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Complexes of Lanthanoid Salts with Macrocyclic Ligands.
Part 25*. Lanthanoid Trifluoroacetate Complexes with 12-Crown-4, 15-Crown-5, and 18-Crown-6 Ethers**

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Abstract

The lanthanoid trifluoroacetates, Ln(TFA)$_3$, react with 12-crown-4, 15-crown-5, and 18-crown-6 ethers to give complexes with various metal:ligand ratios, 1:1, 3:2, and 2:1. The following complexes have been isolated and characterized: $Ln(CF_3CO_2)_3\cdot(C_8H_{16}O_4)$, Ln = La, Ce, Pr; $[Ln(CF_3CO_2)_3]_3\cdot(C_8H_{16}O_4)_2$, Ln = Pr, Eu, Er; $[Ln(CF_3CO_2)_3]_2\cdot(C_8H_{16}O_4)$, Ln = Pr, Nd, Sm; $[Ln(CF_3CO_2)_3]_2\cdot(C_{10}H_{20}O_5)$, Ln = La–Eu; $Ln(CF_3CO_2)_3\cdot(C_{12}H_{24}O_6)$, Ln = La–Eu; $[Ln(CF_3CO_2)_3]_2\cdot(C_{12}H_{24}O_6)$, Ln = Y, Eu–Er, Yb. Thermogravimetric data show that the 2:1 complexes are usually thermally more stable. The 2:1 complexes with the 15-membered polyether undergo a slow hydrolysis in the presence of traces of water, which yields the hydroxo complex $[Ln_2(CF_3CO_2)_3(OH)(C_{10}H_{20}O_5)_2][Ln_2(CF_3CO_2)_8]$. The vibrational spectra confirm the coordination of the coronands; the $\Delta\nu_{as}$(CCO) shifts are not large, which point to a moderate interaction between the polyethers and the metal ions. Magnetic susceptibilities and X-ray powder diagrams have been measured.

High-resolution excitation and emission spectra have been analysed for the europium-containing compounds. The spectrum of $Eu(CF_3CO_2)_3\cdot3H_2O$ indicates the presence of a single species with low symmetry, in agreement with the crystal structure data for the isostructural Pr-salt. The anhydrous salt $Eu(CF_3CO_2)_3$ generates an emission spectrum with broad bands and probably contains several, closely related polymeric species. The spectrum of $[Eu(CF_3CO_2)_3]_2(C_{10}H_{20}O_5)$ is consistent with the presence of two chemically different sites for Eu(III); the emission bands are broad. The double salt $AgEu(CF_3CO_2)_4\cdot3CH_3CN$ has also been investigated; the observed transitions point to the presence of a species with idealized D_{2d} symmetry. The emission spectrum of $[Eu(CF_3CO_2)_3]_2(C_{12}H_{24}O_6)$ displays sharp bands and reveals the presence of two different sites for the metal ion with efficient energy transfers between them. One of the species may have a relatively high symmetry.

In solution, all the complexes are non-electrolytes in acetonitrile and propylene carbonate and close to 1:1 electrolytes in methanol. Some dissociation occurs in acetonitrile for the 2:1 complexes with 18-crown-6 ether. On the other hand, ^{1}H NMR spectra of the lanthanum 1:1 complexes with 12-crown-4 and 18-crown-6 ethers indicate no dissociation of the complexed polyether. Log β_1 is greater than 6 for both complexes; it is equal to 4.4 for the samarium 1:1 complex with 18-crown-6 ether.

Introduction

Trivalent lanthanoids are more or less spherical ions and are well suited for complexation by ionophoric ligands. In particular, complexes between these ions and synthetic macrocyclic polyethers have been isolated with various metal to ligand ratios [4]. With non-coordinating anions, e.g. perchlorate or hexafluorophosphate, 1:1 and 1:2 complexes are formed, depending upon the relative size of the ligand cavity and the ionic diameter. With the small, but strongly coordinating and bidentate nitrate ions, 1:1, 4:3 [5], and 3:2 [6] complexes are isolated. These latter contain complex nitrato species, pentanitrates or hexanitrates. In this communication, we report the synthesis and spectrochemical properties of the complexes between lanthanoid trifluoroacetates and three cyclic polyethers: 12-crown-4, 15-crown-5, and 18-crown-6 ethers. The trifluoroacetate (TFA) anion was chosen for three reasons: (i) it is potentially bidentate and/or bridging, (ii) its donor strength is moderate, and (iii) its steric hindrance is large due to the bulky trifluoromethyl group. It therefore allowed us to complement our study on

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*For Part 24, see [1]; abstracted, in part, from the *Ph.D. Thesis* of A.G.; preliminary communications, see [2, 3].

**Systematic names: 1,4,7,10-tetraoxacyclododecane, 1,4,7,10,13-pentaoxacyclopentadecane, and 1,4,7,10,13,16-hexaoxacyclooctadecane.

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TABLE I. Stoichiometry, Yields of the Syntheses, and Elemental Analyses of $[Ln(TFA)_3]_x\cdot(C_8H_{16}O_4)_y$.

Ln	x:y	Washing[a]	MM	η %	%C		%H		%Ln	
					calc.	exp.	calc.	exp.	calc.	exp.
La	1:1	2	654.18	44	25.71	25.56	2.46	2.48	21.24	21.13
Ce	1:1	3	655.39	56	25.66	25.50	2.46	2.42	21.38	21.12
Pr	1:1	2	656.18	29	25.63	25.16	2.46	2.42	21.47	21.57
Pr	3:2	4	1792.32	17	22.79	22.78	1.80	1.71	23.59	23.60
Nd	2:1	4	1142.80	28	21.02	21.10	1.41	1.41	25.24	25.14
Sm	2:1	4	1155.02	15	20.80	20.84	1.40	1.25	26.04	25.93
Eu	3:2	1	1825.47	15	22.37	21.64	1.77	1.99	24.94	25.27
Er	3:2	1	1871.37	13	21.82	21.96	1.72	1.79	26.81	27.03

[a] The obtained x:y ratio depends upon the exact washing procedure: 1, no washing; 2, CH_2Cl_2 after filtration; 3, C_6H_{12} after filtration; 4 CH_2Cl_2 after drying the complex the first time.

TABLE II. Yields of the Syntheses and Elemental Analyses of the Non-hydrolysed $[Ln(TFA)_3]_2\cdot(C_{10}H_{20}O_5)$ Complexes.

Ln	MM	η %	%C		%H		%Ln	
			calc.	exp.	calc.	exp.	calc.	exp.
La	1176.12	40	22.47	22.50	1.71	1.81	23.62	23.97
Ce	1178.54	13	22.42	22.42	1.71	1.81	23.78	24.10
Pr	1180.12	60	22.39	22.37	1.71	1.71	23.88	24.14
Nd	1186.78	28	22.26	22.12	1.70	1.75	24.31	24.72
Sm	1199.00	24	22.04	22.00	1.68	1.81	25.08	25.96
Eu[a]	1202.22	36	21.98	21.87	1.68	1.73	25.28	25.16

[a] Isolated at 0 °C after a second crystallization.

the influence of the anion upon the metal:ligand ratio in lanthanoid coronates [5].

Experimental

Lanthanoid Trifluoroacetates

The hydrated lanthanoid trifluoroacetates were prepared from the oxides (Nucor Corp. 99.99%) and trifluoroacetic acid (Fluka, 98%, *purum*). The oxide was dissolved into a slight excess of acid (*ca.* 10%), at 70–80 °C; complete dissolution occurred after 2–7 h depending upon the lanthanoid ion. The solution was evaporated to dryness, and the solid obtained was washed with dichloromethane and dried in a vacuum dessicator over KOH for 24 h; this latter operation was repeated three times to eliminate the excess of acid. Additional drying over P_4O_{10} (2×10^{-2} mm Hg) gave the tri- or tetrahydrate. Anhydrous salts could be obtained after heating for 72 h at 70 °C (2×10^{-2} mm Hg). The cerium trifluoroacetate was prepared in the same way from the carbonate (Alfa Products, 99.9%).

The purity of the salts was checked by IR spectrometry, complexometric analysis of the rare earth (Titriplex III, Merck, in the presence of urotropine and xylene-orange), and elemental analyses (Mikrolaboratorium, ETH-Zurich).

12-Crown-4 Complexes

A solution of 5 mmol 12-crown-4 in 15 ml solvent (MeCN:MeOH 3:1) was added dropwise to a solution of 5 mmol hydrated trifluoroacetate in 15 ml solvent. The resulting solution was heated at 60 °C for 24 h, cooled to room temperature, and reduced to a smaller volume (15 ml for La, Ce; 10 ml for Pr, Nd; 5 ml for Sm, Eu, and the heavier lanthanides). The crystallization must be slow in order to avoid the coprecipitation of the starting salt. The solid product was filtered, washed, and dried over P_4O_{10} (2×10^{-2} mm Hg) for 2–3 d. The Ln:L ratio obtained depends upon the exact washing procedure, which is given in Table I along with the elemental analyses.

15-Crown-5 2:1 Complexes

A similar procedure to that described above was used. The solution was evaporated to 10–15 ml. The complex was washed with dichloromethane and dried over P_4O_{10} for 2 d. The complexes with Ln = La–Nd are anhydrous and non-hygroscopic. The

TABLE III. Yields of the Syntheses and Elemental Analyses of $Ln(TFA)_3 \cdot (C_{12}H_{24}O_6)$ and $[Ln(TFA)_3]_2 \cdot (C_{12}H_{24}O_6)$.

Ln	Ln:L	MM	η %	%C		%H		%Ln	
				calc.	exp.	calc.	exp.	calc.	exp.
La	1:1	742.28	49	29.13	29.25	3.26	3.36	18.71	18.54
Ce	1:1	743.49	27	29.08	29.22	3.25	3.17	18.85	18.73
Pr	1:1	744.28	36	29.05	29.05	3.25	3.31	18.93	18.81
Nd	1:1	747.61	9	28.92	28.88	3.24	3.20	19.29	19.11
Sm	1:1	753.72	20	28.68	28.69	3.21	3.10	19.95	19.93
Eu	1:1	755.33	7	28.62	28.51	3.20	3.16	20.12	20.00
Eu	2:1	1246.34	5	23.13	23.07	1.94	1.96	24.38	24.28
Gd	2:1	1256.92	24	22.93	22.75	1.92	1.99	25.02	24.84
Tb	2:1	1260.26	13	22.87	22.69	1.92	1.95	25.22	25.11
Dy	2:1	1267.42	14	22.74	22.65	1.91	1.98	25.64	25.60
Ho	2:1	1272.28	11	22.66	22.48	1.90	2.05	25.93	25.70
Er	2:1	1276.94	4	22.57	22.39	1.89	1.80	26.20	26.28
Yb	2:1	1288.50	9	22.37	22.42	1.88	1.91	26.86	26.96
Y	2:1	1120.23	10	25.73	25.93	2.16	2.31	15.87	15.69

complexes with Ln = Sm, Eu must be dried at 60 °C (2×10^{-2} mm Hg) for 3 d; they are quite hygroscopic and were stored in sealed tubes. Elemental analyses are reported in Table II. The complexes undergo a slow hydrolysis in the presence of traces of water (*vide infra*).

18-Crown-6 Complexes

1:1 Complexes (Ln = La–Eu)

A solution of 5 mmol 18-crown-6 in 25 ml ethanol was added dropwise to a solution of 5 mmol hydrated trifluoroacetate in 50 ml ethanol. The resulting solution was heated 24 h at 60 °C, cooled to room temperature, evaporated to 60 ml (Ln = La, Ce) or 15–20 ml (Ln = Pr–Eu), and filtered. The complexes were dried over P_4O_{10} at 50 °C (2×10^{-2} mm Hg) for 3 d. The Sm and Eu complexes are hygroscopic and were stored in sealed tubes. Elemental analyses are reported in Table III.

2:1 Complexes (Ln = Y, Eu–Er, Yb)

The procedure described above was followed, except that dimethyl ether was used instead of dichloromethane to wash the complexes. For Ln = Ho and Er, a recrystallization at 0 °C is needed. All the complexes are hygroscopic and were stored in sealed tubes. Elemental analyses are reported in Table III.

Spectroscopic Measurements

Luminescence spectra of polycrystalline samples were recorded at 77 K on a previously described laser-spectrofluorimeter [7]. IR spectra were obtained as nujol mulls or KBr pellets with a Perkin-Elmer 577 spectrometer. Raman spectra were recorded with a Ramalog-4 Spex instrument. The ^1H NMR spectra were recorded on a Bruker WP-60 spectrometer equipped with a B-VT-100 variable-temperature unit. Proton chemical shifts are expressed in ppm with respect to tetramethylsilane (TMS).

Other Measurements

Thermogravimetric measurements were performed on a Mettler TA-1 analyzer equipped with a Ni-Cr/Ni thermocouple. The samples were placed into a Pt crucible and heated under a dynamic Ar flow at 2 °C min^{-1}. Baseline correction was performed with respect to an alumine sample heated under the same conditions.

X-ray diffraction patterns were obtained with a Philips PW 1729 diffractometer equipped with a Debye-Scherrer camera. Samples were exposed for 3–8 h to either the Cu K_α (Ni filter) or the Cr K_α (V filter) line.

Magnetic susceptibilities were determined at 21 °C by the Faraday method with a Bruker BE-10 magnet and a Mettler ME-21 electronic balance. Calibration was performed with $HgCo(NCS)_4$ [8]. All the hygroscopic compounds were handled in a KSE glove-box under nitrogen atmosphere with less than 10 ppm water.

Results and Discussion

Stoichiometry of the Complexes

Complexes with metal:ligand ratios equal to 1:1, 3:2, and 2:1 were isolated, generally under the form of polycrystalline powders with the characteristic colours of the Ln(III) ions.

With the 12-crown-4 ether, the isolation of stoichiometric compounds is quite difficult and depends, to a large extent, upon the exact experi-

TABLE IV. Thermogravimetric Data for Ln(TFA)$_3$ Complexes with 12-Crown-4 (12-4), 15-Crown-5 (15-5), and 18-Crown-6 (18-6) Ethers.

L	Ln	Starting compound		Transformation into 2:1 complexes			Remaining mass at 400 °C (%)	
		Ln:L	Stability range (°C)	% calc.	% exp.	Stability range (°C)	exp.	calc. (LnF$_3$)
12-4	La	1:1	→ 100	86.5	86.2	180–250	31.0	30.0
	Pr	3:2	→ 120	95.1	95.1	160–250	33.1	33.7
	Nd	2:1	→ 250				35.2	36.0
	Eu	3:2	→∼100	95.2	[a]	∼250[a]	34.3	36.0
	Er	3:2	→∼ 70	95.3	[a]	∼250[a]	36.0	38.6
15-5	La	2:1	→ 200				36.2	33.1
	Ce	2:1	→ 200				35.9	33.5
	Eu	2:1	→ 160				36.6	34.8
18-6	La	1:1	→ 200				26.0	26.4
	Pr	1:1	→ 180				27.7	26.6
	Sm	1:1	→ 180	82.3	82.3–81.3[b]	240–250[b]	29.5	27.5
	Eu	1:1	→ 140	82.5	80.4–78.9[b]	230–240[b]	30.4	27.7
	Gd	2:1	→ 220				36.4	34.1
	Tb	2:1	→ 170				36.6	34.3

[a] Ill-defined plateau. [b] Non-horizontal plateau.

mental conditions. For praseodymium, for instance, three different metal:ligand ratios are obtained. The complexes with Ln = La–Nd (1:1, La-Pr; 2:1, Nd, Sm; 3:2, Pr) are non-hygroscopic contrary to the coronates with Sm (2:1), Eu, and Er (3:2). The other heavier Ln(III) ions do not yield stoichiometric compounds.

With 15-crown-5 ether, 2:1 complexes are obtained for all the lighter Ln(III) ions (La–Eu); again, non-stoichiometric compounds are isolated with the heavier Ln(III) ions. In fact, the 2:1 complexes are slowly hydrolysed in the presence of traces of water, to give hydroxo compounds:

$$4[Ln(CF_3CO_2)_3]_2(C_{10}H_{20}O_5) + H_2O \longrightarrow CF_3COOH$$

$$+ [Ln_2(CF_3CO_2)_3(OH)(C_{10}H_{20}O_5)_2][Ln_2(CF_3CO_2)_8]$$

The formulation of the hydroxo complex has been demonstrated for Ln = Pr by a single-crystal X-ray diffraction study [9]. The hydrolysis may be followed by IR spectroscopy. When a slightly hydrated complex is placed into a dessicator, a sharp and characteristic absorption band appears at 3610 cm^{-1} after two hours and its intensity steadily increases with time. Elemental analyses of the hydrolysed complexes fall in between the calculated values for 2:1 complexes and for the completely hydrolysed product, which means that the hydrolysis is usually not complete. Freshly prepared complexes have always been used to record the thermal, magnetic, and spectroscopic data discussed below, to avoid complications due to this hydrolysis process. Such hydrolyses have often been noticed with trifluoroacetates [10], but apparently do not occur with the 12-crown-4 and 18-crown-6 complexes, at least at room temperature.

With 18-crown-6 ether, the lighter Ln(III) ions (La–Eu) form 1:1 complexes, whereas the heavier Ln(III) ions (Eu–Yb) and yttrium give 2:1 complexes. For europium, both metal:ligand ratios are observed and mixtures of them are often isolated.

Thermogravimetric analyses have been performed in order to find out if some of the complexes undergo a transformation into another stoichiometry, as has been observed for nitrato and chloro 1:1 coronates, some of which giving 4:3 complexes upon heating [11]. The data are listed in Table IV and typical thermograms are shown in Fig. 1. The thermal decomposition of anhydrous lanthanoid trifluoroacetates proceed in two steps to yield lanthanoid fluoride, carbon mono- and dioxide, carbonyl fluoride, and trifluoroacetyl fluoride [12]. The dehydration of Eu(TFA)$_3$·3H$_2$O occurs stepwise: it starts at 60 °C, the monohydrate is stable between 110 and 120 °C, and the anhydrous salt is obtained at 150 °C. The 1:1 and 3:2 complexes with 12-crown-4 ether undergo a transformation into 2:1 complexes before decomposing completely to yield the fluorides. The 15-crown-5 2:1 complexes do not form stable intermediates; they lose their hydration water between 50 and 100 °C and start to decompose completely between 160 and 200 °C. The 18-crown-6 1:1 complexes with Ln = La–Pr decom-

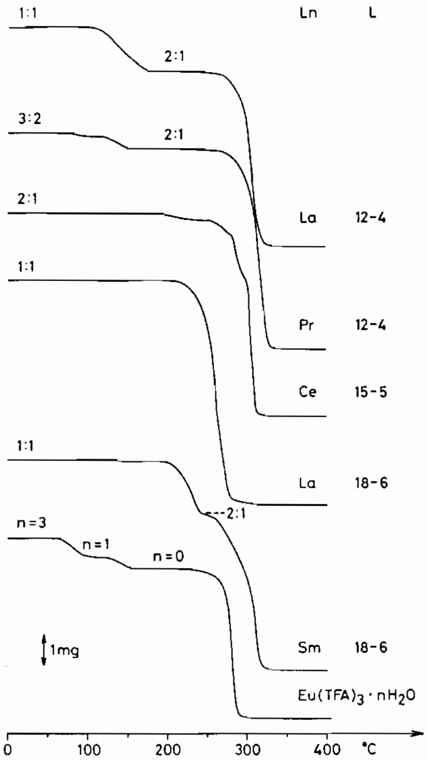

Fig. 1. Thermogravimetric curves for lanthanoid trifluoroacetate coronates with 12-crown-4 (12-4), 15-crown-5 (15-5), 18-crown-6 (18-6) ethers, and for $Eu(CF_3CO_2)_3 \cdot 3H_2O$. The Ln:L ratios are directly indicated on the curves.

pose directly between 180 and 200 °C without going through an intermediate 2:1 compound; on the contrary, such an intermediate is observed, although only on a short temperature range, for Ln = Sm, Eu. All the 2:1 complexes decompose mainly into lanthanoid fluoride. Therefore, with the exception of the 18-crown-6 1:1 complexes with La–Pr, this study shows that the compounds with a 2:1 metal:ligand ratio are thermally more stable than the other 1:1 or 3:2 complexes.

Vibrational, Structural and Magnetic Data

The local symmetry of the trifluoroacetate anion is low, at most C_s. Both the IR and Raman spectra of the complexes are therefore expected to display at least 15 bands arising from the anions. The distinction between the different coordination modes of the trifluoroacetate is not clearcut nd has not yet been unambiguously established [10]. Moreover, the vibrations of the polyether often interfere with the anion vibrations, so that a partial analysis could only be carried out. The ν_{as}(COO) mode of sodium trifluoroacetate appears at 1688 cm^{-1} [13]. This vibration is split into at least three broad components in the anhydrous lanthanoid trifluoroacetates (Ln = Nd: 1620, 1670sh, 1740 cm^{-1}). In the complexes, the corresponding absorptions display two main components and tend to be shifted towards higher wavenumbers. The ν_s(COO) mode appears at 1446 cm^{-1} in $Na(CF_3CO_2)$ and is blue-shifted 15–20 cm^{-1} in both the anhydrous lanthanoid trifluoroacetates and in the complexes, which may point to the presence of bridging and/or bidentate anions [14].

The main features of the ligand vibrations may be summarized as follows (*cf.* [4]):

(i) For 12-crown-4 complexes (Fig. 2), slightly different spectra are obtained for the various metal:ligand ratios. The shift of the ν_{as}(CCO) vibration upon complexation is −15 to −18 cm^{-1} (towards lower wavenumbers) whereas ν_s(CCO) is displaced by *ca.* the same amount towards higher wavenumbers. This is typical of a low to moderate interaction between the polyether and the metal ion.

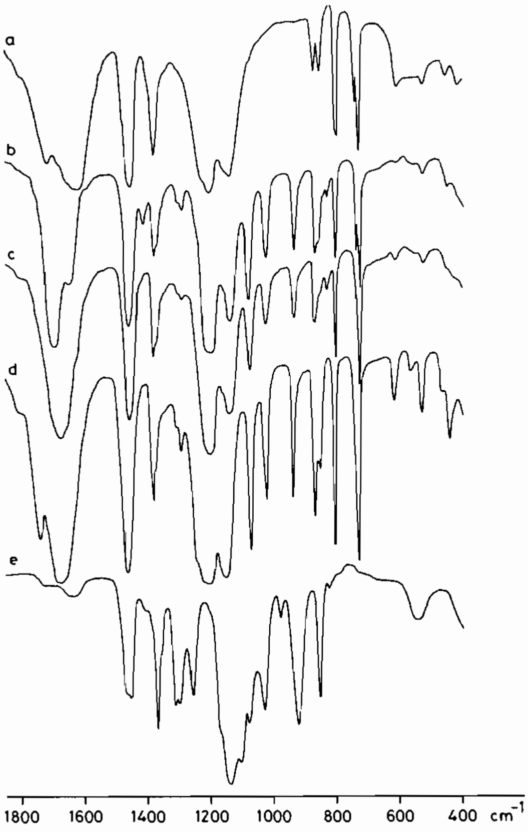

Fig. 2. IR spectra of: (a) $La(TFA)_3 \cdot 3H_2O$, (b) $La(TFA)_3 \cdot (C_8H_{16}O_4)$, (c) $[Pr(TFA)_3]_3 \cdot (C_8H_{16}O_4)_2$, (d) $[Nd(TFA)_3]_2 \cdot (C_8H_{16}O_4)$, and (e) 12-crown-4 ether.

(ii) For the 2:1 complexes with 15-crown-5 ether (Fig. 3), the ν_{as}(CCO) and ν_s(CCO) vibrations are shifted by *ca.* −20 and +14 cm^{-1}, respectively. The spectra of the hydrolysed complexes are essentially similar to the spectra of the 2:1 complexes, with the additional band at 3610 cm^{-1}.

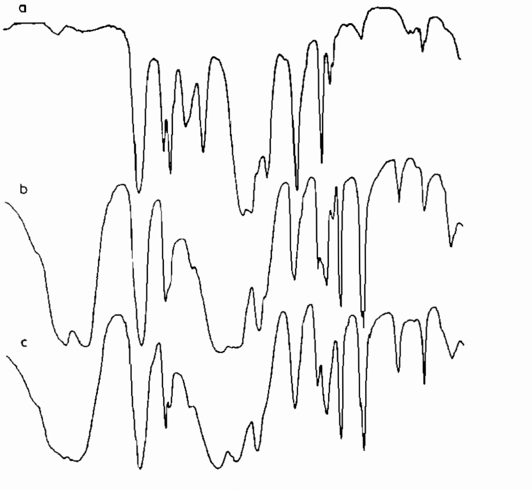

Fig. 3. IR spectra of: (a) 15-crown-5 ether, (b) [La(TFA)$_3$]$_2$·(C$_{10}$H$_{20}$O$_5$), and (c) [Eu(TFA)$_3$]$_2$·(C$_{10}$H$_{20}$O$_5$).

(iii) Beside some intensity changes and wavenumber shifts, the spectra of both 1:1 and 2:1 complexes with 18-crown-6 ether are quite comparable (Fig. 4). The shift of the ν_{as}(CCO) vibration is between –25 and –30 cm^{-1}. The ν_s(CCO) mode is split into several components upon complexation. The ring breathing mode is observed as a strong Raman emission band and a weak IR absorption band at *ca.* 880–885 cm^{-1}.

Combining informations from the vibrational spectra and from X-ray powder diagrams, the following isomorphous series could be characterized. With 12-crown-4 ether, the 1:1 complexes with Ln = La, Ce and the 2:1 complexes with Nd, Sm. With 15-crown-5 ether, all the 2:1 complexes (La–Sm; the Eu-compound is amorphous but its IR spectrum is very similar to the spectrum of the Sm-complex). With 18-crown-6 ether, the 1:1 complexes with Ln = La–Pr and the 2:1 complexes with Ln = Y, Eu, Ho (the Gd–Er complexes are amorphous, but their vibrational spectra are very similar to those of the Eu- and Ho-compounds). It is noteworthy that the 2:1 complexes with 18-crown-6 ether are genuine compounds and not simply a mixture of trifluoroacetates and 1:1 complexes.

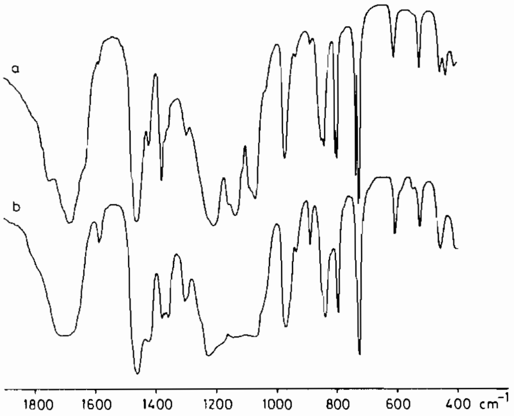

Fig. 4. IR spectra of: (a) [Eu(TFA)$_3$]$_2$·(C$_{12}$H$_{24}$O$_6$), and (b) Eu(TFA)$_3$·(C$_{12}$H$_{24}$O$_6$).

The amount of the ν_{as}(CCO) shift is often taken as a measure of the interaction between the polyether and the metal ion [4]. The values found for all the complexes studied are quite smaller than the largest shifts observed [4], so that this interaction may be characterized as being moderate. This is confirmed by the magnetic moments of the Ln(III) ions in these compounds (Table V). In the complexes with 12-crown-4 ether, these moments are close to the free ion values. For 15-crown-5 complexes, they are 2–7% lower. In the case of the 18-crown-6 1:1 complexes, they are 6–8% lower, whereas this

TABLE V. Corrected Magnetic Moments (Bohr Magnetons, at 21 ± 1 °C) of the Ln(III) Ions in the Ln(TFA)$_3$ Coronates.

Ln	μ_{theor} [a]	12-Crown-4			15-Crown-5 2:1	18-Crown-6		Ln(TFA)$_3$·3H$_2$O [16]
		1:1	2:1	3:2		1:1	2:1	
Ce	2.54	2.54 ± 0.02			2.37 ± 0.02	2.33 ± 0.02		2.66
Pr	3.62			3.56 ± 0.03	3.42 ± 0.03	3.47 ± 0.03		3.34
Nd	3.68		3.59 ± 0.03		3.52 ± 0.03	3.46 ± 0.03		3.56[b]
Sm	1.65		1.78 ± 0.02		1.62 ± 0.02	1.64 ± 0.02		2.10
Eu	3.40			3.32 ± 0.03			3.30 ± 0.03	3.45
Gd	7.94						7.89 ± 0.06	7.77
Tb	9.7						9.60 ± 0.07	9.36
Dy	10.6						10.57 ± 0.07	10.24
Ho	10.6						10.36 ± 0.07	10.48
Er	9.8						9.53 ± 0.07	9.40
Tm	7.6							7.32
Yb	4.5						4.34 ± 0.04	

[a] Free ion values [15]. [b] Anhydrous Nd(TFA)$_3$: 3.55 ± 0.03.

difference is reduced to 1–3% in the 2:1 complexes.

Luminescence Spectra

To complement the structural informations on the trifluoroacetate complexes, we have measured the high-resolution excitation and emission spectra of the europium coronates with 15-crown-5 and 18-crown-6 ethers, of both hydrated and anhydrous europium trifluoroacetates, and of the double salt $AgEu(CF_3CO_2)_4 \cdot 3CH_3CN$. These spectra have been recorded on powdered polycrystalline samples at 77 K, with a bandpass of 0.02 nm (excitation) of 0.01 nm (emission). The excitation spectra in the spectral region of the $^5D_0 \leftarrow {}^7F_0$ allowed us to determine the number of chemically different environments around the metal ion. The different sites have then be selectively excited to the $^5D_0$ level and the $^5D_0 \rightarrow {}^7F_J$ emission bands analysed for J = 1–4. The presence of one sharp $^5D_0 \leftarrow {}^7F_0$ component in the excitation spectrum of $Eu(CF_3CO_2)_3 \cdot 3H_2O$, with a width at half height of 1.9 cm^{-1}, reflects the presence of one metal site only (Fig. 5). The luminescence spectrum (Table VI) is also comprised of sharp bands. All the f–f transitions have a maximum number of components (2J + 1) and the $^5D_0 \rightarrow {}^7F_2$ transition is the more intense, which points to a low site symmetry without inversion centre. The relative intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions are 100, 158, 2, and 115 for J = 1, 2, 3, and 4. These findings are consistent with the crystal structure determination performed on isostructural $Pr(CF_3CO_2)_3 \cdot 3H_2O$ [17]. This salt contains centrosymmetric dimers with four bridging and two monodentate trifluoroacetate anions. The Pr(III) anion is 8-coordinate and its coordination polyhedron is a distorted square antiprism without any symmetry element. The spectra of the anhydrous salt are quite different (Fig. 6,

TABLE VI. Observed ^7F_J Energy Sublevels in cm^{-1} for $Eu(TFA)_3 \cdot 3H_2O$, at 77 K.

$^7F_0$	0	$^7F_4$ (a)	2789
		$^7F_4$ (b)	2839
$^7F_1$ (a)	321	$^7F_4$ (c)	2879
$^7F_1$ (b)	367	$^7F_4$ (d)	2943
$^7F_1$ (c)	421	$^7F_4$ (e)	2971
		$^7F_4$ (f)	3014
$^7F_2$ (a)	930	$^7F_4$ (g)	3027
$^7F_2$ (b)	980		
$^7F_2$ (c)	1049	$^5D_0$	17259
$^7F_2$ (d)	1093		
$^7F_2$ (e)	1148		
$^7F_3$ (a)	1865		
$^7F_3$ (b)	1877		
$^7F_3$ (c)	1900		
$^7F_3$ (d)	1915		
$^7F_3$ (e)	1957		
$^7F_3$ (f)	1980		

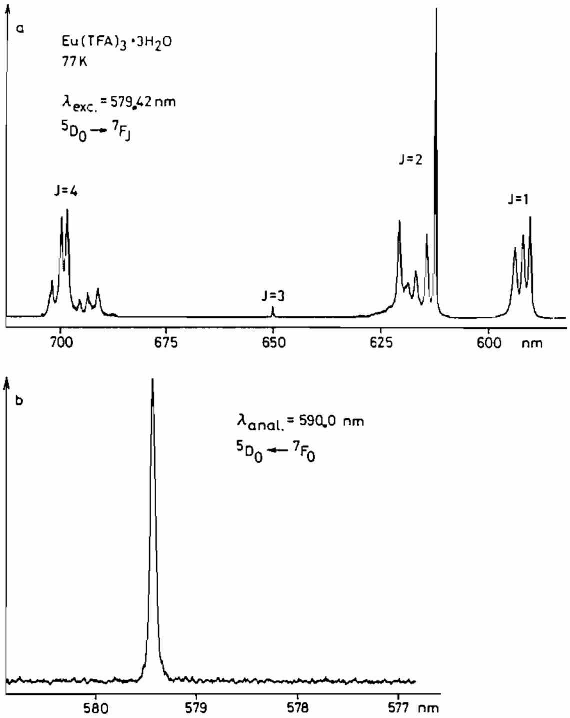

Fig. 5. Emission (a) and excitation (b) spectra of $Eu(CF_3CO_2)_3 \cdot 3H_2O$ at 77 K. Vertical scale: arbitrary units.

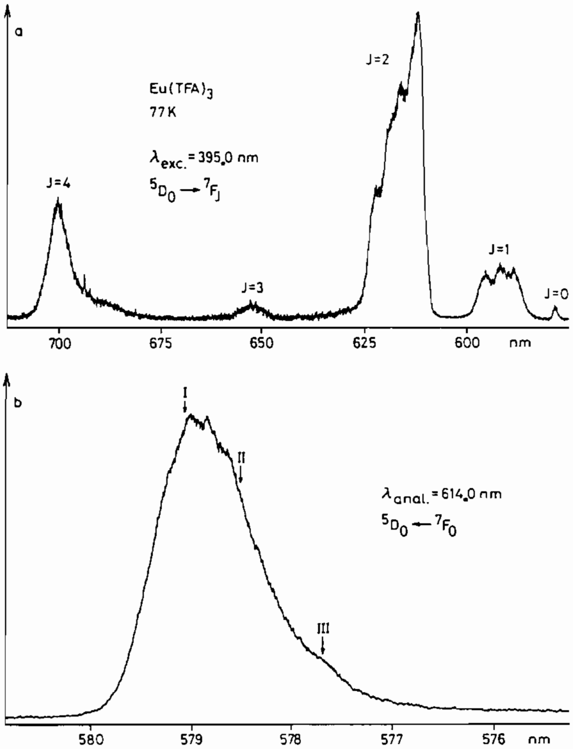

Fig. 6. Emission (a) and excitation (b) spectra of $Eu(CF_3CO_2)_3$, at 77 K. Vertical scale: arbitrary units.

TABLE VII. Emission Spectrum of Eu(TFA)$_3$ (I), [Eu(TFA)$_3$]$_2$·($C_{10}H_{20}O_5$) (II), and [(La:Eu)TFA$_3$]$_2$·($C_{10}H_{20}O_5$) (III), at 77 K.

I		II		III		Assignment
nm	cm^{-1}	nm	cm^{-1}	nm	cm^{-1}	
577.7w	17310	578.9	17274	578.8w	17277	$^5D_0 \rightarrow {^7F_0}$[a]
578.6	17283	579.4	17259	579.25	17264	
578.8	17277			579.45	17258	
579.0	17271			579.7w	17250	
579.2	17265			579.9w	17244	
588.8	16984	590.5	16935	590.0	16949	$^5D_0 \rightarrow {^7F_1}$
591.9	16895	592.3	16883	591.8	16898	
595.6	16790	593.8	16841	594.1	16832	
611.6	16351	612.1	16337	611.7	16348	$^5D_0 \rightarrow {^7F_2}$
613.4	16303	613.7	16295	612.6	16324	
614.6	16271	616.1	16231	613.4	16303	
615.5	16247	618.5	16168	618.7	16163	
622.1	16075			620.3	16121	
651.5	15349	651.5	15349			$^5D_0 \rightarrow {^7F_3}$
699.9	14288	690.4	14484	690.5	14482	$^5D_0 \rightarrow {^7F_4}$
		699.4	14298	692.0	14451	
				693.5	14420	
				698.8	14310	
				700.9	14267	

[a] Measured either on the excitation or on the emission spectrum; w indicates weak components.

Table VII). The $^5D_0 \leftarrow {^7F_0}$ transition is very broad (width at half height: 35 cm^{-1}) and displays several components. The emission bands obtained under excitation to the $^5L_6$ level are also broad and their fine structure cannot be analyzed in details. The relative intensities of the $^5D_0 \rightarrow {^7F_J}$ transitions are 100, 615, 6, and 220 for J = 1, 2, 3, and 4. Selective excitations at the wavelengths denoted by I, II and III, in Fig. 6, yield similar emission spectra that only slightly differ in the structure of the $^5D_0 \rightarrow {^7F_2}$ band. That is, the compound contains several, closely related chemical environments for the Eu(III) ion with efficient energy transfers taking place between them. We conclude that the dehydration of Eu(CF_3CO_2)$_3$·3H_2O leads to the formation of polymeric species containing bridging trifluoroacetate moieties.

The excitation spectrum of [Eu(CF_3CO_2)$_3$]$_2$($C_{10}H_{20}O_5$) (Fig. 7) is consistent with the presence of two chemically different sites for Eu(III), in agreement with the findings of the crystal structure determination for the praseodymium hydroxo complex [9]. Indeed, the two components of the $^5D_0 \leftarrow {^7F_0}$ transition at 17274 and 17259 cm^{-1} have large widths at half height, 15 and 20 cm^{-1}, respectively, which is consistent with the presence of di- and/or polymeric species. According to a recent study [18], the energy of the 0–0 transition may be correlated to the total coordinated ligand charge. When the environment about the Eu(III) ion becomes more negative, this transition is shifted to lower energy, due to the nephelauxetic effect. If such a correlation were valid in our case, the 17274 cm^{-1} component would correspond to a cationic species and the other one to an anionic complex. Selective excitation of either of these two components yields undistinguishable spectra that are dominated by the $^5D_0 \rightarrow$

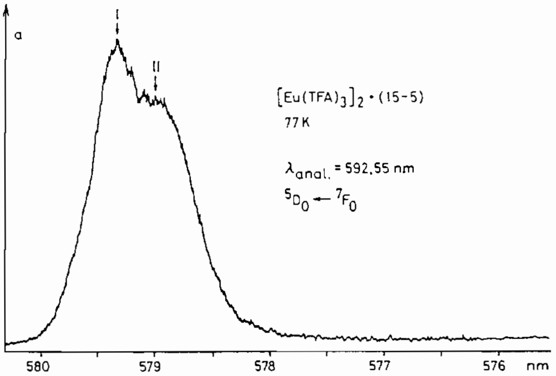

Fig. 7. Excitation spectrum of [Eu(CF_3CO_2)$_3$]$_2$ ($C_{10}H_{20}O_5$) at 77 K. Vertical scale: arbitrary units.

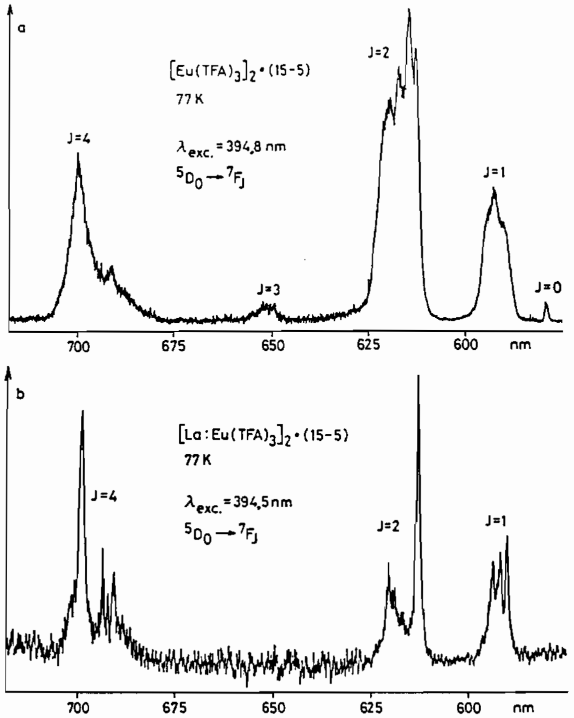

Fig. 8. Emission spectra of (a) $[Eu(CF_3CO_2)_3]_2(C_{10}H_{20}O_5)$ and (b) $[(La:Eu)(CF_3CO_2)_3]_2(C_{10}H_{20}O_5)$ at 77 K. Vertical scale: arbitrary units.

$^7F_2$ transition and which contain broad bands (Fig. 8a, Table VII). The relative intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions are 100, 312, 6, and 145 for J = 1, 2, 3, and 4. The presence of di- or polymeric species in the 2:1 complexes is ascertained by the following experiment. We doped the lanthanum 2:1 complex with 4% Eu and recorded its excitation and emission spectra. In this way, the energy transfers between the different sites are minimized, sharper bands are expected and, indeed, observed. For instance, the main component of the $^5D_0 \leftarrow {}^7F_0$ transition.at 17264 cm^{-1} has a width at half height of 3.3 cm^{-1}. The emission bands are also sharp (Fig. 8b, Table VII); the intensity of the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_2$ transitions are smaller than for $[Eu(CF_3CO_2)_3]_2(C_{10}H_{20}O_5)$ but the overall shapes of all the transitions are similar to the transitions of the Eu-coronate.

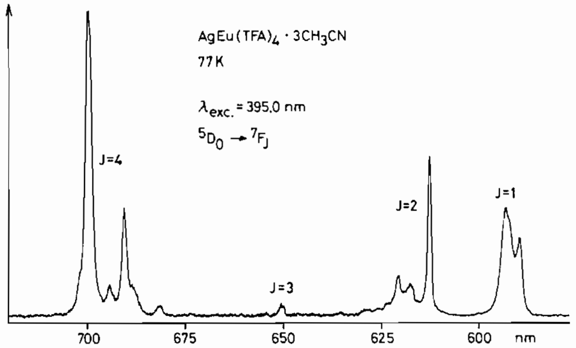

Fig. 9. Emission spectrum of $AgEu(CF_3CO_2)_4 \cdot 3CH_3CN$ at 77 K. Vertical scale: arbitrary units.

TABLE VIII. Emission spectra of $AgEu(TFA)_4 \cdot 3CH_3CN$ (IV) and $[Eu(TFA)_3]_2 \cdot (C_{12}H_{24}O_6)$ (V), at 77 K.

IV		V		Assignment
nm	cm^{-1}	nm	cm^{-1}	
579.2	17265	578.1	17298	$^5D_0 \rightarrow {}^7F_0$[a]
579.3	17262	579.6	17253	
579.4	17259			
579.6	17253			
589.9	16952	586.0	17065	$^5D_0 \rightarrow {}^7F_1$
593.4	16852	590.9	16923	
		592.4	16880	
		592.6	16875	
		597.8	16728	
612.9	16316	609.8	16399	$^5D_0 \rightarrow {}^7F_2$
616.6	16218	611.3	16359	
620.9	16106	612.4	16329	
		617.0	16207	
		617.9	16184	
		618.5	16168	
		619.9	16132	
		620.9	16106	
650.9	15363	650.6	15370	$^5D_0 \rightarrow {}^7F_3$
681.9	14665	684.8	14603	$^5D_0 \rightarrow {}^7F_4$
688.8	14518	685.7	14584	
690.9	14474	686.0	14577	
694.5	14399	689.9	14495	
699.9	14288	694.7	14395	
		696.2	14364	
		698.6	14314	
		700.4	14278	
		701.6	14253	
		702.2	14241	

[a] Measured either on the excitation or on the emission spectrum.

In order to find out if typical bands arising from tetrakis(trifluoroacetato) species may be recognised in the spectra discussed above, we have also studied the double salt $AgEu(CF_3CO_2)_4 \cdot 3CH_3CN$. Its synthesis has been reported by Le Mire *et al.* [19]. According to NMR measurements, a relatively high, cubic symmetry may be assigned to the species $[Ln(CF_3CO_2)_4]^-$ in solution, in contradiction with the IR spectra [19]. The overall emission spectrum of the Eu-containing double salt (Fig. 9, Table VIII) is typically that of a well-defined molecular species. The relative intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions are 100, 87, 2, and 210 for J = 1, 2, 3, and 4. A cubic symmetry cannot be assigned to the complex since the $^5D_0 \rightarrow {}^7F_1$ transition is split into at least two components. On the other hand, the limited number of components of the $^5D_0 \rightarrow {}^7F_J$ transitions and the extremely weak intensity of the $^5D_0 \rightarrow {}^7F_0$ transition are typical of a relatively high symmetry, possibly D_4 or D_{2d}. Blight and Kepert [20] have carried out a detailed analysis of the interligand repulsion of [M(bidentate)$_4$] in which they found that the potential energy surface is critically dependent on the 'bite' of the bidentate ligand. The bite is defined as the distance between two donor atoms of the same ligand divided by the metal–donor distance. For ligands having small bites, there is a single minimum corresponding to the D_{2d} dodecahedron. As the bite of the bidentate ligand increases, a continuous change is predicted towards a polyhedron approximating the D_2 square antiprism. When the bite of the bidentate ligand becomes similar to the distance between donor atoms in [M(monodentate)$_8$] three stereochemistries are equally probable, the D_2 and D_4 square antiprisms and the D_2 dodecahedron. In our case, the bite is small and may be estimated to 0.85 using the data for the bidentate trifluoroacetate found in the polymeric anion $[Pr(CF_3CO_2)_4]_n^{n-}$ [9]. This is comparable to the bite of a bidentate nitrate in $[Eu(NO_3)_5]^{2-}$ [21] which is equal to 0.87. The coordination polyhedron for $[Eu(CF_3CO_2)_4]^-$ is therefore expected to be close to the D_{2d} dodecahedron. A detailed analysis of the emission spectrum has not been carried out because the $^5D_0 \leftarrow {}^7F_0$ transition shows that $AgEu(CF_3CO_2)_4 \cdot 3CH_3CN$ possesses at least four different sites for the metal ion. However, one notes that in D_{2d} symmetry, 0, 2, 2, and 3 transitions are allowed from $^5D_0$ to the ^7F_J manifold for J = 0, 1, 2, and 4, respectively. The corresponding numbers for D_4 and D_2 symmetries are 0, 2, 1, 3 and 0, 3, 3, 6. The observed spectrum is therefore consistent with a coordination polyhedron approximating to a slightly distorted D_{2d} dodecahedron. It is noteworthy that despite some similarities, none of the transitions of $AgEu(CF_3CO_2)_4 \cdot 3CH_3CN$ are seen in the emission spectra of the other studied compounds.

The excitation spectrum of $[Eu(CF_3CO_2)_3]_2(C_{12}H_{24}O_6)$ is displayed in Fig. 10 and contains two well-separated components at 17253 and 17298 cm^{-1}, with widths at half height of 1.5 and 5 cm^{-1}, respectively. According to the above-mentioned criterion, the former component could be assigned to a negatively charged species and the other one to a cationic complex. Surprisingly, selective excitations give rise to almost identical emission spectra with narrow bands (Fig. 10, Table VIII). The $^5D_0 \rightarrow {}^7F_1$ transition is split into five components, which means that one site probably possesses a relatively high symmetry. Since the 18-crown-6 ether has a cavity large enough to encapsulate completely a lanthanide ion (*cf.* $[Eu(NO_3)_2(C_{12}H_{24}O_6)]^+$ [22]), one may think that the trifluoroacetate 2:1 complex contains a similar cation, as well as an anionic species similar to that in $AgEu(CF_3CO_2)_4 \cdot 3CH_3CN$. Indeed, one component of the $^5D_0 \rightarrow {}^7F_0$ transition of this latter also appears at 17298 cm^{-1}. The other transitions, however, do not coincide with those of the silver double salt.

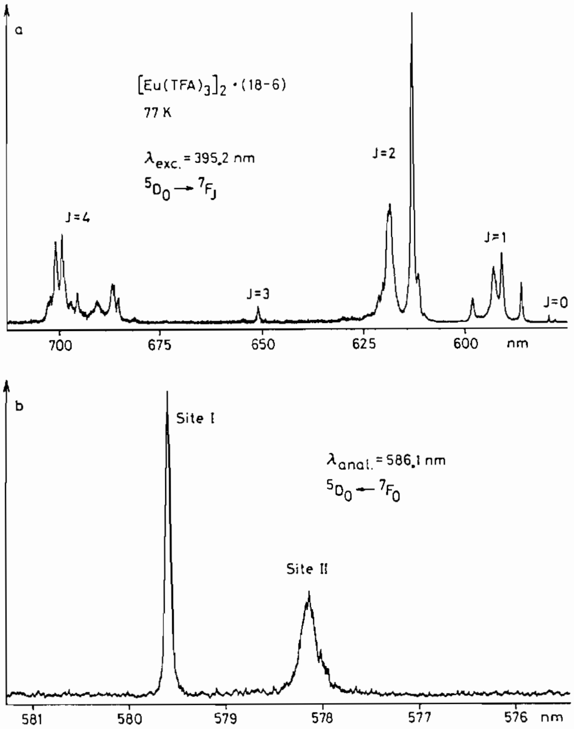

Fig. 10. Emission (a) and excitation (b) spectra of $[Eu(CF_3Co_2)_3]_2(C_{12}H_{24}O_6)$ at 77 K. Vertical scale: arbitrary units.

Solution Study

The molar conductivities of 0.001 M solutions of the complexes, Λ_M, have been measured at room temperature in several organic solvents. In acetonitrile and propylene carbonate, the complexes with 12-crown-4 and 15-crown-5 ethers are non-electrolytes and Λ_M ranges between 3 and 6 Ω^{-1} cm^2 mol^{-1}. Slightly higher values are obtained for both 1:1 and 2:1 complexes with 18-crown-6 ether: *ca.* 15 and 35 Ω^{-1} cm^2 mol^{-1} in acetonitrile, in which 1:1 electrolytes have typical Λ_M between 120 and 160 Ω^{-1} cm^2 mol^{-1} [23]. This indicates that some dissociation takes place in the solutions containing the 2:1 complexes, possibly into complex anions and cations. Molar conductivities between 30 and 65 Ω^{-1} cm^2 mol^{-1} have been observed for solutions of the 4:3 lanthanoid nitrate complexes with 18-crown-6 [11] and 21-crown-7 [24] ethers which contain $[Ln(NO_3)_2L]^+$ cations [4, 25]. In methanol, all the complexes, as well as the anhydrous and hydrated trifluoroacetates have Λ_M between 58 and 66 Ω^{-1} cm^2 mol^{-1}. These values are close to that for 1:1 electrolytes (80–115 Ω^{-1} cm^2 mol^{-1} [23]).

^1H NMR measurements (60 MHz) have been performed on CD_3CN solutions of the complexes having sufficient solubility (5×10^{-3} to 5×10^{-2} M), in order to estimate their apparent formation constants. The 1:1 lanthanum coronate with 12-crown-4 ether exhibits only one singlet from the complexed polyether, at 3.88 ppm with respect to TMS; no free ligand resonance is observed and Log β_1 is estimated to be >7. A similar situation prevails for the 1:1 lanthanum complex with 18-crown-6 ether: the complexed ligand resonance appears at 3.94 ppm and Log β_1 is >6. For $Sm(CF_3CO_2)_3 \cdot (C_{12}H_{24}O_6)$, two singlets are observed at room temperature and assigned to the free (3.52 ppm) and bonded (2.49 ppm) ligand. Their integration yields an apparent formation constant Log β_1 of 4.4. These signals are broadened and displaced at −35 °C (3.50 and 2.68 ppm).

Conclusion

This study has shown that a 2:1 metal:ligand ratio is favored in the solid state for lanthanoid trifluoroacetate coronates with simple crown ethers. We trace the origin of this fact back to the tendency of the trifluoroacetate anion to form bridges between metal ions in order to minimize the steric hindrance of the CF_3 group and hence to form relatively stable di- or polymeric species. At the present time, only one case of a trifluoroacetate anion bidentate to the same metal ion has been found: in the anionic polymeric chain $[Pr(CF_3CO_2)_4]_n^{n-}$ [9]. In view of the many chemically different metal sites observed in $AgEu(CF_3CO_2)_4 \cdot 3CH_3CN$ by luminescence spectroscopy, we therefore question that $[Eu(CF_3CO_2)_4]^-$ may exist as such, at least in the solid state.

Despite the limited number of experimentally available data, it is interesting to compare the apparent formation constants of 1:1 complexes with 18-crown-6 ether, Log β_1. For lanthanum, it amounts to 4.4 (CH_3CN) [11], >6 (CH_3CN), and 8.75 (propylene carbonate [26]) for nitrate, trifluoroacetate and trifluoromethanesulfonate, respectively. The same values for the samarium complexes in the same solvents are *ca.* 3 (interpolated from Nd- and Eu-values [11]), 4.4, and 8.1 [26]. That is, Log β_1 decreases when the donor strength of the anion increases. This study therefore confirms the essential influence of the anion on both the stoichiometry and the formation constants of the lanthanoid coronates.

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