) Å, $c = 14.885$ (5) Å, $\beta = 110.71$ (3)°, $Z = 2$, $R = 0.044$, $R_w = 0.064$. These structures are compared with that previously reported for $\text{Cu}^{\text{II}}([\text{14}] \text{aneS}_4)(\text{ClO}_4)_2$ to provide a continuous series of homologous macrocyclic complexes in which the internal cavity progresses from dimensions that are too small to accommodate the central metal ion to those that exceed optimal size. In the compounds formed with $[\text{12}] \text{aneS}_4$ and $[\text{13}] \text{aneS}_4$, the Cu(II) ion sits 0.53 and 0.38 Å above the plane of the four sulfur donor atoms. In both cases the inner coordination sphere is square pyramidal, being completed by an axially coordinated water molecule. In the complexes formed with the three larger ligands, Cu(II) is coplanar with the four sulfur donor atoms, and two ClO_4^- ions are coordinated axially to form a tetragonal inner coordination sphere. The Cu–S bond lengths increase with increasing ring size, exhibiting average values of 2.30, 2.32, and 2.36 Å for $n = 14, 15$, and 16, respectively. In the last complex, in fact, the four Cu–S bonds are no longer equivalent: one pair of *trans*-Cu–S bonds is 2.33 Å while the other pair is 2.39 Å. In all five complexes, the axial Cu–O bond distances vary inversely with the average Cu–S bond distances so that, within each of the two types of coordination spheres represented, the total of the inner-sphere bond distances remains virtually constant. A comparison between the bond length totals of the two geometric groups indicates a limiting bonding distance of 3.0 Å for an oxygen donor atom axially coordinated to Cu(II). This agrees well with previous studies of Cu(II) complexes containing oxygen and nitrogen within the equatorial plane. Within the macrocyclic ring itself, there appear to be two mechanisms whereby the ligands attempt to adjust to the spatial requirements of the coordinated metal ion: (i) compression of the C–S–C bond angles and (ii) changes in the torsion angles and ring conformations. The progression of these properties is analyzed in considerable detail.

Introduction

In a series of recent studies on the copper(II) complexes of macrocyclic tetrathia ethers, we have investigated the effect of ring size upon various chemical and physical parameters including substitution kinetics,² complex stability constants,³ standard electrode potentials,^{4,5} electron-transfer kinetics,⁵ and

spectral properties.⁶ Whereas the trends observed in several of these properties are presumed to reflect the variations in the coordination geometry forced upon the central metal ion by the constraints of the various macrocyclic ligands, the structural features that account for these variations have not been previously reported except for the copper(II)⁷ and copper(I)⁸ complexes of the 14-membered cyclic tetrathia ether.

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