Eu(III) as a Sensitive Probe of Ligand Conformation in Dicyclohexyl-18-crown-6 Complexes*

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Macrocyclic complexes of the lanthanides have been studied extensively in recent years [1]. A very promising aspect in the study of such complexes is the use of Eu(III) as a spectroscopic probe for the conformation of ligands. Indeed, the energy of the $^5D_0 \leftarrow {}^7F_0$ transition is very sensitive to the chemical environment around the Eu(III) ion. Selective (laser) excitation of each of the observed $^5D_0 \leftarrow {}^7F_0$ transitions results in an emission spectrum characteristic of this environment and also yields information about the symmetry around the Eu(III) ion. This method allows one to distinguish between the different coordination sites in a crystal and between the different conformations of the macrocycle, as was demonstrated in the case of the 18-crown-6 complex [2].

Experimental

The A and **B** isomers (Fig. 1) of dicyclohexyl-18-crown-6 [3] have been separated according to Izatt's procedure [4]. Analytically pure 3:2 (metal:ligand) complexes were obtained by mixing $Eu(NO_3)_3$ and dicyclohexyl-18-crown-6 (pure isomer) in dry ethanol [5], followed by several recrystallizations from the same solvent under an argon atmosphere. The spectroscopic apparatus and measurement technique have been described previously [2].

Results

The 3:2 (metal:ligand) analytical stoichiometry is confirmed by the molecular structure of the complexes (Eu, isomer A [6]; and La, Pr, isomer **B** [5]). As determined from the Eu(III) $^5D_0 \leftarrow {}^7F_0$ excitation spectrum at 295 K (Fig. 2, top), there are three different sites assigned to the $[Eu(NO_3)_5]^{2-}$ pentanitrate anion (**P**) and the two complex cations $[Eu(NO_3)_2(L)]^+$ (**I** and **II**) with L = dicyclohexyl-18-crown-6 ether. It can be seen from consideration of Fig. 2 that the excitation spectra of the complexes with isomers A and **B** are different (values for the maxima appear in Table I). Selective excitations at wavelengths corresponding to these maxima (indicated by arrows in Fig. 2) yield the emission spectra shown in Figs. 3 and 4. The assignment of band P to a polynitrato species (**P**) is supported by the fact that the emission spectra (A-P and B-P in Fig. 3) are

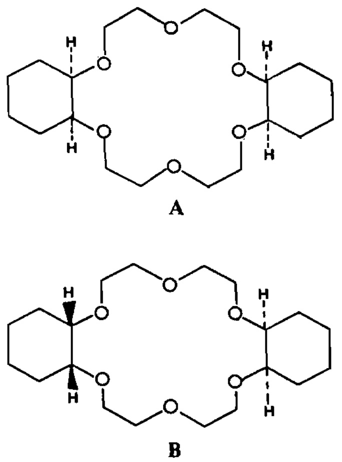

Fig. 1. Schematic of the A and **B** isomers of the ligand dicyclohexyl-18-crown-6.

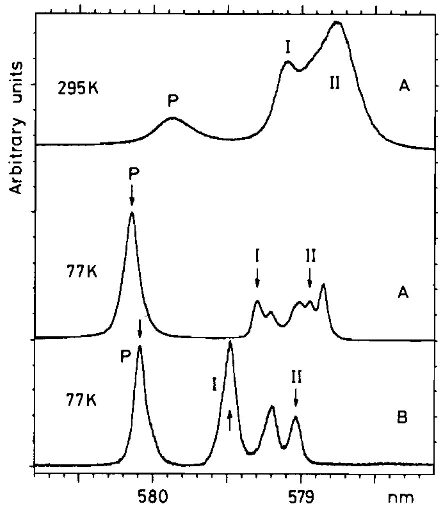

Fig. 2. Excitation spectra ($^5D_0 \leftarrow {}^7F_0$) at 295 K and 77 K of the Eu(III) 3:2 complexes with dicyclohexyl-18-crown-6. A and **B** refer to the isomers of the ligand. **P** corresponds to the polynitrato species $[Eu(NO_3)_5]^{2-}$. **I** and **II** refer to the two $[Eu(NO_3)_2(L)]^+$ complex cations. Arrows point to the excitation wavelengths used to obtain the emission spectra.

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TABLE I. $^5D_0 \leftarrow {}^7F_0$ Maxima (nm) of the $[Eu(NO_3)_2(L)]_2$-$[Eu(NO_3)_5]$ Complexes (L = Dicyclohexyl-18-crown-6)

Complex species	Isomer A	Isomer B
$[Eu(NO_3)_5]^{2-}$ (P)	580.15	580.09
$[Eu(NO_3)_2(L)]^+$ (I)	579.20, 579.30	579.47
$[Eu(NO_3)_2(L)]^+$ (II)	578.85, 578.95	579.03
	579.00, 579.05	579.21

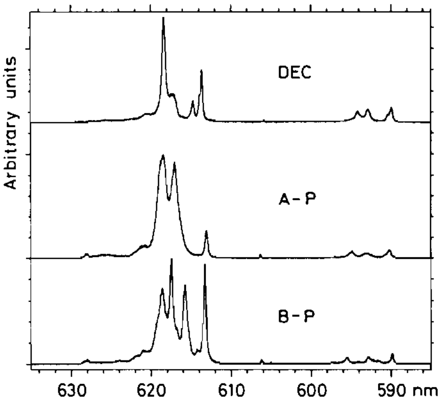

Fig. 3. Emission spectra at 77 K of Eu-polynitrato complexes. DEC = $[(CH_3)_3NC_{16}H_{33}]_4Eu_2(NO_3)_{10}$. **A** and **B** refer to the dicyclohexyl-18-crown-6 isomers. **P** corresponds to the $[Eu(NO_3)_5]^{2-}$ entity in the 3:2 (metal:ligand) complexes with dicyclohexyl-18-crown-6.

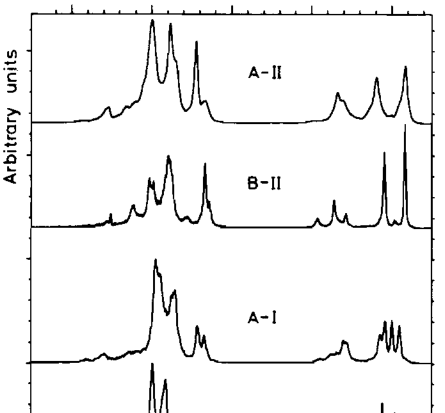

Fig. 4. $^5D_0 \rightarrow {}^7F_1$ (585–600 nm) and $^5D_0 \rightarrow {}^7F_2$ (610–630 nm) transitions of the $[Eu(NO_3)_2(L)]_2[Eu(NO_3)_5]$ complexes (L = dicyclohexyl-18-crown-6) at 77 K. **A** and **B** refer to the two isomers of the ligand. **I** and **II** refer to the two $[Eu(NO_3)_2(L)]^+$ complex cations. Excitation wavelengths are indicated by arrows on Fig. 2.

similar to those of other pentanitrates [7], particularly to that of the decanitrate [8] $[(CH_3)_3NC_{16}H_{33}]_4$-$Eu_2(NO_3)_{10}$ (abbreviated as DEC in Fig. 3). The spectra shown in Fig. 4 arise from the complex cations $[Eu(NO_3)_2L]^+$. There is a significant difference between the spectra generated by isomers **A** and **B**. Moreover, excitation at two different wavelengths I and II for each of the complexes with isomers **A** and **B** yields spectra differing in both the energy and the crystal field splitting of the $^5D_0 \rightarrow {}^7F_J$ transitions ($J = 1, 2$). This reflects the presence, for each isomer, of two complex dinitrato cations (**I** and **II**) having different chemical environments, in agreement with the results of the crystallographic investigations [5, 6]. The additional bands observed in the 77 K excitation spectra (Fig. 2) of the complex cations I and **II** could be due to slight conformational differences in the macrocycles [2]; such differences were observed in solution by ^{13}C NMR spectroscopy [9].

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