of the data available at present.

These points stated, however, we must admit that the argument is not (yet) fully definitive. The Hammett LFER correlation is, as commented earlier, equivalent to the $E°$ approach[47,49] if only a single reducible center (e.g., a pyridinium ion alone) is present. Its potential value lies in its prospect for addressing suitably constructed cases with two potential acceptor sites, such as the metal pyridine complexes, where a single-site reduction potential will, in general, be unavailable. Since reactions of this type are of some general interest and since the method appears to hold considerable promise for making the indicated assignments, we present it at this stage of its development. Other investigations to establish the limits of its validity are currently in progress.

The question we are addressing as regards the mechanism(s) of reduction of the $(H_2O)_5Cr(py)^{3+}$ ions is one that has been considered recently in similar circumstances.[10,58–60] In the cases cited, there was quite credible evidence that certain systems could, indeed, proceed by either mechanism, resonance-transfer or the "chemical" mechanism (i.e., ligand reduction).[61–64] Of course, the latter requires a combination of a donor and a ligand acceptor that together provide a sufficient driving force. In that context, metal pyridine complexes are among the oxidizing substrates that have proved particularly useful in efforts to arrive at general conclusions concerning the controlling factors. The Hammett correlation analysis promises to provide a new tool for assigning mechanisms reliable in such instances.

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Crown Ether–Lanthanide Complexes Studied by CPL and TL. 2. Solution Species in (2R,3R,11R,12R)-2,3,11,12-Tetramethyl-18-crown-6–Europium Nitrate and Perchlorate Systems in MeCN, TFE, and HFiP

David H. Metcalf, Rodney C. Carter, Robert G. Ghirardelli, and Richard Alan Palmer*

The solution behavior of complexes of (2R,3R,11R,12R)-2,3,11,12-tetramethyl-1,4,7,10,13,16-hexaoxacyclooctadecane ((*all-R*)-2,3,11,12-tetramethyl-18-crown-6, I) with europium(III) nitrate and perchlorate in the solvents acetonitrile (MeCN), trifluoroethanol (TFE), and hexafluoroisopropyl alcohol (HFiP) has been investigated by using the techniques of circularly polarized luminescence (CPL) and total luminescence (TL) spectroscopy, as well as conductivity measurements. The nitrate–crown complex is determined to be $[I–Eu(NO_3)_2]^+$, with the europium ten-coordinate, to the hexadentate 18-crown-6 ligand and to the two opposing bidentate nitrate anions. The perchlorate complex, while not as structurally robust as the nitrate, appears to have a similar structure, but with monodentate perchlorate anions. Ligand field splittings of the emission transitions are interpreted in terms of D_2 effective electronic symmetry in the nitrate complex and effective axial symmetry in the perchlorate. Observed changes in the CPL and TL spectra during titrations of $Eu(NO_3)_3$ with I in TFE and MeCN indicate the presence of poly(nitrato) anionic species from the nitrate generated by the formation of the crown complex and the excess $Eu(NO_3)_3$ present in solution. In MeCN, the formation of the stable $[Eu(NO_3)_5]^{2-}$ species limits the formation of additional crown complex, whereas in TFE, the crown complexation goes to completion. In MeCN, the difference in the intensities of the *hypersensitive* $^7F_0 \rightarrow {}^5D_2$ transition used for excitation results in preferential excitation of the pentakis(nitrato) species relative to the crown complex. The data indicate that europium exchange between these two species is slow compared to the lifetime of the europium emission.

Introduction

We have recently been interested in studying the solution interactions of chiral crown ether hosts with cations, through the use of chiroptical techniques.[1] Chiroptical spectroscopy can be quite sensitive to solution complex structure when a normally achiral chromophore gains chirality through association with a chiral ligand. In this study, the solution properties of complexes

of the title tetramethyl-18-crown-6 ether (I) with europium nitrate
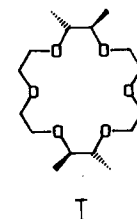
I

and perchlorate have been investigated in several solvents by using circularly polarized luminescence (CPL), the differential emission of left and right circularly polarized light. Simultaneously, total luminescence (TL) spectroscopy has been used to probe *all*

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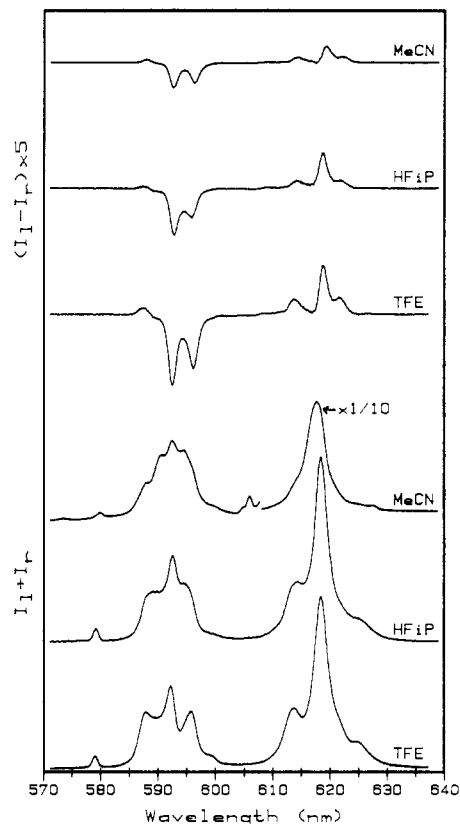
Figure 1. CPL (top) and TL (bottom) spectra for solutions 0.03 M in both I and $Eu(NO_3)_3$ in MeCN, TFE, and HFiP (excitation wavelength 465.8 nm; emission spectral bandwidth 0.8 nm). See text for an explanation of the scaling method for these spectra.

Figure 2. CPL (top) and TL (bottom) spectra for solutions 0.03 M in both I and $Eu(ClO_4)_3$ in MeCN, TFE, and HFiP (excitation wavelength 465.8 nm; emission spectral bandwidth 0.8 nm). See text for an explanation of the scaling method for these spectra.

fluorescing species in solution, and conductivity measurements have been used to probe the ionic nature of these systems. We have previously reported the results of titrations of europium and terbium perchlorate complexes of this crown with nitrate anion in trifluoroethanol (TFE);[2] herein, we extend the investigation to include the solvents aceonitrile (MeCN) and hexafluoroisopropyl alcohol (HFiP) and to characterize achiral as well as chiral species in these solutions.

Experimental Section

Reagents. The synthesis of the crown ether I has been described elsewhere.[1c] The europium(III) salts used were prepared by dissolution of Eu_2O_3 in nitric or perchloric acid and subsequent dehydration of the salts in an Abderhalden drying apparatus (0.01 torr, 25 °C). Purity of the salts was checked by complexometric titration with EDTA (xylenol orange indicator, pH 5 acetate buffer). Acetonitrile (Eastman) was refluxed over CaH_2 for several days and then distilled under N_2 and stored over 4-Å molecular sieves. Reagent grade trifluoroethanol and hexafluoroisopropyl alcohol (Aldrich Gold Label) wee stored over 4-Å molecular sieves and used without further purification. For none of the solvents used was the water content detectable by ^1H NMR. Karl Fischer analysis of the acetonitrile showed water content of <10 ppm.

Safety Note. Lanthanide perchlorates in the presence of organic material, particularly under anhydrous conditions, should be considered potentially *very* hazardous. As reported recently,[3] the vacuum drying of $Nd(ClO_4)_3\cdot4CH_3CN$ at 80 °C may produce $Nd(ClO_4)_3\cdot2CH_3CN$, which detonates violently on slight shock. When a noncoordinating ligand is required, other anions such as triflate or BF_4^- should be used if at all possible. If ClO_4^- must be used, only very small quantities (a few milligrams) should ever be isolated as a solid, and these should be handled only with explosion protection. In the study reported here $Eu(ClO_4)_3$ was kept vigorously free of organic material except when in solution (20–30 mg). Specific effort was made to avoid isolating or producing solid complexes that might have contained ClO_4^-. Only because of the need
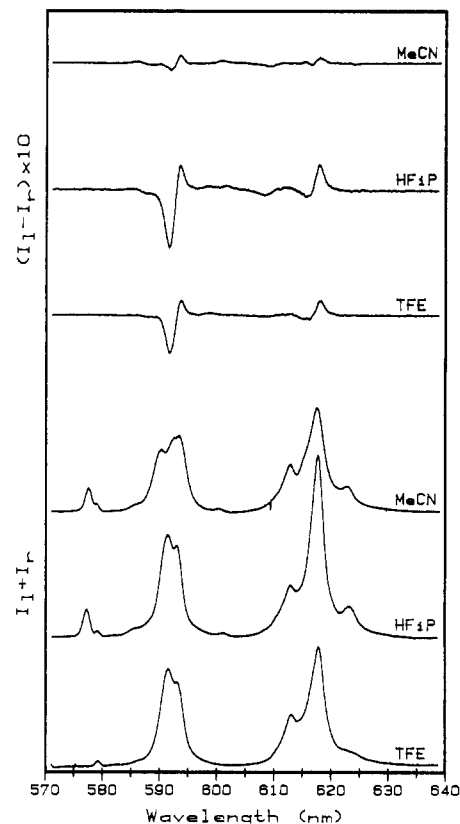
for a high-symmetry, non-fluoride-containing, as well as weakly coordinating, anion was ClO_4^- used for this particular work.

Spectroscopic Samples. Samples for spectroscopic measurement were prepared by addition of an appropriate amount of a stock solution of the crown to a weighed portion of the europium nitrate or perchlorate salt in a fluorescence cuvette. All sample solutions were approximately 0.03 M in both crown and lanthanide. All additions were made in a dry-nitrogen-filled glovebox. Samples for the titration experiments were prepared in the same way and titrated with a solution of the crown in the appropriate solvent by using a Gilmont precision buret (accuraty ±0.0001 mL). The fluorescence cell used for the titration experiments was specially constructed, with two platinum wires approximately 1 mm apart sealed across the cell (above the optical path) to allow for simultaneous measurement of the conductivity. This cell was standarized using a 1.34 × 10^{-4} m aqueous KCl solution at 25 °C. The value of the cell constant was 0.611 cm^{-1}. A Beckman Model RC-18A conductivity bridge was used for the conductance measurements, with the sample maintained at a constant temperature.

Instrumentation. The design of our CPL/TL spectrophotometer generally follows that reported in the literature by several authors.[4] In this design the circularly polarized content of the emitted light and the total intensity of the emitted light are simultaneously measured by using a double-modulation technique. Basically, the spectrophotometer is a high-resolution emission instrument set up with 180° excitation–emission geometry. The excitation source used for these experiments (with europium(III)) is the 465.8-nm line of an argon ion laser (Coherent Innova 90), dispersed through a Pellin-Broca prism–iris combination to eliminate plasma lines. Following the sample, a photoelastic modulator (JCK-FS) and dichroic sheet polarizer (Polaroid) combination produces intensity modulation of any circularly polarized emission, at the modulation frequency of the modulator (42 kHz). A subsequent mechanical chopper provides total intensity modulation of the emitted light at 47 Hz. A high-pass filter is placed after the modulator and before the chopper to block the excitation beam.

The emission monochromator is a McPherson 1-m high-resolution instrument, with a 1200 line/mm grating, blazed at 300 nm. An RCA

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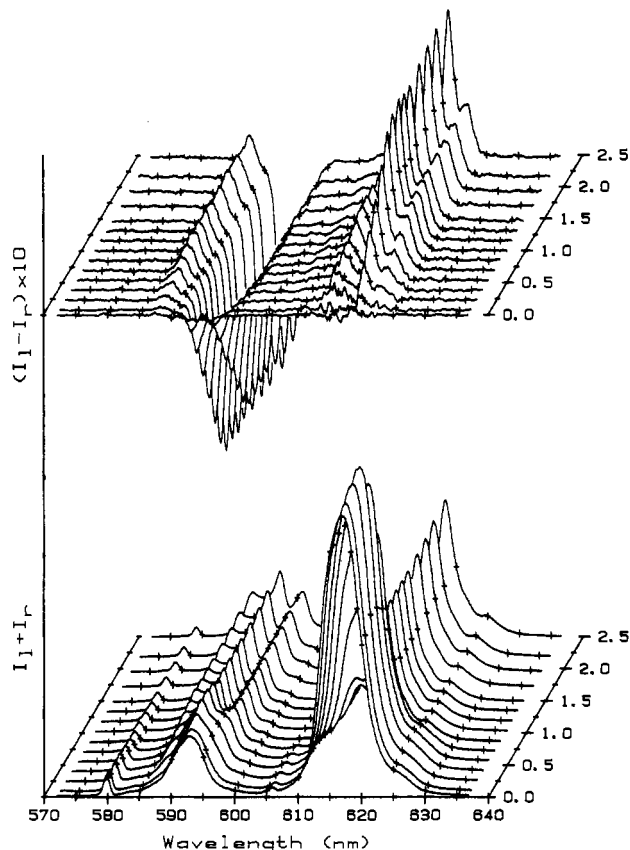
Figure 3. CPL (top) and TL (bottom) spectra obtained during the course of a titration of 1.5 mL of 0.017 M $Eu(NO_3)_3$ with 0.1 M I in TFE, plotted vs. equivalents of I (excitation wavelength 465.8 nm; emission spectral bandwidth 0.8 nm). The scaling of these spectra has been corrected for dilution effects only.

Figure 4. CPL (top) and TL (bottom) spectra obtained during the course of a titration of 1.2 mL of 0.042 M $Eu(NO_3)_3$ with 0.09 M I in MeCN, plotted vs. equivalents of I (excitation wavelength 465.8 nm; emission spectral bandwidth 0.8 nm). The scaling of these spectra has been corrected for dilution effects only, with the scaling of the region above 610 nm in the TL reduced by a factor of 5.

C31034 photomultiplier, thermoelectrically cooled to –30 °C, detects the intensity of the dispersed emission. The current from the tube is converted to a voltage signal (PAR 181 current-sensitive preamp), the modulation of which contains the magnitude and phase information pertaining to the CPL and TL of the sample. Two lock-in analyzers (PAR 5204) are used to determine these quantities, one referenced to the modulation frequency of the photoelastic modulator, the CPL, and the other referenced to the chopper frequency, the TL. The voltage outputs of the lock-ins are sampled by a lab-built A/D converter, which is interfaced to an HP 9825T computer and associated HP 7225A graphics plotter. All experimental spectra presented in this paper represent actual data collected with and plotted directly from this instrument. The emission spectral bandwidth used (0.8 nm) was determined to be sufficient to resolve all the features observed in these solution spectra. (Somewhat lower resolution was used in our earlier report of CPL from these systems.[2]) It should be noted that these spectra are uncorrected for either PMT or emission monochromator response.

Results

Spectral Assignments and Intensities. Figures 1 and 2 show comparison CPL and TL spectra for 1:1 mixtures of the crown I with $Eu(NO_3)_3$ (Figure 1) or $Eu(ClO_4)_3$ (Figure 2) in each of the three solvents used. Excitation at 465.8 nm populates the $^5D_2$ state, which rapidly decays to the $^5D_0$ level, from which most of the emission originates. Observed in these spectra are transitions from the $^5D_0$ state to the $^7F_0$, $^7F_1$, and $^7F_2$ states at ca. 579, 593 and 617 nm, respectively. The intensities of these transitions can be rationalized in terms of "free-ion" selection rules.[5] The electric and magnetic dipole forbidden 0 ← 0 band is unobserved in the CPL and very weak in the TL. Since the 1 ← 0 transition is predicted to be magnetic dipole allowed only, its intensity should remain relatively insensitive to changes in the europium environment. For this reason, this transition has been used as an "internal standard", with the spectra in Figures 1 and 2 scaled
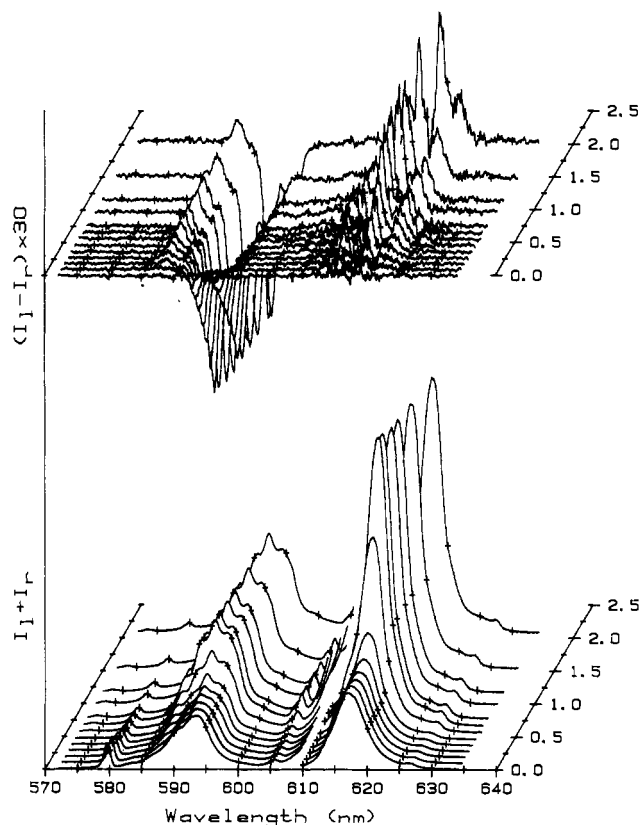
so that this transition has the same integrated TL intensity in each trace within the same figure. (The magnetic dipole allowedness of this transition is also apparent in the relative intensity of the CPL observed for it.[5]) The 2 ← 0 transition is electric dipole allowed and also is *hypersensitive*; therefore, it is expected to show great intensity variation, related to changes in the europium environment.[6] This transition also gains magnetic dipole strength through mixing with the magnetic dipole allowed 1 ← 0 transition, and so displays relatively intense CPL. Transitions to the other J levels of the ground ^7F term show less intense, but measurable, CPL, and spectra showing these transitions are collected in the supplementary material to this paper.

Titration Spectra. Figures 3 and 4 show the CPL and TL spectra obtained during the course of titrations of $Eu(NO_3)_3$ with I in TFE (Figure 3) and MeCN (Figure 4). These spectra are plotted vs. equivalents of titrant added in these three-dimensional plots. The spectra are scaled to account for dilution effects. Measurements of the conductance of these systems were made simultaneously with the spectral data collection, and these data are collected in the supplementary material to this paper.

Discussion

The Crown–Europium Complex Structure. The observation of lanthanide CPL from any of these solutions specifically implies that there is a crown ether–europium interaction. The TL spectra, on the other hand, reflect the luminescence of *all* europium species in solution. In our previous communication on the CPL and TL of crown–lanthanide complexes,[2] we reported the results of titrations of 1:1 mixtures of the crown I and either europium or terbium perchlorate with NO_3^- ion in TFE. The results of these experiments clearly indicated that the crown complex formed is a bis(nitrato) species and that the nitrates are coordinated on either

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side of the lanthanide–crown plane. Strongly suggested by these results is the conclusion that the nitrate complex is 1:1 in crown and lanthanide, although no direct evidence for this stoichiometry was presented. In this study, Figure 3 shows the results of a titration of $Eu(NO_3)_3$ with I in TFE. Examination of the changes in the CPL spectra over the course of the titration shows that the complex is indeed a 1:1 crown:lanthanide complex, since the CPL bands observed increase linearly to a limiting intensity at 1 equiv of crown added. The constancy of band shapes in the CPL throughout the titration is strong evidence for the formation of a single chiral species (i.e., without formation of any intermediates). The linearity of the increase of the CPL transitions is also indicative of a relatively large formation constant for the $[I-Eu(NO_3)_2]^+$ complex in TFE (log $K_f > 3$). The simultaneously measured conductivity shows that the equivalent conductance also increases approximately linearly from the initially nonconductive $Eu(NO_3)_3$ solution to a limiting value of 22 Ω^{-1} mol^{-1} cm^2, which is typical for a 1:1 electrolyte in TFE.[7] This suggests that the third nitrate is not involved in even an outer-sphere interaction with the cationic complex. The behavior of the *TL* spectra during the course of the titration is not as straightforward and will be discussed in more detail below.

The spectra of the nitrate complexes in MeCN, TFE, and HFiP (Figure 1) show that the crown complex structure is similar in each, since the CPL observed is of similar band shape in each solvent. There are some differences between the spectrum in HFiP and in the other solvents, notably in the ligand field splitting of the 1 ← 0 transition, suggesting that the structure is perturbed in some way by this solvent. Presuming comparable absorption strengths and quantum yields for chiral and achiral species, the intensity of the CPL (as compared to the "internal standard" 1 ← 0 TL intensity) is indicative of the degree of formation of the complex in the various solvents. A rough ordering of the complex formation constants in the three solvents based on this presumption is TFE $\approx$ HFiP > MeCN.

The spectra of the I–Eu(ClO$_4$)$_3$ system in the various solvents (Figure 2) also suggest that the structure of this crown complex is similar in each. The CPL spectra observed in TFE and HFiP are quite similar, differing only in the *magnitude* of the CPL. In MeCN, the CPL in the 1 ← 0 and 2 ← 0 regions is much weaker but shows structure similar to that in TFE and HFiP except for some small component-to-component intensity shifts. An examination of the TL observed for this system in these solvents shows one particularly striking feature. This is the observation of a transition at ca. 577 nm, relatively strong in HFiP and MeCN, that is much weaker in TFE. In our earlier reported results in TFE,[2] we assigned this transition to a second 0 ← 0 transition, which would correlate with the existence of at least *two* europium species in solution. However, in light of a later, extensive comparison of the absorbance frequency of the $^7F_0 \rightarrow {}^5D_0$ transition for many different systems, both in solution and in the solid state,[8] it appears *unlikely* that the 577-nm peak is a europium $^7F_0 \leftarrow {}^5D_0$ transition. The observed energy difference between this transition and the "true" 0 ← 0 transition at 579 nm is ca. 60 cm^{-1}, which is larger than any shift observed in this later study.[8] The observation of this transition in these systems, and in others with similar crown ethers,[9] also seems related to the appearance of other currently nonassigned transitions, at ca. 601 nm in the TL and at ca. 601 and 609 nm in the CPL. These transitions may be due to emission from the $^5D_2$ or $^5D_1$ levels of Eu(III) (since the excitation at 466 nm originally populates $^5D_2$). Additional excitation studies are under way to explore this possibility.

The conductivity of 1:1 solutions of the crown and Eu(ClO$_4$)$_3$ in TFE and in MeCN sheds further light on the stoichiometry of the crown–europium–perchlorate complex. The equivalent conductance of a TFE solution 0.0165 M in both I and Eu(ClO$_4$)$_3$

is 24.5 Ω^{-1} mol^{-1} cm^2, clearly in the range of a 1:1 electrolyte.[7] This suggests that this complex, like the nitrate complex, is a bis-anionic species, formulated $[I-Eu(ClO_4)_2]^+$. The equivalent conductance for the same system measured in MeCN is significantly larger, ca. 180 Ω^{-1} mol^{-1} cm^2, which is between the values usually measured for 1:1 (140 Ω^{-1} mol^{-1} cm^2) and 1:2 (220–300 Ω^{-1} mol^{-1} cm^2) electrolytes in MeCN.[10] As noted above, the CPL observed in MeCN is much weaker than in the other solvents, suggesting that perchlorate is not as strongly bound in this solvent and thus that there are several species present. The conductivity results indicate, however, that there is still a significant degree of interaction between the europium and the perchlorate anion.

An examination of the ligand field splitting observed for the 1 ← 0 transition in TFE leads to further conclusions about the structure of both the nitrate and the perchlorate complexes since the number of ligand field components observed in a transition can be related to the symmetry about the ion. For the perchlorate in TFE, we observe two components in both the CPL and the TL of this transition, while the nitrate complex clearly exhibits three well-resolved ligand field components in the 1 ← 0 region. For europium in a *biaxial* field, a maximum of $2J + 1$ components is expected for a transition to a particular J state, while fewer components will be observed if the lanthanide is at a site of *axial* symmetry. While the rigorously determined symmetry of neither the nitrate nor the perchlorate complex can exceed the ideal (biaxial) D_2 symmetry of the crown ether, the observed ligand field splitting in the perchlorate system can be explained in terms of a pseudoaxial field. This is reasonable if the crown ether is assumed to be flattened, and thus to provide an effectively cylindrical component to the ligand field, and if the perchlorates coordinate to the lanthanide in a monodentate fashion, one on either side of the crown–lanthanide plane. This mode of perchlorate coordination is reasonable in light of known lanthanide perchlorate solution behavior.[11] We infer, then, that europium ion in the bis(perchlorato) complex is eight-coordinate, complexed to a six-coordinate 18-crown-6 ether and to two axially bound monodentate perchlorate anions.

If we assume similar cylindrical symmetry for the crown ligand in the bis(nitrato) complex, then the apparent biaxial character of the europium CPL in this case must arise from the coordination of the nitrate anions. This is easily explained by bidentate coordination of the opposing nitrates, which would form a strong biaxial D_2 field around the europium. This coordination mode is quite reasonable again in light of the known binding preference of nitrate anion to lanthanides.[12] Europium in the nitrate complex is thus ten-coordinate, complexed to the hexadentate crown and the two opposing bidentate nitrate anions. The approximate nature of this symmetry assignment in both the nitrate and perchlorate is indicated by the weak but detectable 0 ← 0 emission, which is strictly forbidden (electric dipole and magnetic dipole) in D_2. A similar structure has been observed in the 4:3 Nd(NO$_3$)$_3$:unsubstituted 18-crown-6 "complex", where, in each [18-crown-6-Nd(NO$_3$)$_2$]$^+$ unit, the neodymium is ten-coordinate and is at a site of approximate D_{2d} symmetry.[13]

Other Species in Solution. As described above, the CPL results for the titration of Eu(NO$_3$)$_3$ with I in TFE (Figure 3) show that the addition of crown to the achiral salt causes a linear increase of all the CPL bands, to a limiting spectral band shape and intensity at 1 equiv of crown added, implying the formation of a 1:1 crown:europium species only. However, the spectral changes observed in the TL are not as straightforward. Addition of the crown is marked by an initial intensity *increase* in the hypersensitive $^7F_2 \leftarrow {}^5D_0$ transition, followed by a subsequent *decrease* in the transition strength, until 1 equiv of crown has been added, at which point, the TL spectrum is identical with the spectrum of the 1:1 complex in TFE (Figure 1). The implication of this

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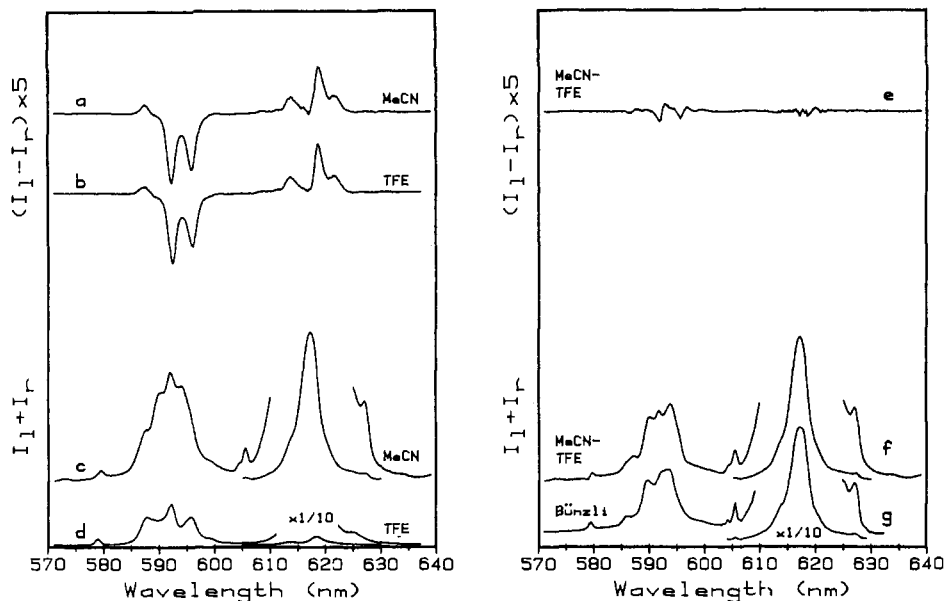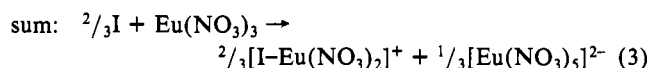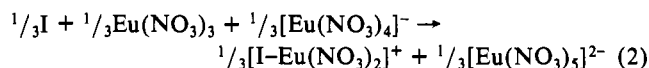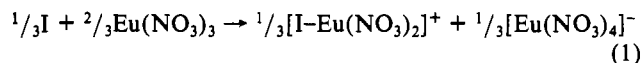
Figure 5. CPL and TL spectra for the I–Eu(NO$_3$)$_3$ system in MeCN. The top left set of CPL and TL spectra (a, c) are the measured data in MeCN (the same as in Figure 1), and the bottom left set (b, d) are the calculated CPL and TL of the [I–Eu(NO$_3$)$_2$]$^+$ complex existing in MeCN. The top right set of spectra (e, f) show the results of subtraction of the left spectra, and the bottom right TL spectrum (g) is redrawn from that obtained by Bünzli for (Me$_4$N)$_2$Eu(NO$_3$)$_5$.[12] See text for full explanation.

result is that complexation of a small amount of crown also causes the formation of an achiral europium species, which is then consumed with further addition of crown.

The spectra obtained during the course of the same titration in MeCN (Figure 4) appear quite different from those seen in TFE. The CPL spectra in MeCN show a linear increase in intensity, but only until $^2/_3$ equiv of crown has been added. The TL spectra exhibit three phases of growth during the course of this titration: an initial stage of limited intensity change to a point corresponding to $^1/_3$ equiv of I added, followed by a large intensity increase between $^1/_3$ and $^2/_3$ equiv of crown added, and a final stage marked by no change (or possibly a slight decrease) in intensity of the europium transitions. The CPL spectra show that the chiral species produced over the course of this complexation is the same [I–Eu(NO$_3$)$_2$]$^+$ species found in TFE, since the CPL is identical with that observed in TFE. However, in MeCN the TL results point to the existence of achiral europium species in solution, which limit the complete formation of the crown complex and persist even in the presence of excess crown.

In order to identify these achiral species, we make the assumption that the crown complex existing in MeCN has the same TL spectrum as it does in TFE, since the CPL spectra are identical. Knowing the integrated intensity of the CPL observed in MeCN, we can then *calculate* the magnitude of the TL spectrum expected for the crown complex in that solvent. Then by subtracting this from the observed TL in MeCN, we should obtain the TL spectrum of the remaining (*achiral*) europium species. The results of this subtraction are shown in Figure 5, using the spectra for 1:1 mixtures of I and Eu(NO$_3$)$_3$ in MeCN (curves a and c) and TFE (curves b and d), redrawn from Figure 1. Curves e and f show the results of the subtraction of these two sets of spectra. As can be seen, the difference CPL (curve e) is effectively nulled, confirming that the remaining europium species is achiral. More importantly, we can identify this species as the [Eu(NO$_3$)$_5$]$^{2-}$ anion, through a comparison of its *calculated* TL spectrum (curve f) with the total luminescence spectrum reported by Bünzli and Yersin for (Me$_4$N)$_2$Eu(NO$_3$)$_5$ dissolved in MeCN,[12] here redrawn as curve g. In 1:1 mixtures of I and Eu(NO$_3$)$_3$ in MeCN, we thus have two dominant ten-coordinate europium species, the chiral [I–Eu(NO$_3$)$_2$]$^+$ complex, and the achiral [Eu(NO$_3$)$_5$]$^{2-}$ species. The presence of an intermediate achiral species is also suggested in the early stages of the titration of Eu(NO$_3$)$_3$ with I MeCN. Equations emphasizing the proposed steps during the titration of Eu(NO$_3$)$_3$ with I in MeCN and the symbiotic relationship between

the crown complex and the pentakis(nitrato) species are shown here:

$$^1/_3\text{I} + {}^2/_3\text{Eu(NO}_3)_3 \rightarrow {}^1/_3[\text{I–Eu(NO}_3)_2]^+ + {}^1/_3[\text{Eu(NO}_3)_4]^- \quad (1)$$

$$^1/_3\text{I} + {}^1/_3\text{Eu(NO}_3)_3 + {}^1/_3[\text{Eu(NO}_3)_4]^- \rightarrow$$
$$^1/_3[\text{I–Eu(NO}_3)_2]^+ + {}^1/_3[\text{Eu(NO}_3)_5]^{2-} \quad (2)$$

$$\text{sum:} \quad {}^2/_3\text{I} + \text{Eu(NO}_3)_3 \rightarrow$$
$$^2/_3[\text{I–Eu(NO}_3)_2]^+ + {}^1/_3[\text{Eu(NO}_3)_5]^{2-} \quad (3)$$

Both the CPL/TL and conductance results indicate that after $^2/_3$ equiv of I has been added, no appreciable additional complex is formed even in the presence of excess crown. This appears to be due to the relatively high stability of [Eu(NO$_3$)$_5$]$^{2-}$ in CH$_3$CN.

If the stability of the pentakis(nitrato)europate species were lowered with respect to the stability of the crown complex, then we would expect the further production of crown complex as the final $^1/_3$ equiv of crown is added. This is precisely what occurs in TFE, where the very acidic, protic nature of this solvent, as well as the low donicity of the carbinol unit due to the electron-withdrawing nature of the trifluoromethyl group, causes the preferential solvation of anions as compared to cations.[7] We *do* observe the production of achiral poly(nitrato)europium species during the initial stages of the titration; however, these species are completely consumed as the full equivalent of crown is added. The following additional step thus is favored in TFE:

$$^1/_3\text{I} + {}^1/_3[\text{Eu(NO}_3)_5]^{2-} \rightarrow {}^1/_3[\text{I–Eu(NO}_3)_2]^+ + \text{NO}_3^- \quad (4)$$
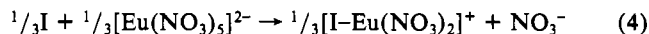
The resulting summation of equations 1, 2, and 4 describes the total complexation of Eu(NO$_3$)$_3$ in TFE:

$$\text{I} + \text{Eu(NO}_3)_3 \rightarrow [\text{I–Eu(NO}_3)_2]^+ + \text{NO}_3^- \quad (5)$$
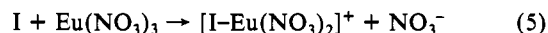
It is worth noting that the conductivity results obtained over the course of these same titrations do not by themselves offer any clue to the *identity* of the ions being produced as crown is added to the system; only the combined use of CPL and TL spectra shows clearly that at least one chiral and one achiral species are produced during the course of the titration. The titration data strongly imply that *only one* chiral species is involved and that both tetrakis- and pentakis(nitrato) achiral species are produced sequentially (and then consumed, partially in MeCN and completely in TFE).

High-resolution TL excitation spectra might also be used to identify the minimum number of europium species present (or

the actual number, presuming the 0 → 0 transitions are not accidentally degenerate). However, the multidimensional data and their analysis presented here can leave little doubt as to not only the existence but also the identity and (in the case of the crown complex) the structure of at least the dominant, if not the only, europium species present in these solutions. It seems unlikely that the excitation spectra, even combined with CPL as well as TL, will offer any further insight into these questions, although they would be useful in probing individual species and studying exchange dynamics in these systems.[14]

Europium Exchange. Of interest in the MeCN–I–Eu(NO$_3$)$_3$ system described above are the coexistence in solution of two ten-coordinate europium species and the possibility of observing europium exchange between them. Examination of the estimated TL spectra for the crown complex (Figure 5, curve d) and the pentakis(nitrato)europate dianion (Figure 5, curves f and g) shows a striking difference in intensities of the *hypersensitive* $^7F_2 \leftarrow {}^5D_0$ transition observed for the two species, with the intensity for the pentakis(nitrato) species being much greater than that of the crown complex. Since the absorbance transition used in the excitation of europium in this system is $^7F_0 \rightarrow {}^5D_2$ (also hypersensitive), it is expected that there should be a similar difference in the oscillator strengths of this transition for the two species.[15] (Although quantum yield is in principle strongly influenced by the efficiency of radiationless deexcitation, it is frequently observed that the $|\Delta J|$ = 2 selection rule for hypersensitivity is valid for emission as well as absorption.) Thus, the expectation is that pentakis(nitrato) anion is preferentially excited during this experiment. This selective excitation can be used for a limited investigation of the exchange dynamics of this system.

If the quantum yields of the fluorescence of each of the two ten-coordinate complexes are in fact similar and if europium exchange between the pentakis(nitrato) species and the crown complex is fast as compared to the lifetime of the europium excited state, we would expect the fluorescence of the crown complex to dominate the spectrum observed, since there is twice as much crown complex as pentakis(nitrato) anion in the final solution (eq 3). On the other hand, if the rate of europium exchange between the two complexes is slow, then we would expect the fluorescence of the pentakis(nitrato) species to dominate, since this species is preferentially excited. The latter is in fact what is observed when we compare the TL spectrum estimated for the crown complex (Figure 5, curve d) with the subtracted spectrum, representing

the TL of the pentakis(nitrato) species (Figure 5, curve f). Thus, the rate of europium exchange between the two complexes appears to be slow compared to the lifetime of the emission. While the emission lifetime of the crown complex has not been measured, that of the pentakis(nitrato) species has (1.25 ms).[12] The lifetime of the chiral crown complex should be similar, and so this represents a lower limit on the lifetime of the europium exchange.

We can further check the validity of the above arguments through excitation of this system using another, *nonhypersensitive* transition. In fact, excitation into the $^5L_6$ level of europium, using arc lamp radiation at 395 nm, produces a spectrum dominated by emission from the crown complex.[17] This confirms that the rate of europium exchange between these two species is slow compared to the lifetime of the emission, since the luminescence from a system in the fast-exchange limit should be independent of the excitation pathway. Similar results have been obtained in NMR studies of crown exchange in europium nitrate–unsubstituted 18-crown-6 systems in MeCN.[18] The hypersensitive transitions thus can be used as an additional probe of lanthanide equilibrium dynamics.[14]

Conclusion

The study of the solution behavior of complex systems can be difficult without a probe of specific interactions between different species. CPL fulfills this requirement, since it can be used to probe luminophores that gain chirality through association with chiral ligands. We have seen in this study how the use of CPL measurements, in conjunction with TL and conductivity results, can allow the determination of the specific nature of the different europium species, chiral and achiral, existing in solution. Extensions of this work to additional chiral 18-crown-6 ligands, as well as to other crown systems, to gain further information about crown–lanthanide chemistry and to investigate the exchange dynamics of these systems are in progress.

Registry No. [I–Eu(NO$_3$)$_2$]$^+$, 94518-35-1; [I–Eu(ClO$_4$)$_2$]$^+$, 101998-09-8; [Eu(NO$_3$)$_5$]$^{2-}$, 55723-40-5; Eu, 7440-53-1.

Supplementary Material Available: Figures of CPL and TL spectra including transitions from the $^5D_0$ state to all states in the ^7F manifold for 1:1 mixtures of I and Eu(NO$_3$)$_3$ or Eu(ClO$_4$)$_3$ in MeCN, HFiP, and TFE and figures illustrating equivalent conductivity data for the titration of Eu(NO$_3$)$_3$ with I in TFE and MeCN (4 pages). Ordering information is given on any current masthead page.

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