examples have been described recently in which the AuPPh$_3$ ligand occupies the role of a hydride in a related compound.[10] As expected, the Re-Au-P group in **2** is nearly linear (Re-Au-P = 175.3°). The Re-Au bond length is 2.615 Å. Other metrical details of the structure (Table III) are unexceptional. The (*p*-methoxyphenyl)diazenide ligand adopts the singly bent structure expected to be present from the ν(NN) value of ca. 1612 cm^{-1} and has reasonable values for Re-N (1.78 Å), N-N (1.27 Å), Re-N-N (171°), and N-N-C(aryl) (119°).

Acknowledgment. This work was supported by NSERC (Canada) through operating grants (to F.W.B.E. and D.S.).

Registry No. **1** (Ar = C$_6$H$_4$-*p*-OMe), 94518-43-1; **2** (Ar = C$_6$H$_4$-*p*-OMe), 94518-44-2; Ph$_3$PAuCl, 14243-64-2.

Supplementary Material Available: Anisotropic thermal parameters (Table S1), calculated positional and thermal parameters for hydrogen atoms (Table S2), additional bond parameters (Table S3), and the observed and calculated structure amplitudes (Table S4) (21 pages). Ordering information is given on any current masthead page.

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Notes

Contribution from the P. M. Gross Chemical Laboratory,
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Crown Ether-Lanthanide Complexes Studied by CPL and TL. 1. Solution Stoichiometry of Europium and Terbium Nitrate Complexes of (2*R*,3*R*,11*R*,12*R*)-2,3,11,12-Tetramethyl-18-crown-6

D. H. Metcalf, R. G. Ghirardelli, and R. A. Palmer*

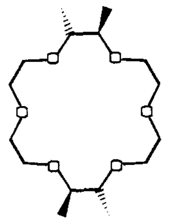
Received May 18, 1984

Although numerous papers describing the syntheses and solid-state structures of crown ether complexes of lanthanide salts have appeared recently,[1] there are few reports of solution studies. Izatt and co-workers determined formation constants for 18-crown-6 complexes of lanthanide chlorides in methanol by calorimetry,[2] Bünzli and Wessner used ^{1}H NMR to find formation constants of lanthanide nitrate-15-crown-5 and -18-crown-6 complexes in acetonitrile,[3] and more recently, Massaux and co-workers described a competitive potentiometric technique for determining the formation constants of lanthanide complexes of several crowns and crown derivatives in propylene carbonate.[4] Other papers have reported the limited success of the use of the ^{1}H NMR shifting properties of paramagnetic lanthanides to determine the solution structure of crown complexes.[5,6] As part of an extensive study of the use of circularly polarized luminescence (CPL) and total luminescence (TL) in probing crown ether-lanthanide interactions in nonaqueous solvents, we describe here the results of an anion-exchange experiment designed to elucidate the solution stoichiometry of a chiral crown ether-lanthanide nitrate complex in trifluoroethanol (TFE).

The CPL experiment measures the differential emission of left and right circularly polarized light by a chiral luminophore when it is excited with unpolarized light.[7] CPL is sensitive to solution structure when a (achiral) luminophore gains chirality through association with a chiral ligand. For lanthanides, CPL is much more easily measured than CD because of the inherent sensitivity of emission measurements and the weakness of f-f transitions in absorption. Although all lanthanides are capable of exhibiting CPL in chiral crystals, only europium(III) and terbium(III) exhibit significant luminescence in solution, and thus solution CPL studies of lanthanides are normally limited to these ions.[8] The more useful CPL-active transitions are the $^7F_2$, $^7F_1 \leftarrow {}^5D_0$ transitions of europium(III) at ca. 618 and 595 nm, respectively, and the $^7F_5 \leftarrow {}^5D_4$ transition of terbium(III) at ca. 545 nm. CPL studies of europium(III) and terbium(III) complexes of various chiral ligands have appeared in the recent literature.[9]

In the case of europium(III) the total luminescence also can be very useful for solution studies. First, since the $^7F_0 \leftarrow {}^5D_0$ transition, at ca. 578 nm, cannot exhibit more than a single line regardless of ligand field, any apparent splitting of this transition is clear evidence of the presence of more than one europium(III) species. Second, the TL of the $^7F_1 \leftarrow {}^5D_0$ transition is predominantly magnetic dipole allowed, and so its intensity is relatively unaffected by the europium environment. However, the crystal field splitting of this transition does give limited information on the symmetry about the lanthanide. In nonaxial ligand fields, i.e., those with lower than threefold axes, three components are expected for this transition. Finally, the $^7F_2 \leftarrow {}^5D_0$ transition is *hypersensitive*, and its intensity can be related to the polarizability of the attached ligands.[10,11] Unfortunately, the TL bands of terbium(III) are more complex and do not lend themselves to such fruitful interpretation.

Our experiments consisted of measuring the CPL and TL spectra of 0.06 M TFE solutions of (2*R*,3*R*,11*R*,12*R*)-2,3,11,12-tetramethyl-18-crown-6 (I) and either europium(III) or terbium(III) perchlorate in a 1:1 crown ether:lanthanide ratio, during the course of a titration with 0.55 M tetraethylammonium nitrate. The details of the synthesis of the crown ether as well as the description of the CPL instrument appear elsewhere.[12] The compounds used in these experiments were dried by using standard techniques, and care was taken to exclude water during the course of the titrations.



I

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(12) Metcalf, D. H.; Palmer, R. A.; Ghirardelli, R. G., unpublished work.

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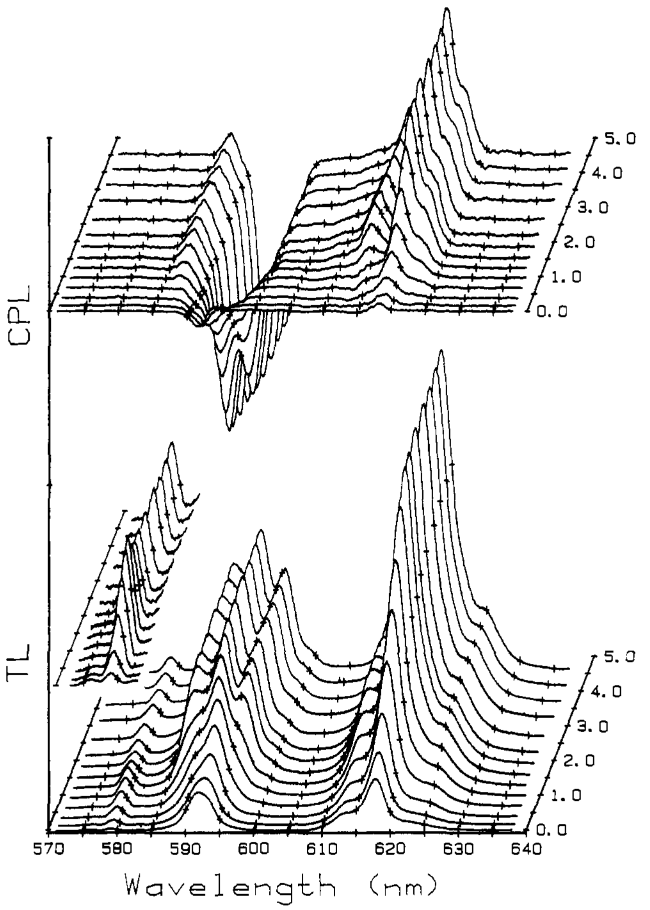

Figure 1. CPL (top) and TL (bottom) spectra plotted vs. equivalents of nitrate for the titration of I–Eu$(ClO_4)_3$ with tetraethylammonium nitrate in TFE. The CPL scale is 15% of the TL scale. The inset in the TL spectrum is an expansion (×5) of the $^7F_0 \leftarrow {}^5D_0$ transition region.

Figures 1 and 2 show the CPL and TL spectra plotted vs. equivalents of nitrate added. These spectra have been scaled so as to correct for dilution effects. As can be seen, changes in both the CPL and TL spectra occur in the europium and terbium solutions until 2 equiv of nitrate are added, at which point no further changes take place. The spectra obtained with an excess of nitrate added are exactly superimposable on spectra for 1:1 solutions of crown–europium nitrate or crown–terbium nitrate in TFE. The implication is clearly that the CPL-active species in solution in both cases has the formulation $[I\text{–}Ln(NO_3)_2]^+$ and that this species is stable with respect to further nitrate addition. The third nitrate is either completely dissociated from the charged crown–lanthanide unit or involved in an outer-sphere interaction with it.

Support for this interpretation has been obtained from the ^{14}N NMR spectra of the europium complex, which show two resonances assignable to nitrates, one broad peak at +91 ppm (relative to a neat CH_3NO_2 external standard) for the Eu-bound nitrates and one narrow resonance at −66 ppm typical of free nitrate. Unfortunately, because of the difference in relaxation times, integration of these peaks gives no useful information as to the amount of nitrate in each environment. The results, however, are clearly consistent with the CPL titration data. The [crown ether–$Ln(NO_3)_2]^+$ unit has been seen before in the crystal structure of the 4:3 "complex" of unsubstituted 18-crown-6 with neodymium nitrate,[13] which involves three $[18\text{-crown-6–}Nd(NO_3)_2]^+$ units and one $[Nd(NO_3)_6]^{3-}$ species. In each of the crown–lanthanide units in this structure a bidentate nitrate is on either side of the crown–Nd plane.

Other information is obtainable from the changes in the TL spectra of the europium complex during the course of the titration.

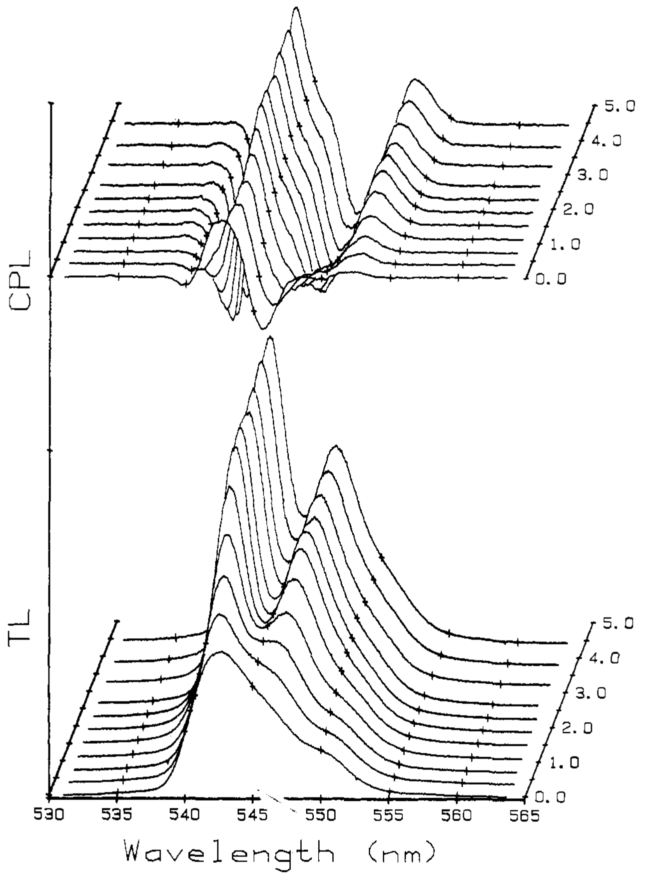

Figure 2. CPL (top) and TL (bottom) spectra plotted vs. equivalents of nitrate for the titration of I–Tb$(ClO_4)_3$ with tetraethylammonium nitrate in TFE. The CPL scale is 15% of the TL scale.

First of all, the $^7F_0 \leftarrow {}^5D_0$ transition (see inset of Figure 1), which is split in the initial (perchlorate) solution, coalesces into a single peak and increases in intensity until 1 equiv of nitrate is added. Its intensity then *decreases* until 2 equiv of nitrate have been added, at which point no further changes take place. This shows the stepwise formation first of a mono(nitrato)- and then a bis(nitrato)(crown)europium complex. The mono(nitrato) complex is further from centrosymmetry than the bis(nitrato) species, and so the intensity of the transition, which is predicted to be greater in noncentrosymmetric systems, is larger than in the bis(nitrato) complex. Also, its initial bifurcation in the perchlorate shows the existence of at least two europium species. The bis(nitrato) complex appears to be a single species. Second, increases in intensity are apparent in the $^7F_1$, $^7F_2 \leftarrow {}^5D_0$ transitions with nitrate addition. As noted above, the intensity of the magnetic dipole allowed $^7F_1 \leftarrow {}^5D_0$ transition should be insensitive to changes in the lanthanide ligand field. Its small increase in strength may be due to decreased quenching of the luminescence as nitrate anions exclude solvent molecules and/or perchlorate anions from the primary coordination sphere of the lanthanide. However, such an explanation cannot account for the large intensity increase of the $^7F_2 \leftarrow {}^5D_0$ transition. In the perchlorate, this transition is about as intense as the $^7F_1 \leftarrow {}^5D_0$ transition, but it gains strength with nitrate addition. This can be explained by its *hypersensitive* nature. For such $\Delta J = \pm 2$ transitions, dramatic dependence of both absorption and emission intensity on the polarizability of the ligands is usually observed.[10,11] Thus, as the more polarizable nitrate replaces perchlorate and/or TFE in the first coordination sphere of the europium ion, there is a profound increase in emission intensity.

The strength of the CPL seen for these complexes during the course of the titration is interpretable in terms of the degree of chirality about the lanthanide cation, which is related to the strength and the geometry of the crown–lanthanide association. Table I gives the emission anisotropies $g_{em} = 2\Delta I/I$ for the major transitions of the europium and terbium perchlorate and ni-

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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}; δ(^{95}Mo) −1350 ppm relative to 2 M Na$_2$MoO$_4$, pH 11, line width ca. 30 Hz. Anal. Calcd for C$_9$H$_{12}$O$_3$S$_3$Mo: 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.

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(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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