$Cs_3Yb_2Cl_9$ $2J = -3.25\ (3)\ cm^{-1}$

$Cs_3Yb_2Br_9$ $2J = -2.87\ (3)\ cm^{-1}$

5. Discussion

In most dimeric transition metal ion systems a Heisenberg description is most adequate, and it is usually argued that a complete or partial quenching of the orbital angular momentum is responsible for this. Rare-earth-metal ions, on the other hand, usually have unquenched orbital angular momenta. For the Yb^{3+} systems studied here, the anisotropy of *g* values in the ground state is not very pronounced. It is therefore not surprising that the exchange splitting in the title compounds can be described by a Heisenberg Hamiltonian. This cannot be generalized, however, as was shown in ref 16 for $Cs_3Ho_2Br_9$. Neither a Heisenberg nor an anisotropic Hamiltonian of the type in eq 1 could account for the observed splittings in three crystal field states. An exchange-tensor formalism was then successfully used.[16,19] A more fundamental treatment has to take explicit account of the orbital functions of the electrons involved in the coupling. There have been numerous theoretical approaches to this,[20] and we are planning to explore some of these models in order to gain a better understanding of the observed exchange splittings in the whole series of $Cs_3(RE)_2Br_9$ dimer compounds.

The difference of approximately 10% between $Cs_3Yb_2Cl_9$ and $Cs_3Yb_2Br_9$ is reminiscent of exchange-coupled transition metal ion systems with face-sharing octahedra. In the dimers $M_2X_9^{3-}$ ($M = Ti^{3+}, V^{3+}, Cr^{3+}$; $X = Cl^-, Br^-, I^-$) it was found that the relative orbital contributions to the exchange parameter *J* varied greatly upon variation of either the metal ion or the halide ion.[21] In the chloride dimers the dominant contribution was J_{aa}, the orbital parameter involving the trigonal a orbitals on the metal centers, i.e. those orbitals that point directly toward each other. This interaction was strongly reduced in the bromide dimers as a result of the increased metal-metal distance. We conclude, by analogy, that a similar mechanism is responsible for the coupling in the $Yb_2Cl_9^{3-}$ and $Yb_2Br_9^{3-}$ dimers.

Acknowledgment. We are indebted to N. Furer for synthesizing the compounds. Financial support by the Swiss National Science Foundation is gratefully acknowledged.

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Crown Thioether Ligands Containing Rigid Xylyl Units. Synthesis and Structures of 2,5,8-Trithia[9]-*o*-benzenophane (TTOB), 2,5,8-Trithia[9]-*m*-benzenophane (TTMB), and *fac*-Mo(CO)$_3$(TTOB)·DMSO

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The crown thioethers 2,5,8-trithia[9]-*o*-benzenophane (TTOB) and 2,5,8-trithia[9]-*m*-benzenophane (TTMB) were prepared by the reaction of the dipotassium salt of 3-thiapentane-1,5-dithiol with α,α'-dibromo-*o*-xylene and α,α'-dibromo-*m*-xylene, respectively. These compounds were characterized by ^1H and $^{13}C\{^1H\}$ NMR, GCMS, and X-ray crystallography methods. The ortho isomer crystallized in the space group $P2_1/n$, with $a = 8.840$ (2) Å, $b = 15.866$ (5) Å, $c = 10.600$ (2) Å, $\beta = 119.34$ (6)°, $V = 1295.9$ (6) Å^3, and $Z = 4$. The structure was refined to $R = 4.80\%$ and $R_w = 5.51\%$ for 1034 reflections with $F_o^2 > 3\sigma(F_o^2)$. The meta isomer crystallized in the space group $P2_12_12_1$, with $a = 9.107$ (5) Å, $b = 8.851$ (7) Å, $c = 31.90$ (2) Å, $V = 2571$ (1) Å^3, and $Z = 8$. The structure refined to $R = 6.59\%$ and $R_w = 7.04\%$ for 1384 reflections with $F_o^2 > 3\sigma(F_o^2)$. In both structures, the S atoms are exodentate to the ring with a $-SCH_2CH_2SCH_2CH_2S-$ "bracket" bridging the xylyl group and the plane of the aromatic ring approximately perpendicular to the mean plane of the S atoms. Molecular mechanics calculations (MMX) indicated the possibility of a conformation for TTOB, with all S atoms endodentate, which would be ideal for facial coordination to a metal center. The reaction of TTOB with *fac*-Mo(CH$_3$CN)$_3$(CO)$_3$ gave the complex *fac*-Mo(CO)$_3$(TTOB), showing that the predicted facial coordination mode is possible in octahedral geometry. The complex *fac*-Mo(CO)$_3$(TTOB)·DMSO crystallized in the space group $P2_1/c$, with $a = 7.732$ (4) Å, $b = 18.69$ (2) Å, $c = 15.00$ (1) Å, $\beta = 104.05$ (6)°, $V = 2103$ (1) Å^3, and $Z = 4$. The structure was refined to $R = 4.52\%$ and $R_w = 5.44\%$ for 2174 reflections with $F_o^2 > 3\sigma(F_o^2)$. The analogous coordination mode for TTMB was neither indicated by molecular mechanics calculations nor observed in similar complexation studies.

Introduction

It is now well established that crown thioethers favor the adoption of "inside-out" or exodentate conformations with the sulfur donor atoms oriented out of the macrocyclic cavity.[1-3] This results from the tendency of $-SCH_2CH_2SCH_2CH_2S-$ chains to adopt a "bracket" structure that prefers anti placements for carbon-carbon bonds and gauche placements for carbon-sulfur bonds.[4] Each thioether molecule must then undergo substantial conformational change in order to attain the "crown" conformation of the macrocycle essential for metal ion coordination.[1-12] The need for these large conformational changes often results in the formation of complexes with limited stability or complexes in which

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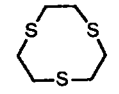
the ligand acts to bridge metal ions by employing exodentate sulfur atoms rather than coordinating to a single metal center.[1,2,12-15]

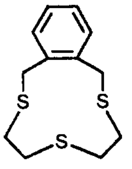
A notable exception to this general observation is the small ring tridentate ligand 1,4,7-trithiacyclononane (9S3). This particular



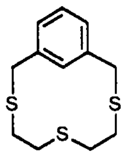
9S3

crown thioether is quite rigid and exhibits an all endodentate or crown conformation in the free ligand which very closely resembles that required for facial coordination.[16] As a result, complexation requires almost no conformational change and it can be assumed that this thermodynamic barrier to complex formation is effectively removed. 9S3 is an excellent ligand, and several complexes of the type $[M(9S3)_2]^{n+}$ exhibit unique redox chemistry and enhanced stability.[2,6,12,15-24]

This paper describes the synthesis, structure, conformational analysis and complexation of the small ring crown thioethers 2,5,8-trithia[9]-*o*-benzenophane (TTOB) and 2,5,8-trithia[9]-*m*-benzenophane (TTMB). These potentially tridentate thioether



TTOB



TTMB

ligands are similar in design to 9S3 except that the macrocyclic ring is slightly larger (11 and 12 atoms versus 9 atoms) and the ring contains either a rigid *o*- or *m*-xylyl fragment. These rigid structural units have been added in order to limit the flexibility of the ligand and reduce the number of possible ring conformations. This provides a measure of steric control and predictability in ligand design. The planar aromatic system should contribute significantly to the overall structure and perhaps even dictate the preferred conformations. This would be in marked contrast to the crown thioether ligands containing only aliphatic chains for which the conformations are dependent on the structural preferences of the $-SCH_2CH_2SCH_2CH_2S-$ linkages.[4] The thioether macrocycles TTMB and TTOB will be relatively inflexible, and this may result in either the favoring of an endodentate conformation, similar to 9S3, or the accessibility of such a conformation via some low-energy conformational change.

Table I. Crystallographic Data for TTMB, TTOB, and $Mo(CO)_3(TTOB)\cdot DMSO$

chem formula	$C_{12}H_{16}S_3(m)$	$C_{12}H_{16}S_3(o)$	$C_{17}H_{22}MoO_4S_4$
fw	256.5	256.5	514.37
a, Å	9.107 (5)	8.840 (2)	7.732 (4)
b, Å	8.851 (7)	15.866 (5)	18.69 (2)
c, Å	31.90 (2)	10.600 (2)	15.00 (1)
β, deg		119.34 (6)	104.05 (6)
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$
V, Å^3	2571 (1)	1295.9 (6)	2103 (1)
ρ(calcd), g/cm^{-3}	1.33	1.31	1.62
Z	8	4	4
μ, cm^{-1}	4.85	4.81	9.39
λ, Å	0.71069	0.71069	0.71069
T, °C	24	24	24
R, %	6.59	4.80	4.52
R_w, %	7.04	5.51	5.44

Experimental Section

fac-$Mo(CH_3CN)_3(CO)_3$ was prepared by the literature method.[25] 3-Thiapentane-1,5-dithiol, α,α'-dibromo-*o*-xylene, and α,α'-dibromo-*m*-xylene were purchased from Aldrich and used as received. Absolute ethanol was purified by distillation from CaH_2 under N_2. All reactions were conducted under an atmosphere of N_2 by using standard Schlenk techniques, and all other solvents were degassed prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.1 and 75.4 MHz, respectively, on a Bruker AM300 spectrometer locked to the deuterated solvent. ^1H NMR simulation calculations were performed by using the program LAOCOON3. Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrometer. GCMS experiments were performed on a HP5970 Series MSD instrument coupled to a HP5890a gas chromatograph. Elemental analysis were performed by Microanalytical Services, New Westminister, British Columbia, Canada.

Structure building, structure manipulation, and molecular mechanics calculations were performed on an IBM-386 compatible computer using Serena Software's program PCMODEL-MMX employing MMX and MMP force fields and parameters provided with the program.

Preparation of 2,5,8-Trithia[9]-*m*-benzenophane (TTMB). 3-Thiapentane-1,5-dithiol (13.50 g, 87 mmol) was added to anhydrous ethanol (200 mL) in which K metal (6.84 g, 175 mmol) had been dissolved and the resulting solution stirred for 1 h. α,α'-Dibromo-*m*-xylene (22.96 g, 87 mmol) was dissolved in anhydrous ethanol (500 mL). Both solutions were simultaneously added dropwise to anhydrous ethanol (300 mL), over a period of 4 h, by using constant-addition funnels. During this time, a white precipitate formed. The solvent was removed in vacuo and the residue extracted with benzene (300 mL). After filtration, the benzene solution was reduced in volume to ca. 100 mL, which resulted in the formation of colorless crystals of the product. Yield: 10.14 g, (46%). Mp: 144-145 °C (lit. mp: 143-144 °C).[28] MS: m/e 256. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.06, 130.65, 130.54, 128.13 (aromatic); 35.51 (benzylic CH_2S); 30.98, 30.09 (SCH_2CH_2S). ^1H NMR ($CDCl_3$): δ 7.00-7.47 (m, 4 H, aromatic), 3.77 (s, 4 H, benzylic CH_2), 2.19-2.41 (m, 8 H, SCH_2CH_2S). Anal. Calcd for $C_{12}H_{16}S_3$: C, 56.19; H, 6.30; S, 37.51. Found: C, 56.21; H, 6.14; S, 37.29.

Preparation of 2,5,8-Trithia[9]-*o*-benzenophane (TTOB). 3-Thiapentane-1,5-dithiol (16.08 g, 104 mmol) was added to anhydrous ethanol (250 mL) in which K metal (8.15 g, 208 mmol) had been dissolved, and the resulting solution stirred for 1 h. α,α'-Dibromo-*o*-xylene (27.51 g, 104 mmol) was dissolved in anhydrous ethanol (500 mL). These two solutions were simultaneously added dropwise to anhydrous ethanol (500 mL), over a period of 72 h, by using constant-addition funnels. During this time, a white precipitate formed. The mixture was stirred for a further 12 h and then filtered. The solvent was removed in vacuo and the residue extracted with benzene (300 mL). After the filtering, the benzene was evaporated to give a semisolid residue. The crude product was dissolved in a minimum amount of hot anhydrous ethanol and this hot solution filtered. Cooling this solution gave the product as colorless needles. Yield: 5.55 g, (21 %). Mp: 98.5-100.0 °C. MS: m/e 256. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 136.91, 130.26, 127.60 (aromatic); 32.27 (benzylic CH_2S); 32.10, 31.80 (SCH_2CH_2S). ^1H NMR ($CDCl_3$): δ 7.39 (m, 4 H, aromatic), 3.94 (s, 4 H, benzylic CH_2), 2.68 (m, 8 H, SCH_2CH_2S). Anal. Calcd for $C_{12}H_{16}S_3$: C, 56.19; H, 6.30; S, 37.51.

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Found: C, 55.93; H, 6.29; S, 37.93.

Preparation of *fac*-$Mo(CO)_3$(TTOB). $Mo(CO)_6$ (634 mg, 2.4 mmol) was dissolved in CH_3CN (20 mL) under N_2. The initially colorless solution turned yellow after a few minutes and was refluxed for 4 h. TTOB (487 mg, 1.9 mmol), dissolved in CH_3CN (10 mL), was added dropwise, while the mixture was being stirred vigorously, to the resulting yellow solution of *fac*-$Mo(CH_3CN)_3(CO)_3$. The color of the solution changed to yellow-brown and after a few minutes a yellow-brown precipitate formed. The mixture was refluxed for a further hour and then cooled to room temperature. The solvent was removed in vacuo, leaving a beige residue. Yield: 802 mg (97%). Diffusion of diethyl ether into a DMSO solution of the complex yielded yellow crystals of the DMSO adduct suitable for X-ray diffraction. $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 134.96, 130.85, 128.26, 37.42, 34.77, 31.85. ^1H NMR (CD_3CN): δ 7.28 (s, 4 H), 4.13–3.77 (q, 4 H), 3.3–2.6 (m, 8 H). IR: ν(CO) 1818, 1935 cm^{-1} (CH_3NO_2); ν(CO) 1810, 1925 cm^{-1} (KBr). Anal. Calcd for: $C_{17}H_{22}MoO_4S_4$: C, 39.69; H, 4.31; S, 24.93. Found: C, 39.57; H, 3.91; S, 22.87.

General X-ray Diffraction Data Collection, Solution, and Refinement. Diffraction experiments were performed on a four-circle Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrices were obtained from 15 machine-centered reflections selected from rotation photographs. Partial rotation photographs around each axis were used to determine the crystal systems. Ultimately, 30 high-angle reflections were used to obtain the final lattice parameters and orientation matrices. Machine parameters, crystal data, and data collection parameters are summarized in Table I and detailed in Table S-I (deposited as supplementary material). The intensities of standard reflections were recorded every 197 reflections and showed no statistically significant changes over the duration of the data collections. The data were processed by using the SHELX-76 program package on the computing facilities shared with the University of Manitoba. The absorption coefficients were small, and ψ scans recorded showed no significant absorption effects. Thus, no absorption corrections were applied to the data. Refinement was carried out by using full-matrix least-squares techniques on F minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors[26] and anomolous dispersion terms[27] were taken from the usual sources. Fixed H atom contributions were included with C–H distances of 0.95 Å and thermal parameters 1.1 times the isotropic thermal parameter of the bonded C atoms. No H atoms were refined, but all values were updated as refinement continued.

Structure Determination of TTMB. Colorless crystals were grown by slow evaporation of an acetone solution of the compound. Preliminary photography was consistent with an orthorhombic crystal system. Observed extinctions were consistent with the space group $P2_12_12_1$. Intensity data $(+h,+k,+l)$ were collected in one shell $(4.5° < 2\theta < 45°)$. A total of 1972 reflections were collected and 1384 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The six S atom positions were determined by direct methods from the E map with the highest figure of merit. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. This resulted in the identification of a 2-fold disorder for the $-SCH_2CH_2SCH_2CH_2S-$ carbon atoms. This was successfully modelled with site occupancy factors of 0.65 and 0.35 for molecule one and site occupancy factors of 0.55 and 0.45 for molecule two. H atom contributions were not included for the disordered carbon atoms. In the final cycles of refinement, sulfur atoms were refined anisotropically and the carbon atoms were assigned isotropic thermal parameters. The correct enantiomorph was determined by inversion of the atomic positions and comparison of the resulting R and R_w values for the possible enantiomorphs at convergence. This resulted in $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0659$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.0704$ at final convergence.

The Δ/σ value for any parameter in the final cycle was less than 0.002. A final difference Fourier map calculation showed no peaks of chemical significance; the largest was 0.35 e/Å^3 and was associated with the C2 and C3 carbon atoms. Selected atomic positional parameters are summarized in Table II and selected bond distances and angles are summarized in Table III. Complete listings of atomic positional parameters (Table S-II), nonessential bond distances and angles (Table S-III), thermal parameters (Table S-IV), hydrogen atom parameters (Table S-V), and values of $10|F_o|$ and $10|F_c|$ (Table S-XIV) are deposited as supplementary material.

Structure Determination of TTOB. Colorless crystals of TTOB were grown by slow diffusion of diethyl ether into an acetone solution of the compound. Preliminary photography was consistent with a monoclinic crystal system. Observed extinctions were consistent with space group $P2_1/n$. Intensity data $(\pm h,+k,+l)$ were collected in one shell $(4.5° < 2\theta$

Table II. Selected Positional Parameters[a] for TTMB

atom	x	y	z
S1	6986 (4)	1395 (4)	1360 (1)
S2	2731 (3)	3897 (3)	1524 (1)
S3	0797 (4)	1322 (4)	2575 (1)
S4	9291 (5)	−1768 (3)	4961 (1)
S5	1591 (4)	0472 (4)	3911 (1)
S6	248 (4)	4772 (3)	4000 (1)
C7	706 (1)	050 (2)	1860 (4)
C8	495 (2)	202 (2)	1293 (6)
C8d	564 (4)	278 (3)	1571 (9)
C9	462 (2)	331 (2)	1574 (6)
C9d	406 (3)	249 (3)	1379 (9)
C10	175 (2)	252 (2)	1825 (6)
C10d	228 (3)	328 (4)	206 (1)
C11	187 (2)	283 (2)	2281 (6)
C11d	117 (3)	199 (4)	202 (1)
C12	241 (1)	030 (1)	2751 (3)
C19	815 (1)	033 (1)	5177 (4)
C20	991 (3)	−113 (3)	4388 (8)
C20d	1070 (2)	−074 (2)	4688 (6)
C21	1122 (3)	−027 (3)	4428 (8)
C21d	1029 (3)	−059 (3)	4205 (8)
C22	1019 (2)	195 (2)	3847 (6)
C22d	1111 (3)	237 (3)	4087 (8)
C23	1069 (2)	324 (2)	4110 (7)
C23d	981 (3)	982 (3)	3835 (9)
C24	823 (1)	457 (1)	4480 (3)

[a] Multiplied by 10^4. d = Atom for the minor component in disorder model.

Table III. Selected Bond Distances and Angles for TTMB[a]

Molecule 1			
Distances (Å)			
S1–C7	1.78 (1)	S1–C8	1.95 (2)
S1–C8d	1.86 (3)	S2–C9	1.80 (2)
S2–C9d	1.79 (3)	S2–C10	1.79 (2)
S2–C10d	1.85 (4)	S3–C11	1.87 (2)
S3–C11d	1.91 (4)	S3–C12	1.82 (1)
C1–C12	1.52 (1)	C5–C7	1.52 (2)
C8–C9	1.48 (2)	C8d–C9d	1.58 (4)
C10–C11	1.48 (3)	C10d–C11d	1.53 (5)
Angles (deg)			
C7–S1–C8	105.0 (7)	S1–C3d–C9d	110 (2)
C7–S1–C8d	90 (1)	C8–C9–S2	111 (1)
C9–S2–C10	103.3 (8)	C8d–C9d–S2	113 (2)
C9B–S2–C10d	101 (1)	S2–C10–C11	112 (1)
C11–S3–C12	96.2 (7)	S2–C10d–C11d	106 (2)
C11d–S3–C12	107 (1)	C10–C11–S3	110 (1)
C5–C7–S1	113.4 (8)	C10d–C11d–S3	105 (2)
S1–C8–C9	110 (1)	S3–C12–C1	115.5 (7)
Molecule 2			
Distances (Å)			
S4–C19	1.77 (1)	S4–C20	2.00 (3)
S4–C20d	1.80 (2)	S5–C21	1.81 (3)
S5–C21d	1.78 (3)	S5–C22	1.84 (2)
S5–C22d	1.83 (3)	S6–C23	1.92 (2)
S6–C23d	1.88 (3)	S6–C24	1.80 (1)
C17–C19	1.50 (1)	C13–C24	1.50 (1)
C20–C21	1.42 (3)	C20d–C21d	1.59 (3)
C22–C23	1.49 (3)	C22d–C23d	1.48 (4)
Angles (deg)			
C19–S4–C20	108.2 (1)	S4–C20d–C21d	108.2 (1)
C19–S4–C20d	104.1 (7)	C20–C21d–S5	105 (2)
C21–S5–C22d	103.2 (1)	C20d–C21d–S5	114 (2)
C21d–S5–C22d	100 (1)	S5–C22–C23	106 (2)
C23–S6–C24	97.5 (1)	S5–C22d–C23d	105 (2)
C23–S6–C24	106.9 (9)	C22–C23–S6	103 (2)
C17–C19–S4	116.3 (8)	C22d–C23d–S6	107 (2)
S4–C20–C21	108 (2)	S6–C24–C13	115.9 (7)

[a] d = atom for the minor component in disorder model.

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(26) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974.

(27) Cromer, D. T.; Mann, J. B. *Acta. Crystallogr., Sect. A: Cryst. Phys. Diffr., Theor. Gen. Crystallogr.* (a) **1968**, *A24*, 321; (b) **1968**, *A24*, 390.

Table IV. Selected Positional Parameters[a] for TTOB

atom	x	y	z
S1	−0550 (2)	2673 (1)	4969 (2)
S2	1351 (3)	1758 (1)	2087 (2)
S3	3502 (2)	4339 (1)	2784 (2)
C7	0548 (6)	3650 (3)	5054 (5)
C8	−0576 (8)	2204 (4)	3411 (6)
C9	1155 (9)	1870 (4)	3712 (7)
C10	1615 (7)	2860 (4)	1773 (6)
C11	3361 (7)	3212 (4)	2801 (7)
C12	2573 (6)	4633 (3)	3903 (5)

[a] Multiplied by 10^4.

Table V. Selected Bond Distances and Angles for TTOB

	Distances (Å)		
S1–C7	1.807 (5)	S1–C8	1.801 (6)
S2–C9	1.822 (7)	S2–C10	1.816 (6)
S3–C11	1.793 (7)	S3–C12	1.803 (5)
C6–C7	1.502 (7)	C8–C9	1.499 (8)
C10–C11	1.495 (7)	C1–C12	1.515 (6)
	Angles (deg)		
C7–S1–C8	99.5 (2)	C8–C9–S2	113.2 (5)
C9–S2–C10	99.2 (3)	S2–C10–C11	113.9 (4)
C11–S3–C12	101.3 (3)	C10–C11–S3	114.7 (4)
C6–C7–S1	116.0 (3)	S3–C12–C1	116.1 (3)
S1–C8–C9	113.5 (4)		

< 45°). A total of 1827 reflections were collected, and 1034 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The three S atom positions were determined by direct methods from the E map with the highest figure of merit. The remaining carbon atoms were located from successive difference Fourier map calculations. In the final cycles of refinement, sulfur atoms and $-SCH_2CH_2SCH_2CH_2S-$ carbon atoms were refined anisotropically, and the remaining carbon atoms were assigned isotropic thermal parameters. This resulted in $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0480$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.0551$ at final convergence.

The Δ/σ value for any parameter in the final cycle was less than 0.001. A final difference Fourier map calculation showed no peaks of chemical significance; the largest was 0.26 e/Å^3 and was associated with the C3 and C4 carbon atoms. Selected atomic positional parameters are summarized in Table IV and selected bond distances and angles in Table V. Complete listings of atomic positional parameters (Table S-VI), nonessential bond distances and angles (Table S-VII), thermal parameters (Table S-VIII), hydrogen atom parameters (Table S-IX), and values of $10|F_o|$ and $10|F_c|$ (Table S-XV) are deposited as supplementary material.

Table VI. Selected Positional Parameters[a] for $Mo(CO)_3(TTOB)\cdot DMSO$

atom	x	y	z
Mo	4321 (1)	2933 (1)	4197 (1)
S1	2014 (2)	2216 (1)	4775 (1)
S2	1722 (2)	3061 (1)	2807 (1)
S3	5170 (2)	1942 (1)	3219 (1)
C7	2340 (9)	1242 (4)	4929 (6)
C8	−0074 (9)	2243 (5)	3881 (5)
C9	−0203 (9)	2891 (5)	3275 (6)
C10	1770 (9)	2252 (4)	2143 (5)
C11	366 (1)	2073 (4)	2103 (5)
C12	448 (1)	1063 (4)	3547 (5)
C13	3613 (9)	3732 (4)	4844 (5)
C14	6265 (9)	2740 (4)	5278 (5)
C15	5884 (9)	3630 (4)	3816 (5)
O13	3219 (8)	4223 (3)	5241 (4)
O14	7406 (7)	2646 (3)	5918 (4)
O15	6793 (7)	4073 (3)	3646 (4)

[a] Multiplied by 10^4.

Table VII. Selected Bond Distances and Angles for $Mo(CO)_3(TTOB)\cdot DMSO$

	Distances (Å)		
Mo–S1	2.546 (2)	Mo–S2	2.531 (2)
Mo–S3	2.545 (2)	Mo–C13	1.931 (8)
Mo–C14	1.958 (7)	Mo–C15	1.954 (7)
C13–O13	1.173 (8)	C14–O14	1.149 (9)
C15–O15	1.155 (8)	C6–C7	1.49 (1)
C7–S1	1.844 (8)	S1–C8	1.831 (7)
C8–C9	1.50 (1)	C9–S2	1.820 (8)
S2–C10	1.817 (7)	C10–C11	1.52 (1)
C11–S3	1.810 (7)	S3–C12	1.831 (7)
C12–C1	1.47 (1)		
	Angles (deg)		
S1–Mo–S2	81.3 (1)	Mo–S3–C12	111.4 (2)
S1–Mo–S3	96.5 (1)	Mo–S1–C7	118.5 (2)
S2–Mo–S3	81.9 (1)	Mo–S3–C11	103.7 (2)
C13–Mo–C14	88.9 (3)	Mo–S2–C9	103.1 (3)
C14–Mo–C15	87.7 (3)	Mo–S2–C10	104.8 (2)
C15–Mo–C13	84.4 (3)	C1–C6–C7	120.8 (6)
S1–Mo–C13	85.9 (2)	C6–C7–S1	111.8 (5)
S1–Mo–C14	94.7 (2)	C7–S1–C8	100.9 (4)
S1–Mo–C15	170.0 (2)	S1–C8–C9	112.5 (5)
S2–Mo–C13	94.3 (2)	C8–C9–S2	115.7 (5)
S2–Mo–C15	96.9 (2)	C9–S2–C10	101.1 (4)
S2–Mo–C14	174.6 (2)	S2–C10–C11	110.7 (5)
S3–Mo–C14	95.2 (2)	C10–C11–S3	113.9 (4)
S3–Mo–C15	93.0 (2)	C11–S3–C12	101.9 (3)
S3–Mo–C13	175.1 (2)	S3–C12–C1	108.1 (5)
Mo–S1–C8	107.6 (3)	C12–C1–C6	121.9 (6)

Structure Determination of *fac*-$Mo(CO)_3(TTOB)\cdot DMSO$. Yellow crystals of the complex were grown by slow diffusion of diethyl ether into a DMSO solution of the compound. Preliminary photography was consistent with a monoclinic crystal system. Observed extinctions were consistent with space group $P2_1/c$. Intensity data ($\pm h,+k,+l$) were collected in one shell ($4.5° < 2\theta < 45°$). A total of 2904 reflections were collected, and 2174 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The Mo atom position was determined by conventinal heavy-atom methods and the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. This resulted in the location of a molecule of DMSO exhibiting 2-fold disorder. In the final cycles of refinement, all non-hydrogen atoms, except for the solvent molecule, were refined anisotropically. The solvent molecule was refined isotropically with site occupancy factors of 0.78 and 0.22. At final convergence this resulted in $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0452$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.0544$.

The Δ/σ value for any parameter in the final cycle was less than 0.002. The largest peak in the final difference Fourier map calculation was relatively large (1.23 e/Å^3) and associated with the solvent molecule. Selected atomic positional parameters are summarized in Table VI, and selected bond distances and angles are summarized in Table VII. Complete listing of atomic positional parameters (Table S-X), nonessential bond distances and angles (Table S-XI), thermal parameters (Table S-XII), hydrogen atom parameters (Table S-XIII), and values of $10|F_o|$ and $10|F_c|$ (Table S-XVI) are deposited as supplementary material.

Results

Ligand Synthesis and Characterization. The crown thioethers TTMB and TTOB are easily prepared by the reaction described in eq 1. This method employs high dilution techniques and takes advantage of the template fit of the xylyl fragment and the $-SCH_2CH_2SCH_2CHS_2-$ chain to favor ring closure.

$$2KSCH_2CH_2SCH_2CH_2SK + BrCH_2(C_6H_4)CH_2Br \xrightarrow{\text{ethanol}} \text{TTMB (or TTOB)} + 2KBr \quad (1)$$

The isolation of products as clean crystalline solids is straightforward and does not require chromatographic techniques. The yields of 46% for TTMB and 21% for TTOB reflect the relative fits of the *o*-xylyl and *m*-xylyl fragments with the $-SCH_2CH_2SCH_2CHS_2-$ chain during the ring closure step. This phenomenon has been previously noted by Vögtle in the preparation of crown thioethers containing rigid groups, including TTMB for which a yield of 37% was reported.[28] It should be noted that there are no isolable side products in the synthesis of TTMB other than insoluble and presumably polymeric materials. However in the formation of TTOB, the yield is dependent upon addition rates, and at lower dilutions small amounts of the larger

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(28) Vögtle, F. *Liebigs Ann. Chem.* **1976**, 891.

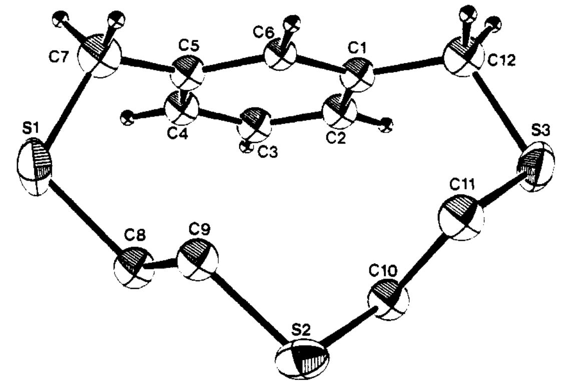


Figure 1. Perspective ORTEP drawing of TTMB, molecule 1, showing the atom-numbering scheme. Thermal ellipsoids of 20% are shown.

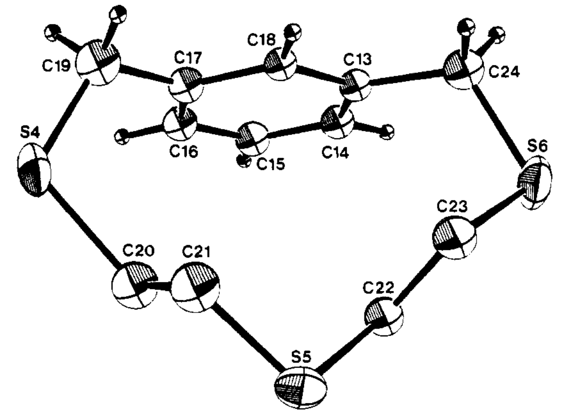
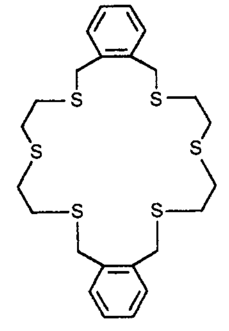


Figure 2. Perspective ORTEP drawing of TTMB, molecule 2, showing the atom-numbering scheme. Thermal ellipsoids of 20% are shown.

24-membered ring 2,5,8,13,16,19-hexathia[9.9]-*o*-benzenophane (HTOB) can be isolated.



HTOB

We have also prepared this macrocycle and the meta analog, in >80% yield, employing a multiple-step synthesis which employs a Cs^+-mediated ring closure reaction for the final step.[3,29] The molecular structures of these large ring crown thioethers have been verified by X-ray crystallography and will be the subject of future publications.

The ^1H NMR spectra for TTOB and TTMB show the expected patterns for ortho and meta aromatic substitution, a single resonance due to the benzylic CH_2 groups and an AA′BB′ pattern for the SCH_2CH_2S chain. We have shown previously that this second-order multiplet is probably related to retention of the $-SCH_2CH_2SCH_2CH_2S-$ bracket in solution.[3] The S–C–C–S torsional angles estimated from calculated coupling constants are comparable to those observed in the solid state and are consistent with an anti conformation.

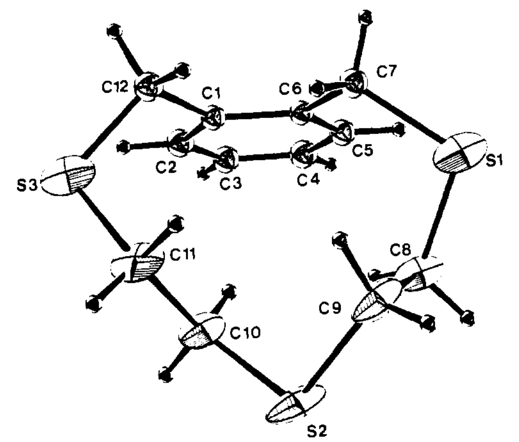
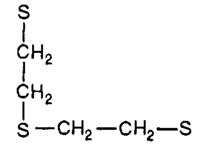


Figure 3. Perspective ORTEP drawing of TTOB, showing the atom-numbering scheme. Thermal ellipsoids of 20% are shown.

X-ray Structure of TTMB. The unit cell contains eight molecules of TTMB such that the asymmetric unit contains two crystallographically independent molecules. Perspective views of the two molecules, indicating the numbering scheme, are shown in Figures 1 and 2. The closest intermolecular nonbonded contact is 2.97 Å between S3 and H2. Selected interatomic distances and angles are found in Table III. Sulfur–carbon distances range from 1.77 (1) to 2.00 (1) Å and carbon $C(sp^2)-C(sp^2)$ bonds range from 1.34 (1) to 1.41 (1) Å. The $C(sp^3)-C(sp^3)$ bonds range from 1.42 (3) to 1.59 (3) Å, and the $C(sp^2)-C(sp^3)$ bonds range from 1.50 (1) to 1.52 (1) Å. The wide variation in chemically equivalent bond distances is primarily a result of a disorder for the carbon atom positions in the $-SCH_2CH_2SCH_2CH_2S-$ portion of the molecule. The disorder is such that the thermal ellipsoids are extremely elongated along the S–C bonds and is presumably related to the fact that the S–C–C–S chains can adopt either of two conformations, reminiscent of the λ and δ configurations associated with five-membered chelate rings. This type of disorder and the effect on structural parameters has been observed for other crown thioethers.[4,30,31]

The conformations of crown thioethers are usually described in terms of torsional angles, particularly those associated with the $-SCH_2CH_2SCH_2CH_2S-$ brackets that form a right triangle in projection.[3,4]



$$\begin{array}{l} \mathrm{S} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{S{-}CH_2{-}CH_2{-}S} \end{array}$$

These brackets are formed due to the propensity of S–C bonds to favor gauche placement and C–C bonds to favor anti placement when part of a $-SCH_2CH_2SCH_2CH_2S-$ chain.

These small, relatively rigid, crown thioether molecules are composed of a xylyl fragment and a $-SCH_2CH_2SCH_2CH_2S-$ bracket, fused at the benzylic carbon to sulfur bonds. Therefore, the overall structures of these molecules are best described in terms of (1) the torsional angles associated with the $-SCH_2CH_2SCH_2CH_2S-$ bracket, (2) the S1 to S3 distance across the xylyl unit, and (3) the dihedral angle between the planar xylyl fragment and the bracket structure. For TTMB, the S–C–C–S torsional angles average 177 (3)°, as would be predicted for an anti conformation about the C–C bonds, the average nonbonding S1···S3 distances across the xylyl ring average 6.84 (6) Å, and the average dihedral angle between the plane defined by the aromatic ring carbon atoms and the plane defined by the three sulfur atoms is 101 (4)°.

X-ray Structure of TTOB. The unit cell contains four molecules of TTOB. A perspective view of the molecule, indicating the atom numbering scheme, is shown in Figure 3. The closest intermolecular nonbonded contact is 3.07 Å between S2 and H12B. Selected interatomic distances and angles are found in Table V.

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(29) Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1981**, *46*, 4481–4485.

(30) Olmstead, M. M.; Musker, W. K.; Kessler, R. M. *Inorg. Chem.* **1981**, *20*, 151–157.

(31) Rubin, B. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 2088–2092.

Table VIII. Structural Parameters for Complexes of the Type Mo(CO)$_3$L

L	Mo–S, Å	Mo–S[a], Å	S–Mo–S, deg	S–Mo–S,[b] deg	S···S, Å	S···S,[c] Å	S–C–C–S, deg
9S3	2.52 (2)		82.8 (2)		3.354 (8)		48 (2)
TTN	2.528 (1)	2.578 (4)	81.8 (4)	83.83 (2)	3.35 (1)	3.445 (1)	47 (2)
10S3	2.518 (1)	2.545 (1)	81.96 (6)	90.59 (4)			
TTOB	2.531 (2)	2.545 (1)	81.6 (4)	96.5 (1)	3.32 (1)	3.798 (2)	54 (6)

[a] Average of the Mo–S1 and Mo–S3 distances associated with the unique fragment. [b] The S1–Mo–S3 angle associated with the unique fragment. [c] The S1···S3 nonbonding distance across the unique fragment.

Sulfur–carbon distances range from 1.793 (7) to 1.822 (7) Å, and carbon C(sp^2)–C(sp^2) bonds range from 1.359 (7) to 1.399 (7) Å. The two C(sp^3)–C(sp^3) bonds are 1.499 (8) and 1.495 (7) Å and the two C(sp^2)–C(sp^3) bonds are 1.515 (6) and 1.502 (7) Å. These distances compare well to those found previously for other macrocyclic thioethers.[2-4]

The S–C–C–S torsional angles are 166.7 (5)° and 158.5 (5)°, the S1···S3 distance is 5.76 Å and the dihedral angle between the plane defined by the aromatic ring carbon atoms and the plane defined by the three sulfur atoms is 96.1°.

Molecular Mechanics Calculations. The number of possible conformations for a particular macrocyclic ligand is numerous. In order to avoid some of the design-based errors that occur when molecular models are used in the design of macrocyclic ligands, we have applied molecular mechanics calculations to the design of some crown thioether ligands. In particular, our approach has been to (1) determine the most probable conformation for the crown thioether molecule by molecular mechanics energy minimization and to (2) determine whether a conformation, of relatively low energy, exists that would allow for the crown thioether to coordinate a metal ion in a designed geometry.

For the relatively rigid crown thioethers described in this paper, there are two general conformations which are most likely. One conformation has the three sulfur atoms exodentate to the ring, and the other has the three sulfur atoms endodentate to the ring. By "building" models of the "all-endodentate" and "all-exodentate" conformations for TTMB and TTOB and using these as input for molecular mechanics energy minimizations, we determined the potential for each ligand to act as a facial-coordinating tridentate ligand. For both TTMB and TTOB, the lowest energy conformation was that with all sulfur atoms exodentate. After minimization, the total energies of TTMB and TTOB for the all exodentate conformation were 49.4 and 70.3 kJ mol^{-1}, respectively. These conformations are essentially unchanged from the ones determined by X-ray analysis. The same result was also obtained when the X-ray structure positional parameters were used as input geometries for the molecular mechanics energy minimizations.

The corresponding minimization energies for the all-endodentate conformations were 74.1 and 82.8 kJ mol^{-1} for TTMB and TTOB, respectively. Analysis of the calculated geometry for the all endodentate conformations showed that, for TTOB, the S1···S2 and S2···S3 distances, containing the ethylene chains, were 3.31 Å and the S1···S3 distance spanning the *o*-xylyl fragment was 3.64 Å. For TTMB, the S1···S2 and S2···S3 distances were 3.53 Å and the S1···S3 distance across the *m*-xylyl fragment was much larger, 5.94 Å. As a comparison, similar calculations for 9S3 minimized with an all-endodentate geometry at a value of 53.1 kJ mol^{-1}. The conformation is essentially that found by X-ray crystallography[16] with S···S distances of 3.34 Å and S–C–C–S torsional angles of 53.5° compared to 3.451 (2) Å and 58.5° found from the crystal structure determination.

Complexation Studies. The organometallic fragment *fac*-Mo(CO)$_3$, generated from the labile complex -fac-Mo(CH$_3$CN)$_3$(CO)$_3$, was chosen as the complexation target because this offered a simple test for facial coordination at an octahedral metal center. Also, direct structural comparisons could be made to the compounds *fac*-Mo(CO)$_3$L where L = 1,4,7-trithiacyclononane (9S3),[18] 1,4,7-trithianonane (TTN),[32] and 1,4,7-trithiacyclodecane (10S3).[9]

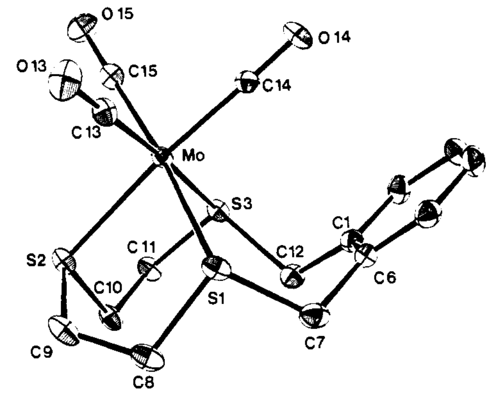

Figure 4. Perspective ORTEP drawing of *fac*-Mo(CO)$_3$(TTOB), showing the atom-numbering scheme. Thermal ellipsoids of 20% are shown.

The complex *fac*-Mo(CH$_3$CN)$_3$(CO)$_3$ was prepared in situ by the literature method and 1 equiv of the crown thioether ligand added as an acetonitrile solution. In the case of TTOB, a brownish yellow solid precipitated and was recrystallized from DMSO/diethyl ether to give the desired complex, *fac*-Mo(CO)$_3$(TTOB), as the DMSO solvate. The ^{1}H NMR spectrum for Mo(CO)$_3$(TTOB) shows the same general features as the free ligand except that the AA′BB′ pattern associated with the SCH$_2$CH$_2$S portion of the molecule has separated into two distinct multiplets and the benzylic protons show a pair of doublets due to the adoption of axial and equatorial positions in the seven-membered chelate ring.

For TTMB, the solution remained yellow in color upon addition of the ligand, and only starting materials were detected by ^{1}H NMR and infrared spectroscopy and eventually isolated.

X-ray Structure of *fac*-Mo(CO)$_3$(TTOB)·DMSO. The unit cell contains four molecules of *fac*-Mo(CO)$_3$(TTOB) and four disordered molecules of DMSO. A perspective view of *fac*-Mo(CO)$_3$(TTOB), indicating the atom-numbering scheme, is shown in Figure 4. Selected interatomic distances and angles are found in Table VII.

The Mo atom is in an octahedral environment with facial coordination of both the TTOB ligand and three carbonyl groups. The Mo–S distances are 2.546 (2) and 2.545 (2) Å for S1 and S3 and 2.531 (2) Å for the central sulfur atom, S2. The S–Mo–S angles for the two five-membered chelate rings are 81.3 (1) and 81.9 (1)° for S1–Mo–S2 and S2–Mo–S3, and the S1–Mo–S3 angle, involving the *o*-xylyl fragment, is 96.5 (1)°. The Mo–C bonds average 1.95 (1) Å and the C–Mo–C angles average 87 (2)° for the carbonyl groups. These are as expected for Mo–CO bonds and compare well to those found for similar structures.[9,18,32]

The S–C–C–S torsional angles are 58.7 (6) and 49.8 (6)°, the S1···S3 distance is 3.80 Å, and the dihedral angle between the plane defined by the aromatic ring and the plane defined by the three sulfur atoms is 148.5°.

Discussion

In the study of macrocyclic ligands and their metal complexes, it is often assumed that the conformation and molecular structure of the free ligand is relatively unimportant. However, it is becoming increasingly apparent that one must consider carefully the conformational preferences of certain ligands if one is to have insight into their complexation chemistry. The crown thioethers are a good example of this since the conformation of the free ligand seems to have a very large influence on the nature and stability of the complex formed. For example, the formation of bridging

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(32) Ashby, M. T.; Enemark, J. H.; Lichtenberger, D. L.; Ortega, R. B. *Inorg. Chem.* **1986**, *25*, 3154–3157.

complexes of limited stability employing exodentate sulfur donors is in marked contrast to the remarkable stability of complexes of 9S3 for which the sulfur atoms are preorganized in an endodentate arrangement prior to coordination.[1,2]

Since the conformational preferences of the free crown thioether ligands can profoundly influence their coordination chemistry, we have undertaken a careful study of the molecular mechanics and solid-state structures of TTMB and TTOB.

For TTMB, the X-ray structure and the structure calculated from molecular mechanics minimization indicate that there is an excellent match of the spatial requirements of the *m*-xylyl and the $-SCH_2CH_2SCH_2CH_2S-$ bracket fragments. The sulfur to sulfur distance (6.74 Å, MMX; 6.84 Å, X-ray), which could be described as the "bite" of the bracket, matches exactly the corresponding spacing between benzylic carbon atoms. The results are that neither of the fragments shows appreciable distortion (S–C–C–S of approximately 180°) as a result of their fusion to form the intact TTMB molecule and the three sulfur atoms are exodentate to the ring.

Both X-ray analysis and molecular mechanics calculations show that the basic conformation of TTOB is the same as for TTMB with the three sulfur atoms exodentate to the ring. However, the experimental (166.7 (4)/158.5 (4)°, X-ray) and calculated (174.2/154.4°, MMX) S–C–C–S torsional angles associated with the bracket portion and the smaller S1···S3 spacing (5.76 Å, MMX; 5.80 Å, X-ray) indicate that the $-SCH_2CH_2SCH_2CH_2S-$ bracket must be distorted significantly to adapt to the smaller spatial requirements of the *o*-xylyl fragment.

In order to determine whether TTMB and TTOB could adopt a ligand conformation suitable for facial coordination to a metal, molecular mechanics calculations were performed on the all endodentate conformations of these macrocycles. These results and those obtained similarly for 9S3 indicated that only TTOB could adopt an endodentate geometry that would be suitable for facial coordination. For TTOB, the S1···S2 and S2···S3 distances (3.31 Å) are very close to those obtained for 9S3 (3.34 Å) and the S1···S3 distance across the *o*-xylyl fragment is only slightly longer (3.64 Å). However for TTMB, the S1···S2 and S2···S3 distances are longer (3.53 Å) and the S1···S3 distance (5.94 Å) is clearly incompatible with the proposed geometry.

The predictive value of the molecular mechanics calculations was tested by attempting to coordinate TTOB and TTMB, as a tridentate ligand, to the organometallic fragment *fac*-$Mo(CO)_3$. Only the complex *fac*-$Mo(CO)_3$(TTOB) could be obtained. By comparison of the molecular mechanics calculated geometry for the all-endodentate conformation of TTOB with the conformation of TTOB found in the X-ray structure of $Mo(CO)_3$(TTOB)·DMSO, some conclusions as to the reliability and usefulness of these calculations can be attained. In the complex *fac*-$Mo(CO)_3$(TTOB), the ligand TTOB adopts the all-endodentate conformation and coordinates to the metal by employing all three S donor atoms. The S1···S2 and S2···S3 distances are 3.31 and 3.33 Å, and the S1···S3 distance is 3.80 Å. These are very close to those predicted by molecular mechanics for the all-endodentate conformation in the absence of the metal atom. At least in the simple case of TTOB and TTMB, it appears that molecular mechanics calculations may be useful in the design of crown thioether ligands.

A comparison of the structure of *fac*-$Mo(CO)_3$(TTOB) to those of *fac*-$Mo(CO)_3$(9S3),[18] *fac*-$Mo(CO)_3$(10S3),[9] and *fac*-$Mo(CO)_3$(TTN)[32] shows that TTOB binds in essentially the same geometry as the other crown thioether ligands. Table VIII shows a comparison of various structural parameters within the coordination sphere of these complexes. The major differences are due to the seven-membered chelate ring containing the *o*-xylyl ring. For example, the S1–Mo–S3 angle within the larger chelate is 96.5 (1)° as compared to 82.8 (2)° found for the five-membered chelate in $Mo(CO)_3$(9S3). Although some of these differences are significant, the stability of the complex *fac*-$Mo(CO)_3$(TTOB) seems to be quite comparable to that of *fac*-$Mo(CO)_3$(9S3) and *fac*-$Mo(CO)_3$(10S3). Further studies in our laboratories are under way to determine whether TTOB can function as a ligand for other transition metals. If this comparison to 9S3 can be extended to other metals and complex geometries, this may result in the observation of some unique reaction and redox chemistry.

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Supplementary Material Available: Listings of crystallographic data collection parameters (Table S-I), atomic positional parameters (Tables S-II, S-VI, and S-X), non-essential bond distances and angles (Tables S-III, S-VII, and S-XI), thermal parameters (Tables S-IV, S-VIII, and S-XII), and hydrogen atom parameters (Tables S-V, S-IX, and S-XIII) (9 pages); listings of observed and calculated structure factors (Tables S-XIV–S-XVI) (27 pages). Ordering information is given on any current masthead page.

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Silver(II) Tetraneopentoxyphthalocyanine and Its Redox Chemistry

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The synthesis and characterization of the title complex is described. This new silver(II) phthalocyanine is soluble in most organic solvents, rendering it suitable for extended study. The complex can be oxidized electrochemically to a silver(III) phthalocyanine that is also indefinitely stable. Further oxidation is possible to the silver(III) phthalocyanine cation radical, also showing substantial stability. Reduction to a silver(I) phthalocyanine leads to demetalation on the electrochemical time scale. In support of this electrochemical study, the electrochemistry of metal-free tetraneopentoxyphthalocyanine is also reported. Both silver(II) and metal-free tetraneopentoxyphthalocyanine are extensively aggregated in solution. The FTIR spectrum of the title complex is compared with the spectra of the corresponding cobalt(II), copper(II), and zinc species. The electronic spectra of the several silver species are reported. When diluted with metal-free tetraneopentoxyphthalocyanine, silver(II) tetraneopentoxyphthalocyanine yields a highly resolved electron spin resonance spectrum. Spin-Hamiltonian parameters are reported.

Introduction

The +2 and +3 oxidation states of silver can be stabilized by N_2-heterocyclic and tetraazamacrocyclic ligands and porphyrins,[1-6] but relatively little is known about these higher oxidation state silver species. While silver porphyrins have been studied in some

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