Table I. Emission Anisotropies (g_{em}) for the Complexes Studied

complex	transition	λ, nm	$10^2 g_{em}$
I-Eu$(ClO_4)_3$	$^7F_1 \leftarrow {}^5D_0$	591.7	−5.7
		594.4	2.6
	$^7F_2 \leftarrow {}^5D_0$	618.2	2.1
I-Eu$(ClO_4)_3$ + excess NO_3^-	$^7F_1 \leftarrow {}^5D_0$	587.5	3.0
		592.8	−22.3
		596.2	−23.7
	$^7F_2 \leftarrow {}^5D_0$	614.2	6.3
		619.2	7.1
I-Tb$(ClO_4)_3$	$^7F_5 \leftarrow {}^5D_4$	539.9	−2.2
		542.7	5.8
		545.7	−7.5
		552.3	3.3
I-Tb$(ClO_4)_3$ + excess NO_3^-	$^7F_5 \leftarrow {}^5D_4$	541.6	−5.7
		543.6	10.2
		548.5	−9.3
		552.5	15.9

trate–crown complexes. The perchlorate CPL is seen to be much weaker than the nitrate in both cases. This weakness of the CPL when only perchlorate anions are present can be accounted for by partial dissociation of the crown–lanthanide complex or by the existence in solution of multiple crown–lanthanide structures (or conformations). As was noted for the europium perchlorate–crown complex, the evidence suggests the existence of at least two species in TFE (vide supra). On the other hand, the nitrate complexes appear to be very robust, with well-defined stoichiometries. The CPL for the nitrate also is quite intense, showing very clearly the ligand field components for these transitions, especially for the $^7F_1 \leftarrow {}^5D_0$ transition of europium. Here, the maximum number of components possible (three) is seen, showing the complex to be nonaxially symmetric. A structure such as observed in the neodymium nitrate–18-crown-6 crystal,[13] with two opposing nitrates reducing the potential axial symmetry to a maximum of D_2 by their strong bidentate coordination to the europium, would be consistent with this result. The less structured emission in the case of perchlorate correlates with the weaker influence of this ion on the electronic structure of the lanthanide ion.

One further note should be added as to the source of the chirality induced in the f-electron structure of these complexes. Of the three types of chirality generally considered for metal complexes, *configurational* chirality, with its usual formulation in terms of the orientation of chelate rings, seems an inappropriate model for these 1:1 macrocyclic complexes, and the CPL associated with *vicinal* chirality is usually extremely weak, 1 order of magnitude or so below that seen for conformationally induced chirality.[14] In these complexes then, the chirality seen is best described as arising from a *conformational* twist of the crown ring as it seeks to accommodate its four chiral centers as well as the lanthanide and the other ligands in the metal ion's coordination sphere.

This study shows the usefulness of CPL and TL measurements in conjunction with NMR in characterizing subtle aspects of the solution behavior of crown–lanthanide systems that otherwise would be difficult to study. The TL spectra indicate a 2:1 interaction between the nitrate anions and the lanthanide cation, but it is the CPL spectra that clearly confirm that the NO_3^- has replaced the ClO_4^- and/or TFE in the first coordination sphere, leaving the (chiral) crown macrocycle still complexed. Other work in progress indicates that by varying the positions of substituents and chiral centers on the crown ring and comparing the CPL and TL results for different anions, and a variety of solvents, an increasingly systematic picture of the stochiometric and structural properties of these macrocyclic lanthanide complexes may be developed.

Acknowledgment. Support from the U.S. Army Research Office under Contract DAAG29-79-D-1001 is gratefully acknowledged.

Registry No. [I-Eu$(NO_3)_2$]NO_3, 94518-36-2; [I-Tb$(NO_3)_2$]NO_3, 94518-38-4; I-Eu$(ClO_4)_3$, 94518-42-0; I-Tb$(ClO_4)_3$, 94518-40-8.

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Cyclic Polythioether Complexes: Preparation and Crystal Structure of Tricarbonyl(1,4,7-trithiacyclononane)molybdenum(0)[1]

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In contrast to the conformation adopted by most of the free mesocyclic polythioethers, the sulfur atoms in 1,4,7-trithiacyclononane (TTCN) are endodentate.[2] The geometric conformation of these sulfur atoms and the mechanical flexibility of the molecule indicate that it should serve as a versatile tridentate ligand. Reports of $M(TTCN)_2$ (M = Co(II), Ni(II), Cu(II)) have appeared; however, these compounds do not allow one to completely investigate the distortion of the ring upon complexation.[3] Interest in transition-metal complexes of 1,4,7-triazacyclononane,[4] TTCN's nitrogen analogue, and the recent success in preparing a macrocyclic triphosphine using molybdenum tricarbonyl as a metal template[5] have prompted us to explore the coordination chemistry of TTCN. In an attempt to do so, we have prepared and structurally characterized the title compound, $(TTCN)Mo(CO)_3$. This is the first zerovalent metal complex of a cyclic polythioether for which the crystal structure has been determined.[6] The facial configuration of the carbonyls provides a unique point of reference when describing the distortion of the ligand upon coordination.

Experimental Section

Preparation. Under argon, $Mo(CO)_6$ (157.9 mg, 0.60 mmol) was stirred in refluxing acetonitrile (ca. 1 mL) for 2 h to give $Mo(CO)_3(NCCH_3)_3$. The pale yellow solution was cooled to room temperatures, and 1,4,7-trithiacyclononane[3] (81.7 mg, 0.45 mmol dissolved in ca. 0.5 mL of acetonitrile) was added. The reaction mixture turned dark brown, and within minutes the pale yellow $(TTCN)Mo(CO)_3$ precipitated. Filtration under argon yielded 52.8 mg (32% yield based on TTCN) of the product: ν_{CO}(KBr) 1915, 1783 cm^{-1}; ν_{CO}(nitromethane) 1935, 1825 cm^{-1}; $\delta(^{95}Mo)$ −1350 ppm relative to 2 M Na_2MoO_4, pH 11, line width ca. 30 Hz. Anal. Calcd for $C_9H_{12}O_3S_3Mo$: C, 30.01; H, 3.33; S, 26.70. Found: C, 30.25; H, 3.29; S, 26.44; N, 0.59.[7] The CO stretching frequencies for $(TTCN)Mo(CO)_3$ are similar to those of (3,6,9-trithiaundecane)$Mo(CO)_3$[8] and other $Mo(CO)_3$ complexes with S-donor ligands.[9] $(TTCN)Mo(CO)_3$ shows no sign of decomposition when exposed to the air for several days; however, it decomposes upon heating or long-term storage to yield uncomplexed TTCN.

X-ray Crystallography. Ethyl ether was vapor diffused into a nitromethane solution of $(TTCN)Mo(CO)_3$ at 0 °C to give a mixture of slender yellow hexagonal-shaped needles and thin yellow plates in an approximate 10:1 ratio. An attempt to solve the structure of one of the hexagonal needles was unsuccessful.

Table I contains the crystallographic data for one of the square plates. The crystal was mounted on a Syntex $P2_1$ autodiffractometer, with the longest dimension approximately parallel to the ϕ axis. Automatic centering, indexing, and least-squares routines[10] gave the cell dimensions listed in Table I. The axial photos showed the lattice to be monoclinic, and an unique quadrant was collected by using the conditions listed in Table I.[11] Examination of the collected data set revealed the systematic

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(1) This work was presented at the 183rd National Meeting of the American Chemical Society, March 28–April 2, 1982, Las Vegas, NV.

(2) Glass, R. S.; Wilson, G. S.; Setzer, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 5068.

(3) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266.

(4) Chaudhuri, P.; Wieghardt, K.; Tsai, Y; Krüger, C. *Inorg. Chem.* **1984**, *23*, 427.

(5) Diel, B. N.; Haltiwanger, R. C.; Norman, A. D. *J. Am. Chem. Soc.* **1982**, *104*, 4700.

(6) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365.

(7) Chemical analysis performed by MICANAL, Tucson, AZ 85717.

(8) Mannerskantz, H. C. E.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4454.

(9) Cotton, F. A.; Zingales, F. *Inorg. Chem.* **1962**, *1*, 145.

(10) Programs used for centering, autoindexing, least-squares refinement of the cell parameters, and data collection were written by Syntex Analytical Instruments (now Nicolet XRD Corp.), Cupertino, CA.

(11) At the time that this data set was collected, means were not available to apply an absorption correction.

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Table I. Crystallographic Data for (TTCN)Mo(CO)$_3$ at 25 °C[a]

(A) Cell Parameters	
formula	$C_9H_{12}O_3S_3Mo$
fw	360.33
cryst color	pale yellow
cryst shape	square plate
cryst size, mm	0.15 × 0.15 × 0.08
cryst orientation	[101]
cryst syst	monoclinic
space group	$P2_1/n$
a,[b] Å	9.17 (2)
b, Å	11.11 (2)
c, Å	12.57 (2)
V, Å^3	1279.4
β, deg	92.35 (15)
Z	4
d_{calcd}, g cm^{-3}	1.88
μ, cm^{-1}	12.06
(B) Measurement and Treatment of Intensity Data	
radiation	Mo Kα (λ = 0.710 73 Å), monochromatized by a graphite crystal
data collcn method	$\theta/2\theta$ scan
scan speed, deg min^{-1}	variable (2.0-29.3) as a function of reflcn intens
scan range (2θ), deg	Mo Kα_1 −1.0 to Mo Kα_2 +1.0
ratio of total bkgd time to peak scan time	0.5
std reflcns	(2,0,0), (0,2,0), (0,0,2) recollcd every 97 reflcns
max dev of std, %	<2
max 2θ, deg	50
no. of unique data	2502
no. of data used	1298, $I > 2\sigma(I)$
final residuals R	0.067
R_w	0.073
final GOF	2.02

[a] The estimated standard deviation of the least significant figure is given in parentheses in this table and in the tables that follow. [b] The cell dimensions were obtained from a least-squares refinement of setting angles of 15 reflections in the 2θ range 5.67-15.50°.

Table II. Atomic Coordinates for the Non-Hydrogen Atoms in (TTCN)Mo(CO)$_3$

atom	x	y	z
Mo	0.41544 (16)	0.24447 (18)	0.11725 (11)
S1	0.3533 (5)	0.4179 (4)	−0.0045 (4)
S2	0.4704 (5)	0.1410 (4)	−0.0535 (3)
S3	0.1555 (5)	0.1810 (4)	0.0660 (3)
O1	0.3535 (16)	0.3913 (14)	0.3191 (9)
O2	0.7480 (14)	0.3027 (12)	0.1452 (11)
O3	0.4515 (15)	0.0279 (12)	0.2726 (9)
C1	0.3726 (19)	0.3375 (17)	0.2424 (15)
C2	0.6251 (19)	0.2822 (15)	0.1348 (13)
C3	0.4399 (17)	0.1079 (15)	0.2116 (13)
C4	0.3965 (20)	0.3700 (17)	−0.1370 (13)
C5	0.5042 (17)	0.2674 (18)	−0.1407 (13)
C6	0.2987 (18)	0.0807 (16)	−0.1047 (12)
C7	0.1858 (21)	0.0549 (17)	−0.0248 (14)
C8	0.0843 (18)	0.2960 (16)	−0.0241 (13)
C9	0.1543 (21)	0.4178 (18)	−0.0089 (16)

Table III. Selected Bond Distances (Å)

Mo-S1	2.512 (6)	S1-C4	1.84 (2)	O1-C1	1.15 (2)
Mo-S2	2.504 (6)	S1-C9	1.82 (2)	O2-C2	1.15 (2)
Mo-S3	2.543 (7)	S2-C5	1.82 (2)	O3-C3	1.18 (2)
Mo-C1	1.94 (2)	S2-C6	1.81 (2)	C4-C5	1.49 (3)
Mo-C2	1.97 (2)	S3-C7	1.84 (2)	C6-C7	1.49 (3)
Mo-C3	1.93 (2)	S3-C8	1.82 (2)	C8-C9	1.51 (3)

Table IV. Selected Bond Angles (deg)

S1-Mo-S2	83.0 (4)	C1-Mo-C2	91.4 (9)	C4-S1-C9	103 (1)
S1-Mo-S3	82.6 (4)	C1-Mo-C3	86.8 (9)	C5-S2-C6	103.9 (9)
S2-Mo-S3	82.8 (4)	C2-Mo-C3	90.5 (9)	C7-S3-C8	102.2 (9)
S1-Mo-C1	92.1 (8)	Mo-S1-C4	106.4 (9)	S1-C4-C5	115 (1)
S1-Mo-C2	95.8 (8)	Mo-S1-C9	102.7 (9)	S1-C9-C8	115 (1)
S1-Mo-C3	173.6 (8)	Mo-S2-C5	101.9 (8)	S2-C5-C4	116 (1)
S2-Mo-C1	175.0 (8)	Mo-S2-C6	105.8 (8)	S2-C6-C7	117 (1)
S2-Mo-C2	88.0 (8)	Mo-S3-C7	101.7 (8)	S3-C7-C6	114 (1)
S2-Mo-C3	98.2 (7)	Mo-S3-C8	105.9 (7)	S3-C8-C9	114 (1)
S3-Mo-C1	97.7 (8)	Mo-C1-O1	177 (2)		
S3-Mo-C2	170.8 (8)	Mo-C2-O2	179 (2)		
S3-Mo-C3	91.3 (7)	Mo-C3-O3	177 (1)		

Table V. Selected Torsional Angles[a] (deg)

S1-C4-C5-S2	46.7	C9-S1-C4-C5	−129.1
S2-C6-C7-S3	50.0	C5-S2-C6-C7	−132.4
S3-C8-C9-S1	50.0	C7-S3-C8-C9	−132.4

[a] Torsion angles for A-B-C-D are defined as positive for clockwise rotation of C-D toward A-B while looking down the B-C bond.

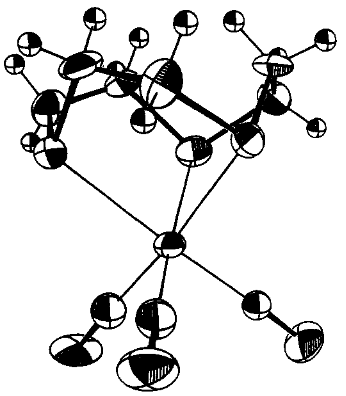

Figure 1. ORTEP drawing of the (TTCN)Mo(CO)$_3$ molecule. Atoms are represented by thermal vibration ellipsoids at the 50% level. Hydrogen atoms have been assigned an arbitrary thermal parameter.

absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$, which unambiguously determined the space group to be $P2_1/n$.

The data were reduced to F_o^2 and $\sigma(F_o^2)$ by procedures previously described.[12] Lorentz-polarization corrections were made on the assumption of 50% mosaic and 50% perfection of the monochromator crystal. Neutral atomic scattering factors of Cromer and Waber[13a] were used for all the atoms except hydrogens, for which the values of Stewart, Davidson, and Simpson[14] were used. The effect of the real and imaginary components of anomalous dispersion for the molybdenum and sulfur atoms were included in the structure factor calculations by using the tabulated values of Cromer.[13b]

The structure was solved by direct methods.[15] From 220 reflections with the larget values of $|E|$, a solution based on the highest figure of merit (2.00) and the lowest residual index (18.7%) clearly revealed 14 of the 16 non-hydrogen atoms. The remaining two atoms were located in the first difference electron density map. The non-hydrogen atoms were refined isotropic in three cycles with $R_1 = 0.079$ and $R_2 = 0.095$ and anisotropic in three cycles with $R_1 = 0.069$ and $R_2 = 0.078$.[16] Two of the carbonyl carbons were found to have thermal parameters that were nonpositive definite. The thermal parameters for these two atoms could only be described isotropically, and therefore, all three carbonyl carbons were refined isotropically for the remainder of the calculations. After convergence of the carbonyl carbons isotropically, a difference electron

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(12) Yamanouchi, K.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 1981.

(13) (a) Cromer, D. T.; Waber, J. T. In "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2a, p 149. (b) Cromer, D. T. *Ibid.* Table 2.3.1, p 72.

(14) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, 42, 3175.

(15) All computations were performed on the CDC Cyber 175 computer at the University of Arizona Computer Center. The major programs used were MULTAN (direct method program by Germain, Main, and Woolfson), FORDAP (Fourier summation program by Zalkin), and NUCLS (structure factor calculations and full-matrix least-squares refinement, a modification by Ibers of ORFLS by Busing, Martin, and Levy).

(16) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, and GOF $= [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, where n is the number of reflections used in the refinement, m is the number of variable parameters, and $w = 4F_o^2/[\sigma^2(F_o^2)+(pF_o^2)^2]$ where p, the factor to prevent overweighting of strong reflections, was set equal to 0.03.

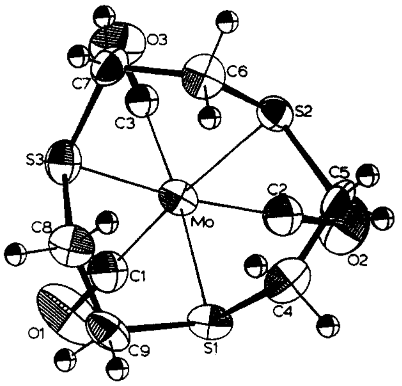


Figure 2. ORTEP view of (TTCN)Mo(CO)$_3$ down the molecule's noncrystallographic threefold axis. Atoms are represented by thermal vibration ellipsoids at the 50% level, and the labeling scheme is defined. Hydrogen atoms have been assigned an arbitrary thermal parameter.

Table VI. Comparison of Selected Structural Features of Uncomplexed TTCN to Those in (TTCN)Mo(CO)$_3$

	uncomplexed	complexed
	Distances (Å)	
S-C	1.822 (5)	1.82 (1)
C-C′	1.510 (6)	1.50 (1)
S···S′	3.451 (2)	3.334 (8)
	Angles (deg)	
C-S-C′	102.8 (3)	103.0 (9)
S-C-C′	117.0 (4)	115 (2)
C-C′-S′	113.0 (4)	115 (1)
	Torsional Angles (deg)	
S-C-C′-S′	58.5	48 (2)
C′-S-C-C′	131.1	−131 (2)

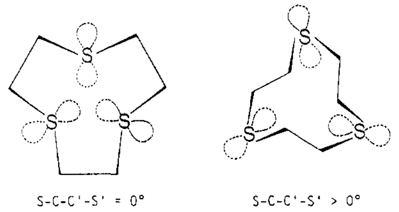
density map failed to clearly reveal the hydrogen atoms. All 12 hydrogen atoms were included as fixed contributors in idealized positions, assuming tetrahedral geometry about the carbon and a carbon–hydrogen bond length of 0.95 Å.[17] Each hydrogen atom was assigned an isotropic thermal parameter 1 Å^2 greater than the value for its bonded carbon. The final cycles converged with $R_1 = 0.067$, $R_2 = 0.073$, and GOF = 2.02. The largest residuals in the final difference electron density map were 1.27 and 1.10 e Å^{-3}, which were both near the molybdenum atom.

Results and Discussion

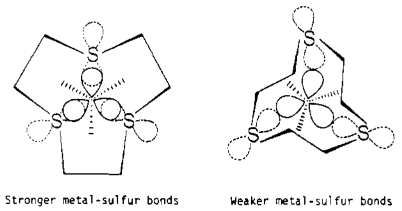
Tables II–V give the final positional parameters for the nonhydrogen atoms, selected interatomic distances, selected interatomic angles, and selected torsion angles for (TTCN)Mo(CO)$_3$. Figure 1 is a side view of the molecule while Figure 2 looks down the noncrystallographic threefold axis.

The angles between the carbonyl groups are essentially 90°, and the Mo–C–O fragments are essentially linear, reflecting a pseudooctahedral electronic symmetry at the metal center. The metal–carbon bond distances are approximately 0.1 Å shorter than the reported bond distance in Mo(CO)$_6$ (2.06 (2) Å)[18], and the CO stretching frequencies are reduced by approximately 200 cm^{-1}, suggesting that TTCN is an ineffective π acid in comparison to carbonyls.

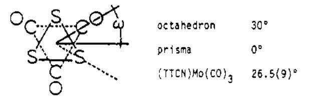
The features of most interest in this structure are those that describe the distortion distortion of the cyclic polythioether upon coordination to the metal. Table VI compares the crystal structure results for uncomplexed TTCN[2] with those obtained for (TTCN)Mo(CO)$_3$. In uncomplexed TTCN the three sulfur atoms are endodentate.[2] The molecule compensates for the repulsive interaction between the sulfurs by increasing the S–C–C′–S′ torsion angle. An increase in this angle effects an increase in the inter-sulfur distance and also rotates the interior lone pair on the sulfur away from the molecules rotational axis:



The S–C–C′–S′ torsion angle and the rotation of the ring on the metal tricarbonyl fragment is related to the metal–sulfur orbital overlap. The S–C–C′–S′ torsion angle for uncomplexed TTCN is 58°. The torsion angle for (TTCN)Mo(CO)$_3$ is 48°. The reduction in this torsion angle is the result of stabilization provided by formation of the metal–sulfur bonds, which partly overcomes the repulsion between the sulfur lone pair. Stronger shorter metal–sulfur bonds would result in a smaller torsion angle:



One may view the small rotational or trigonal distortion in (TTCN)Mo(CO)$_3$ by looking down the molecule's noncrystallographic threefold axis (Figure 2). The mean angular difference between a given sulfur atom, the metal atom, and the carbonyl carbon on either side of the sulfur is 6.8°.[19] This type of distortion has been described in many different ways,[20–24] one of which is defined in the following diagram:[20]



The twist angle as so defined is 30° for octahedral geometry and 26.5 (9)° for (TTCN)Mo(CO)$_3$.[25]

Acknowledgment. We thank the Department of Energy, Contract DE-AC0280ER10746, the University of Arizona Computer Center for a generous allocation of computing time, and Prof. Richard S. Glass for providing us with a sample of TTCN.

Registry No. Mo(CO)$_3$(NCCH$_3$)$_3$, 15038-48-9; (TTCN)Mo(CO)$_3$, 92314-34-6.

Supplementary Material Available: Table VII showing the anisotropic thermal parameters of the hydrogen atoms, Table VIII showing the positional and thermal parameters of the hydrogen atoms, and Table IX listing the calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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(17) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(18) Beach, N. A.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5713.

(19) The mean angular difference between a given sulfur atom, the metal atom, and the carbonyl oxygen on either side of the sulfur is 7.5°.

(20) Wieghardt, K.; Bossek, U.; Chandhuri, P.; Herrmann, W.; Menke, B. C.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 4308.

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(24) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

(25) This calculation was made with the carbonyl oxygen as a reference. If the carbonyl carbon is used, the angle is 26.8 (8)°.