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Crown Ether–Lanthanide Complexes Studied by CPL and TL. 3. Chirality in Europium Nitrate and Chloride Complexes of Methyl-Substituted 18-Crown-6 Ligands. Optical Activity of Two-Bladed Nitrate Propellers

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Circularly polarized luminescence (CPL) and total luminescence (TL) have been used to investigate the solution structures of $EuCl_3$ and $Eu(NO_3)_3$ complexes of chiral 18-crown-6 ligands dissolved in trifluoroethanol. The sources of dissymmetry sensed by the lanthanide cation in these complexes are discussed, with specific emphasis on the influence of the anion on the complex chirality. The chirality of the nitrate complexes contains a contribution arising from the presence of a dissymmetric two-bladed propeller formed by the opposing nitrate chelate rings. In contrast, the optical activity of the corresponding chloride complexes is due only to configurational and conformational contributions from the crown ether.

Introduction

Studies using circularly polarized luminescence (CPL) in conjunction with total luminescence (TL) have provided detailed information concerning the solution structures of lanthanide complexes of the chiral crown ether (2*R*,3*R*,11*R*,12*R*)-2,3,11,12-tetramethyl-1,3,7,10,13,16-hexaoxacyclooctadecane (I).[1,2] Of interest in understanding more about the solution structures of these complexes is a determination of the nature of their effective chirality and its relation to their CPL spectra. To address this point more fully, we have measured the CPL and TL spectra of a series of europium nitrate and choride complexes of I and of three other chiral methyl-substituted 18-crown-6 ligands (II–IV, Figure 1). These experiments have been designed to determine the influence of the anion and of the number and placement of ring substituents on the overall solution structure of the complex. CPL and TL spectroscopy are ideally suited to these studies since they combine the conformational sensitivity of chiroptical spectroscopy with the detection sensitivity and specificity inherent in emission spectroscopy.[3]

The enantiomerically pure 18-crown-6 ligands employed in this study (Figure 1) derive their chirality from stereospecific placement of methyl substituents directly onto the crown ring. This stereospecificity has been achieved through the use of two different chiral precursors: (2*R*,3*R*)-2,3-butanediol for crowns I and II and (2*S*,2′*S*)-1,1′-oxybis(2-propanol) for the ethers III and IV. Thus, the 2,3-type ligands (crowns I and II) differ from the 2,6-type crowns (III and IV), not only in the proximity of adjacent methyl groups but also in the absolute configuration of their chiral centers. The stereospecific introduction of pairs of methyl groups onto the crown ring insures that the resulting macrocycles are formally homeotopic. The tetramethyl crowns I and III have idealized D_2 symmetry and the dimethyl crowns II and IV, idealized C_2 symmetry.

Experimental Section

Reagents. Details of the preparation and purification of the ligands I–IV have been described elsewhere.[4] Europium nitrate was prepared and dried as described previously.[2] Anhydrous europium chloride (99.9+%, Aldrich gold label) was used without further purification since an infrared spectrum of this material showed no –OH stretch. 2,2,2-Trifluoroethanol (TFE; 99+%, Aldrich gold label) was dried over activated 4-Å molecular sieves and used without further purification.

CPL/TL Sample Preparation. All sample manipulations were carried out in a dry-nitrogen-filled glovebox. Samples for spectroscopic measurement were prepared by addition of a measured amount of a stock solution of the appropriate crown (dissolved in TFE) to a weighed portion of either $Eu(NO_3)_3$ or $EuCl_3$, in standard Teflon-stoppered fluorescence cuvettes. All solutions were approximately 0.03–0.05 M in both crown and lanthanide.

Instrumentation. The design and construction of our high-resolution CPL/TL spectrophotometer has been described previously.[2] All samples were excited by using the 465.8-nm output of an argon ion laser (ca. 100-mW power) and the emission measured by employing emission slits of 1 mm (0.8-nm spectral bandwidth). This bandwidth was found to be sufficient to resolve all features of these room temperature solution CPL and TL spectra. No corrections for emission monochromator throughput or PMT response were made.

Results

CPL ($I_l - I_r$) and TL ($(I_l + I_r)/2$) spectra obtained on 1:1 crown:lanthanide solutions of $EuCl_3$ and the crown ethers I–IV in TFE are shown in Figure 2. The corresponding spectra for the $Eu(NO_3)_3$ complexes are displayed in Figure 3. The spectral region examined encompasses the Eu(III) $^7F_J \leftarrow {}^5D_0$ (J = 0–2) emission transitions, all of which occur in the visible portion of the spectrum. The data are represented in arbitrary intensity units, with the CPL being multiplied by an additional factor for plotting purposes. In both figures, all spectra are scaled such that the magnetic dipole allowed, electric dipole forbidden $^7F_1 \leftarrow {}^5D_0$ transition (590 nm) has the same integrated TL intensity for each, making the relative intensities of all spectra within a given figure comparable. The rationale for this scaling method has been discussed previously.[2]

Discussion

In the crown ether–europium complexes investigated in this report, specific multiplet-to-multiplet transitions, localized on the europium(III) cation, are exploited as probes of the complex structure and chirality. Optical activity is induced into the inherently achiral luminescent f–f transitions of the guest cation as a result of its inclusion into the cavity of the chiral crown host. Indeed, the very observation of CPL from these solutions indicates a specific crown–lanthanide interaction. This situation is analogous to that observed in studies of host–guest complexation of neutral organic molecules by optically active cyclodextrins, for example.[5] The ultimate source of the optical activity observed in the europium emission bands is the chirality of the crown ligand, due to the presence of asymmetric carbon atoms within the polyether skeleton. The chirality sensed by the europium can arise by one or more of the following mechanisms: (1) *vicinal* chirality, induced by proximity of the metal to a chiral center; (2) *conformational* chirality, induced by a twist within a chelate ring; (3) *configurational* chirality, caused by a dissymmetric arrangement of chelate rings about the europium ion. Because these chiral crowns are hexadentate ligands, potentially forming *six* chelate rings with

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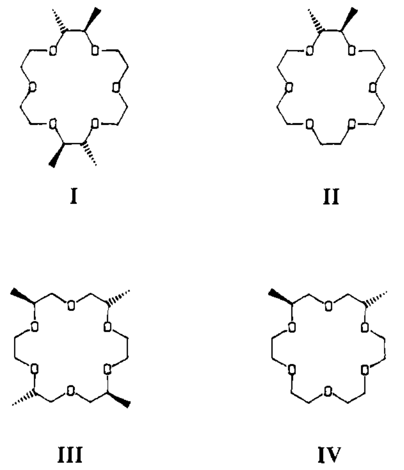

Figure 1. Chiral, polymethyl macrocycles employed in this study.

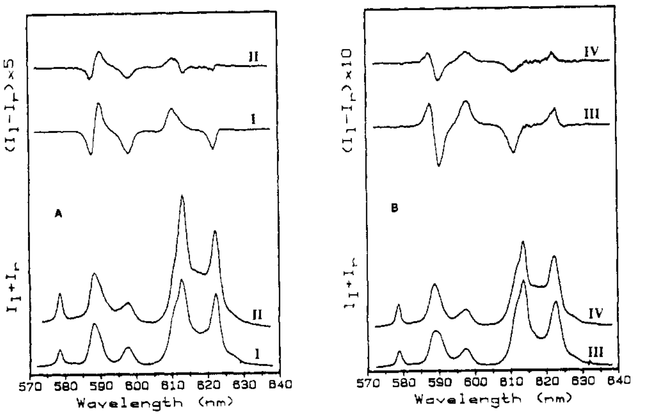

Figure 2. CPL (top traces) and TL (bottom traces) spectra for 1:1 solutions of $EuCl_3$ with (A) crowns I and II and (B) crowns III and IV in TFE.

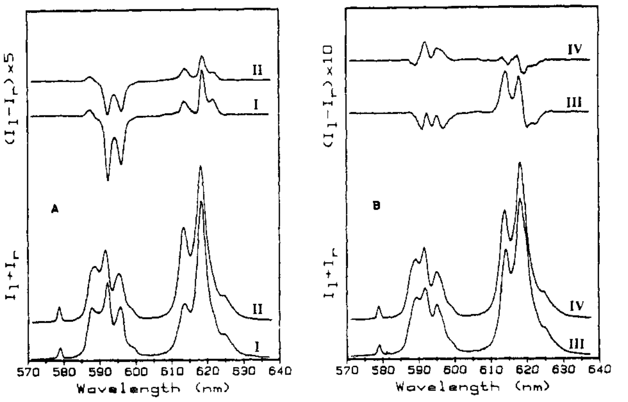

Figure 3. CPL (top traces) and TL (bottom traces) for 1:1 solutions of $Eu(NO_3)_3$ with (A) crowns I and II and (B) crowns III and IV in TFE.

a centrally bound metal, all three of the above sources of chirality should be considered. They are, in fact, intimately related in that the *configurational* chirality of the system arises from the twisting of the entire ring to accommodate the *conformational* chirality within the methyl-substituted polyether subunits, which in turn is brought about by the accommodation of the asymmetric carbon atoms within these subunits. It thus becomes difficult to separate the various forms of chirality within these complexes. However, to the extent that such a separation is meaningful, it is expected that the *configurational* and *conformational* contributions to the chirality will be greater than that of *vicinal* chirality in these complexes.

An examination of the CPL and TL spectra of the $EuCl_3$ complexes of crowns I–IV in TFE (Figure 2) leads to important conclusions about the chirality of these systems. The *TL* spectra (bottom traces) are quite similar, differing primarily in slight intensity shifts between the crystal field components. On the other hand, the *CPL* spectra associated with these complexes show distinctive differences, reflecting the great sensitivity of this technique to molecular geometry. Particularly striking is the mirror image relationship between the CPL spectra of the *S*-type crown complexes (complexes of crowns III and IV) and those of the *R*-type complexes (of crowns I and II). This is at first glance consistent with a *vicinal* mechanism for the complex chirality, since the absolute configuration of the chiral centers is opposite in the two types of complexes. The fact that the optical activity observed for the tetramethyl crown complexes of each type is ca. twice that of the corresponding dimethyl crown complexes is also consistant with *vicinal* chirality. However, if a vicinal mechanism were solely responsible for the observed optical activity, then the *magnitude* of the CPL associated with the corresponding di- and tetramethyl complexes of each type would be the same, since the optical activity would be related only to the distance of the chiral centers on the crown ligand to the europium, which should be equivalent (or nearly so) for all four crown complexes. As seen in Figure 2, this is clearly not the case; in fact, the CPL of the *R*-type crown complexes is in every case ca. twice that of the corresponding *S*-type complex. (This is also true for the nitrate complex spectra in Figure 3, as discussed below.) It is thus clear that, consistent with expectation, the chirality in the chloride systems arises from *conformational* and *configurational* mechanisms involving the twisting of the crown ligands in order to accommodate their chiral centers. This twist will be of the opposite sense for the *R*-type crowns as compared to the *S*-type crowns, but also will be larger for the *R*-type crowns than the *S*-type crowns, since the steric interaction of the methyl substituents of the former will be greater (methyls two atoms apart) than of the latter (methyls four atoms apart).

In order to understand better the relation of the structure of these complexes to their chiroptical properties, we now compare the spectra of the chloride complexes to those of the analogous complexes of $Eu(NO_3)_3$. Previously reported results[1,2] clearly show that the nitrate complex of I is properly formulated as $[EuI(NO_3)_2]^+NO_3^-$ and that the solution structure is closely related to that found in the crystal of $CaI(NO_3)_2$, in which two nitrates are associated with the metal ion, each through two oxygens, on opposite faces of the crown-metal ion plane.[4] Similar evidence strongly supports the same solution structure for the europium chloride complexes of I–IV. This is also the solid state structure adopted by the gadolinium chloride complex of unsubstituted 18-crown-6, i.e., $[GdLCl_2]^+Cl^-$.[6] Thus comparison of the TL and CPL of the complexes of I–IV with those of europium chloride and nitrate should reveal the extent to which the shape and steric requirements of the planar, "bidentate" nitrate influence the structure and chiroptical properties.

Examination of the TL spectra measured for the 1:1 solutions of $Eu(NO_3)_3$ with the other 18-crown-6 derivatives (II–IV) indicates that the solution structures of these crown complexes formed in TFE are similar to that of I with this salt,[1,2] since the observed splittings and relative intensities of the various transitions are similar for each complex. Trends observed in the CPL of the $EuCl_3$ complexes of I–IV described earlier are also present in the $Eu(NO_3)_3$ complexes of these macrocycles. For example, the CPL for the $Eu(NO_3)_3$ complexes of crowns I and II are similar, with the same doubling of intensity between the dimethyl and tetramethyl ligand being observed. Furthermore, the CPL intensity of the *R*-type crowns is roughly double that of the corresponding *S*-type macrocycles. However, in comparison with the CPL of the chloride complexes, a significant difference in the pattern of the optical activity of the nitrate complexes is obvious. Although, as in the chloride complexes, the CPL spectra of the $Eu(NO_3)_3$ complexes of II and IV are very nearly mirror images, the optical activity of the nitrate complexes of the two tetramethyl crowns, I and III, fails to show this quasi-enantiomeric relationship. This

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[6] Forsellini, E.; Benetollo, F.; Bombieri, G.; Cassol, A.; De Paoli, G. *Inorg. Chim. Acta* **1985**, *109*, 167.

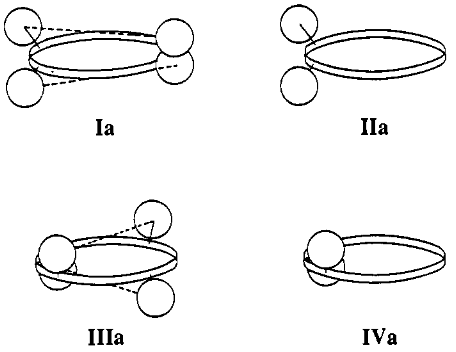

Figure 4. Schematic representation of the "channels" formed by the methyl substituents on the faces of the chiral crowns. The methyl groups are represented as spheres. In the tetramethyl-substituted crowns, the dashed lines connect methyl groups on the same face of the macrocycle. The numbers correspond to those of the structures in Figure 1.

suggests another contribution to the complex chirality, related specifically to the nitrate anions.[7]

In fact, a pattern similar to that seen in the CPL of the europium nitrate complexes of I–IV has been observed in the circular dichroism of the nitrate n → π* transition in alkaline-earth-metal nitrate complexes of the same four crowns.[4] As noted above, the structure of these complexes has been determined to be essentially the same as that of the lanthanide nitrates with these crowns, i.e., a centrally coordinated cation with two "bidentate" nitrate anions associated on opposite sides of the mean plane of the polyether ligand. Infrared measurements also are consistent with this structure, and further confirm the presence of bidentate nitrate anions. Furthermore, the X-ray data show that, in complexes of I, the methyl substituents occupy axial positions, forming "channels", on each face of the macrocycle. These channels are expected to lie roughly perpendicular to the line connecting the methyls (see Figure 4). In the tetramethyl crown I, the crystal structure reveals that these channels are oriented approximately parallel to each other because of the relatively close spacing of the pairs of methyl substituents. In contrast, the more widely spaced methyl substituents of the other tetramethyl crown III produce channels which are oriented more nearly perpendicular to each other. Due to steric interactions with the anions, the methyl groups will cause the chelating nitrate anions to occupy these channels, thereby controlling their relative orientation. (The steric influence of the methyls in the dimethyl crown complexes is similar but less well-defined than in the complexes of I and III.)

The opposing, bidentate nitrates in the europium complexes of I–IV may be envisioned as forming two-bladed propellers, the symmetry of which will depend solely on the relative twist of the opposing nitrate planes. If the angle between these two planes is represented by ϕ, then for $0 < \phi < 90°$, the symmetry of the propeller is D_2. This arrangement will therefore lead to an additional source of chirality in these complexes, a configurational contribution due to the chiral arrangement of the nitrate rings. This contribution to the complex chirality will pass through a maximum for $\phi = 45°$ and will be nonexistent for $\phi = 0°$ (coplanarity of the anions, effective symmetry D_{2h}) and for $\phi = 90°$ (orthogonality, symmetry D_{2d}). It should be noted that this arrangement of the nitrate chelate rings (for $0 < \phi < 90°$) functions as an independent source of chirality and does not require the presence of a chiral host ligand except as the macrocycle determines that the propeller will be either right- or left-handed and not racemic. (Specifically, the $(NO_3^-)_2$ propeller will be right-handed for the *R*-crown complexes and left-handed for the *S*-crown complexes.)

It is also obvious from an examination of Figure 4 that the channels formed by the methyl groups on the crown faces will favor different nitrate twist angles, particularly in the complexes of I and III. The twist angle ϕ is expected to be much larger in the europium nitrate complex of III, because of the more even spacing of the methyls around the macro ring. This increased twist angle will lead to a significantly different $(NO_3^-)_2$ configurational contribution to the complex chirality in the case of III, as compared to the corresponding complex of I. As seen in Figures 2 and 3, among the quasienantiomeric pairs of complexes of $EuCl_3$ and $Eu(NO_3)_3$, it is, in fact, only the europium *nitrate* complexes of I and III that show no trace of mirror image relationship in their CPL spectra.

It is also interesting to note that the apparent (and for the crystal structure of $[CaI(NO_3)_2]$, observed) twist of the macrocycle ring in these complexes makes the ring itself into a two-bladed propeller, the pitch of which will be affected by the steric interactions of the methyl groups as well as by interactions with the axially associated anions. Thus, the nitrate complexes involve the orthogonal intersection of two two-bladed propellers, while the chlorides have only the one formed by the twist of the marocycle ring.

Conclusion

Comparison of the CPL spectra of the $EuCl_3$ and $Eu(NO_3)_3$ complexes of the chiral 18-crown-6 ligands I–IV shows clearly that the optical activity of the nitrate complexes contains a contribution due to the dissymmetric two-bladed propeller formed by the opposing nitrate chelate rings, which is especially significant in the complex of $Eu(NO_3)_3$ with III. The corresponding $EuCl_3$ complexes contain no such contribution to the overall complex chirality, the optical activity in these complexes being produced by configurational and conformational contributions from the crown ether alone.

Registry No. $[EuICl_2]^+Cl^-$, 111582-95-7; $[EuIICl_2]^+Cl^-$, 111582-96-8; $[EuIIICl_2]^+Cl^-$, 111615-28-2; $[EuIVCl_2]^+Cl^-$, 111615-29-3; $[EuI(NO_3)_2]^+NO_3^-$, 94518-36-2; $[EuII(NO_3)_2]^+NO_3^-$, 111582-98-0; $[EuIII(NO_3)_2]^+NO_3^-$, 111583-00-7; $[EuIV(NO_3)_2]^+NO_3^-$, 111583-02-9.

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[7] The mirror image relationship between the spectra of the nitrate complexes of II and IV indicates that the nitrate has no more direct conformational influence on the macrocycle ring than does the chloride.