

Trifluoromethanesulfonate as Non-coordinating Anion in Lanthanide Complexes

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Lanthanide(III) trifluoromethanesulfonates and their complexes with neutral ligands containing one or two oxygen and nitrogen atoms have been prepared and characterized. IR spectra, absorption and emission f-f spectra of the trifluoromethanesulfonates indicated that the sulfonate groups are not coordinated to the cation in all cases. The complexes have 8-coordinated arrangements of the [LnO₈], [LnO₄N₄] and [LnN₈] types. Absorption and emission f-f spectra of the complexes have also been performed and discussed. Information on the basicity of the ligand and symmetry of the complexes have been drawn out.

Introduction

The trifluoromethanesulfonic acid is one of the strongest of all known acids. On the basis of conductivity measurements in anhydrous acetic acid it has been found to be a stronger acid than the perchloric and fluorosulfonic acids [1, 2]. Studies on the stability of the olefin-silver(I) π -complexes indicated the following series of acid strength: $\text{CF}_3\text{SO}_3\text{H} > \text{HSbF}_6 > \text{HBF}_4 > \text{HClO}_4$ [3–5]. The use, thus, of trifluoromethanesulfonates to prepare metal complexes should minimize the anion coordination and achieve full ligand coordination.

Lanthanide(III) trifluoromethanesulfonates having general formula $\text{Ln}(\text{CF}_3\text{SO}_3)_3 \cdot n\text{H}_2\text{O}$ have been prepared by reaction of oxides or carbonates with the acid, but only some U.S. Patents and analytical and thermoanalytical properties are known [6–8].

In this paper we report the synthesis, characterization and spectroscopic properties of lanthanide(III) trifluoromethanesulfonates and their complexes with some neutral ligands having 8-coordinated structures.

Experimental

Lanthanide(III) trifluoromethanesulfonates were prepared by treating a slight excess of the oxide or carbonate in ethanol or acetonitrile suspension with the acid in the same solvent. The solution was filtered and evaporated in a rotating evaporator until copious

crystalline precipitates formed; they were filtered off, washed with small amounts of the appropriate solvent and dried *in vacuo* at room temperature.

Synthesis of the Complexes

The complexes of lanthanide(III) trifluoromethanesulfonates with the following ligands: cyclic ethylene urea (EU), cyclic propylene urea (PU), 2,2'-bipyridine N,N'-dioxide (bipyO₂), pyridine N-oxide (pyO), picolinamide (PA) and 1,10-phenanthroline (phen) were prepared.

Complexes with PU and EU

To 1 mmol of the lanthanide ion (Ln = La, Pr, Nd, Eu, Ho, Er) in 10 ml of anhydrous ethanol were added 8 mmol of the ligand dissolved in the minimum required volume of ethanol (150 ml). The boiling solutions were stirred and evaporated until the volume was reduced to 50 ml. From the cooled solutions fine crystals separated; they were filtered off, washed with ethanol and dried *in vacuo* at room temperature.

Complexes with BipyO₂

To 1 mmol of the hydrated cation (Ln = La, Nd, Sm, Eu, Tb, Ho) in 10 ml of boiling anhydrous ethanol were added 5 mmol of bipyO₂ in 50 ml of hot ethanol. The complexes precipitated slowly as crystalline powder. The precipitates were filtered off, washed with ethanol and dried *in vacuo* at room temperature.

Complexes with PyO and PA

To 1 mmol of the cation (Ln = La, Pr, Nd, Eu, Tb, Ho) in 5 ml of anhydrous ethanol were added 10 ml of triethylorthophosphate as dehydrating agent and the resulting solution refluxed under dry nitrogen for 2 h. To the boiling solution were added 9 mmol of pyO or 5 mmol of PA in 20 ml of ethanol and refluxed for 30 min. Microcrystalline products formed on cooling the solution or by addition of successive small amounts of anhydrous diethyl ether; they were filtered off, washed with ethanol-diethyl ether mixture (1:5) and dried *in vacuo* at room temperature.

Complexes with Phen

To 1 mmol of the cation (Ln = La, Pr, Nd, Eu) in 5 ml of anhydrous ethanol were added 6 mmol of phen in 10 ml of ethanol and the solution refluxed for 10 min. Microcrystalline products separated from the cooled solutions; they were filtered off, washed with ethanol and dried *in vacuo* at room temperature.

Analysis

Lanthanides were determined by gravimetric (oxalate) method. The water molecules content was determined by the Karl Fisher method and the results compared with the thermoanalytical results.

Physico-chemical Measurements

IR spectra were obtained by a Perkin-Elmer 577 spectrophotometer by KBr pellets and nujol mulls. Electronic absorption spectra were recorded with an Optical CF4NI spectrophotometer equipped with 5 cm quartz cells; the diffuse reflectance spectra were recorded with the same instrument equipped with a single-beam reflectance attachment using solid compounds pasted with nujol and spread on a disk of filter paper [9]. The absorption intensity, presented as oscillator strength, was calculated from the expression:

$$P = 4.31 \times 10^{-9} \left[\frac{9\eta}{(\eta^2 + 2)^2} \right] \int \epsilon(\nu) \delta\nu$$

where η is the refractive index of the solution and ϵ the molar extinction coefficient at the wavelength ν . Electrolytic conductivity was measured with an Amel 951 conductivity bridge at 25 ± 0.1 °C with a conventional closed cell. Thermal analysis was performed with a Mettler vacuum thermoanalyzer in dynamic nitrogen and with an heating rate of 2 °C min^{-1} . The fluorescence spectra were obtained by a Perkin-Elmer MPF-3L fluorescence spectrophotometer from solid compounds and acetonitrile, ethanol and aqueous solutions exciting with near ultraviolet radiations at room and liquid nitrogen temperatures. Resolution was better than 10 cm^{-1} .

Results and Discussion

According to previous reports [8] the trifluoromethanesulfonates we obtain, contain nine molecules of water, but species containing less than nine molecules can be obtained by heating the enneahydrated species to over 100 °C under reduced pressure; these are, however, hygroscopic and exposure to the moist air causes the formation of the final stable enneahydrated species.

Selected analytical data and molar conductivity of the prepared compounds are reported in Table I.

The Lanthanide(III) Trifluoromethanesulfonates

The lanthanide(III) trifluoromethanesulfonates are soluble in water, alcohols and acetonitrile. Molar conductivity values obtained from aqueous solutions vary between 360 and 380 $\text{ohm}^{-1} \text{cm}^2 M^{-1}$ for $1-2 \times 10^{-3} M$ and between 395 and 415 $\text{ohm}^{-1} \text{cm}^2 M^{-1}$ for $1-2 \times 10^{-4} M$ solutions. In acetonitrile the ranges of values are $280-300$ $\text{ohm}^{-1} \text{cm}^2 M^{-1}$ for $0.9-1 \times 10^{-3} M$ and $390-370$ $\text{ohm}^{-1} \text{cm}^2 M^{-1}$ for $0.9-1 \times 10^{-4} M$ solutions. Some data are lower than those reported for 1:3 electrolytes, but they can be attributed to ion pairs.

One intense and broad band at $1270-1265$ cm^{-1} and two weaker and sharp ones at $1038-1035$ cm^{-1} and $640-638$ cm^{-1} appear in the IR spectra of the enneahydrated trifluoromethanesulfonates; they can be assigned, respectively, to the stretching ν_4 (E), ν_1 (A₁) and deformation ν_3 (A₁) modes of the C_{3v} symmetry -SO₃ group (six normal modes of vibrations for the tetrahedral ZXY₃ type molecule). The ν_4 mode is frequently mixed with the ν_1 mode of the -CF₃ group and appears as a very intense and broad band around 1250 cm^{-1} . The weak band appearing at $780-775$ cm^{-1} is due to the stretching ν_2 (A₁) (C-S) mode while the two medium intensity bands at $530-528$ and $352-350$ cm^{-1} are assigned respectively to the bending (ν_5 (E)) and rocking (ν_6 (E)) modes of the -SO₃ group [10]. This spectral pattern is relatively simple (six bands arising from the -SO₃ group) and indicate the presence of only one type of sulfonate group; on the other hand, the three oxygen atoms are equivalent thus suggesting that only ionic trifluoromethanesulfonate groups act in these systems. If replacement of inner-sphere water molecules by trifluoromethanesulfonate groups occur on dehydration, both A₁ and E modes of the -SO₃ group (C_{3v} symmetry) should split and more than six bands must be assigned (nine normal modes of vibrations for the ZXY₂W type molecule). The IR spectra of the lanthanide(III) trifluoromethanesulfonates heated from 130 to 200 °C for 30 min under reduced pressure ($\sim 10^{-2}$ mm Hg) are similar to the spectra of the enneahydrated species, except for a broadness of the band at 1260 cm^{-1} and a small splitting of the bands at 1035 and 640 cm^{-1} . This spectral pattern indicates that distortion from the C_{3v} symmetry occurs for the sulfonate group on dehydration, but the dimension of the changes suggests that it must be more reasonably attributed to solid state effects rather than to coordination with cation.

The intensity of the hypersensitive transitions $^4I_{9/2} \rightarrow ^4G_{5/2}$ in Nd³⁺ ion and $^5I_8 \rightarrow ^5G_6$ in Ho³⁺ ion has been measured in aqueous, ethanolic and acetonitrile solutions. Changes in the band shape and intensity occur on passing from the aqueous to the non-aqueous solutions and, for these, from the enneahydrated to the partially or completely [8] dehydrated species. These changes are, however, slight

TABLE I. Selected Analytical Data and Molar Conductivity ($\text{ohm}^{-1} \text{cm}^2 \text{M}^{-1}$, at 25 ± 0.1 °C) in Acetonitrile of Lanthanide(III) Trifluoromethanesulfonates and Their Complexes (in parenthesis the calcd. values).

	% C	% H	% N	% Ln	Λ_M ($\text{c} \times 10^3$)	
Nd(CF ₃ SO ₃) ₃ ·9H ₂ O	5.03(4.78)	2.48(2.41)		19.37(19.14)	270	1.15
Eu(CF ₃ SO ₃) ₃ ·9H ₂ O	5.13(4.73)	2.39(2.38)		20.12(19.96)	300	0.95
Ho(CF ₃ SO ₃) ₃ ·9H ₂ O	4.80(4.65)	2.47(2.34)		21.02(21.30)	295	0.98
Tm(CF ₃ SO ₃) ₃ ·9H ₂ O	4.50(4.63)	2.41(2.33)		21.57(21.71)	285	1.02
La(PU) ₈ (CF ₃ SO ₃) ₃	30.94(30.31)	4.58(4.65)	15.98(16.16)	10.32(10.01)	210 ^c	1.10
Nd(PU) ₈ (CF ₃ SO ₃) ₃			16.00(16.10)	10.48(10.36)	235 ^c	1.00
Eu(PU) ₈ (CF ₃ SO ₃) ₃			15.87(16.01)	11.03(10.86)	230 ^c	1.05
Er(PU) ₈ (CF ₃ SO ₃) ₃	30.55(29.70)	4.60(4.56)	16.03(15.83)	11.68(11.82)	210 ^c	1.20
Eu(EU) ₈ (CF ₃ SO ₃) ₃	26.12(25.18)	3.70(3.76)	17.01(17.40)	11.76(11.80)	220 ^c	1.03
Ho(EU) ₈ (CF ₃ SO ₃) ₃	25.31(24.93)	3.80(3.73)	16.92(17.23)	13.03(12.69)	240 ^c	0.97
La(pyO) ₈ (CF ₃ SO ₃) ₃			8.27(8.32)	10.45(10.31)	305	1.30
Nd(pyO) ₈ (CF ₃ SO ₃) ₃	39.12(38.17)	3.03(2.98)	8.12(8.28)	10.33(10.66)	290	1.35
Eu(pyO) ₈ (CF ₃ SO ₃) ₃			8.03(8.24)	11.25(11.17)	310	1.12
Ho(pyO) ₈ (CF ₃ SO ₃) ₃	36.75(37.60)	2.87(2.94)	7.98(8.16)	11.87(12.01)	305	1.20
La(bipyO ₂) ₄ (CF ₃ SO ₃) ₃	38.51(38.57)	2.37(2.41)	8.00(8.37)	10.34(10.38)	310	1.20
Nd(bipyO ₂) ₄ (CF ₃ SO ₃) ₃			7.99(8.34)	10.61(10.73)	335	0.98
Eu(bipyO ₂) ₄ (CF ₃ SO ₃) ₃	38.15(38.20)	2.47(2.39)	8.31(8.29)	11.37(11.24)	330	1.01
Ho(bipyO ₂) ₄ (CF ₃ SO ₃) ₃	36.81(37.84)	2.53(2.36)	7.95(8.21)	12.15(12.45)	340	0.95
La(PA) ₄ (CF ₃ SO ₃) ₃ ·H ₂ O ^a			9.81(10.26)	13.01(12.71)	330	1.05
Nd(PA) ₄ (CF ₃ SO ₃) ₃ ·H ₂ O ^a	28.73(29.53)	2.50(2.39)	10.35(10.21)	12.99(13.14)	345	0.95
Eu(PA) ₄ (CF ₃ SO ₃) ₃ ·2H ₂ O ^a			9.66(9.97)	13.72(13.53)	315	1.18
Ho(PA) ₄ (CF ₃ SO ₃) ₃ ·2H ₂ O ^a	27.62(28.53)	2.46(2.48)	10.13(9.86)	14.66(14.51)	320	1.05
La(phen) ₄ (CF ₃ SO ₃) ₃	47.92(46.87)	2.38(2.47)	8.34(8.57)	10.75(10.63)	315	1.20
Nd(phen) ₄ (CF ₃ SO ₃) ₃			8.12(8.54)	11.09(10.99)	300	1.40
Eu(phen) ₂ (CF ₃ SO ₃) ₃ ·4H ₂ O ^b	30.82(31.43)	2.40(2.34)	5.34(5.43)	15.07(14.73)	310	1.30

^aThe thermogravimetric and differential thermal analysis show that the dehydration begins endothermically at 70–80 °C and is complete at 110 °C; this suggests only un-coordinated water molecules. ^bThe dehydration begins at 110 °C and is complete at 160 °C. ^cIn nitromethane–ethanol mixture (9:1).

TABLE II. Intensity, as Oscillator Strength ($10^6 \times P$), of the $^4I_{9/2} \rightarrow ^4G_{5/2}$ in Nd³⁺ Ion and $^5I_8 \rightarrow ^5G_6$ in Ho³⁺ Ion Hypersensitive Transitions.

Complex	$10^6 \times P$		
	H ₂ O	C ₂ H ₅ OH	CH ₃ CN
Nd(CF ₃ SO ₃) ₃ ·9H ₂ O	8.03	9.35	11.09
Nd(CF ₃ SO ₃) ₃ ·9H ₂ O + CF ₃ SO ₃ H (c = 4 M)	8.35	10.84	12.76
Ho(CF ₃ SO ₃) ₃ ·9H ₂ O	4.95	8.14	11.95
Ho(CF ₃ SO ₃) ₃ ·9H ₂ O + CF ₃ SO ₃ H (c = 4 M)	5.70	10.16	13.60
Nd(PU) ₈ (CF ₃ SO ₃) ₃	8.91	10.22 ^a	14.85
Ho(PU) ₈ (CF ₃ SO ₃) ₃		11.84 ^a	16.38
Nd(EU) ₈ (CF ₃ SO ₃) ₃		10.03 ^a	14.70
Nd(pyO) ₈ (CF ₃ SO ₃) ₃		27.92	28.65
Ho(pyO) ₈ (CF ₃ SO ₃) ₃	7.74	29.74	34.86
Nd(bipyO ₂) ₄ (CF ₃ SO ₃) ₃		57.31	57.88
Ho(bipyO ₂) ₄ (CF ₃ SO ₃) ₃ ·H ₂ O		113.08	112.37
Nd(PA) ₄ (CF ₃ SO ₃) ₃ ·H ₂ O	8.55	28.05	28.74
Ho(PA) ₄ (CF ₃ SO ₃) ₃ ·2H ₂ O		34.57	35.10
Nd(phen) ₄ (CF ₃ SO ₃) ₃			22.35

^aIn nitromethane–ethanol mixture (1:1).

and can be reasonably attributed to changes in the solvation molecules. The intensity values measured for the various solutions are approximately the same as found for the perchlorates and tetrafluoroborates and point out the non-coordinating (or very weak) property of the trifluoromethanesulfonate group. The addition of $\text{CF}_3\text{SO}_3\text{H}$ to the cation in acetonitrile, so that total CF_3SO_3^- concentrations from 0.01 to 4.0 M are realized, causes more pronounced changes in the band shape and intensity of the hypersensitive transitions (Fig. 1, Table II). The enneahydrated ion $[\text{Ln}(\text{OH}_2)_9]^{3+}$ has been described in terms of tricapped trigonal prism and D_{3h} site symmetry [11]. The europium trifluoromethanesulfonate in aqueous solution upon excitation to the $^5\text{L}_6$ level (~ 395 nm) exhibits an emission spectrum which consists of two poorly resolved bands associated with the $^5\text{D}_0 \rightarrow ^7\text{F}_{1,2}$ transitions. No line appears in the region of the $^5\text{D}_0 \rightarrow$

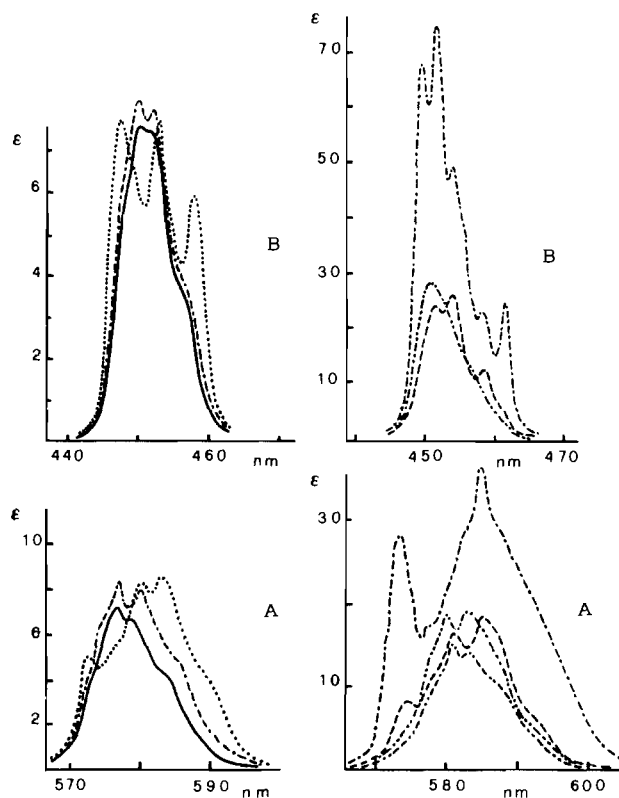


Fig. 1. $f-f$ absorption spectra in acetonitrile solution. The $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$ in Nd^{3+} ion and $^5\text{I}_8 \rightarrow ^5\text{G}_6$ in Ho^{3+} ion hypersensitive transitions. A: (—) $\text{Nd}(\text{CF}_3\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$; (---) $\text{Nd}(\text{CF}_3\text{SO}_3)_3 \cdot 9\text{H}_2\text{O} + \text{CF}_3\text{SO}_3\text{H}$ ($c_{\text{CF}_3\text{SO}_3^-} = 4.0$ M); (····) $\text{Nd}(\text{PU})_8(\text{CF}_3\text{SO}_3)_3$; (----) $\text{Nd}(\text{pyO})_8(\text{CF}_3\text{SO}_3)_3$; (· · · · ·) $\text{Nd}(\text{PA})_4(\text{CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$; (---) $\text{Nd}(\text{bipyO})_2(\text{CF}_3\text{SO}_3)_3$; (---) $\text{Nd}(\text{phen})_4(\text{CF}_3\text{SO}_3)_3$. B: (—) $\text{Ho}(\text{CF}_3\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$; (---) $\text{Ho}(\text{CF}_3\text{SO}_3)_3 \cdot 9\text{H}_2\text{O} + \text{CF}_3\text{SO}_3\text{H}$ ($c_{\text{CF}_3\text{SO}_3^-} = 4.0$ M); (····) $\text{Ho}(\text{PU})_8(\text{CF}_3\text{SO}_3)_3$; (----) $\text{Ho}(\text{pyO})_8(\text{CF}_3\text{SO}_3)_3$; (· · · · ·) $\text{Ho}(\text{PA})_4(\text{CF}_3\text{SO}_3)_3 \cdot 2\text{H}_2\text{O}$; (---) $\text{Ho}(\text{bipyO})_2(\text{CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$.

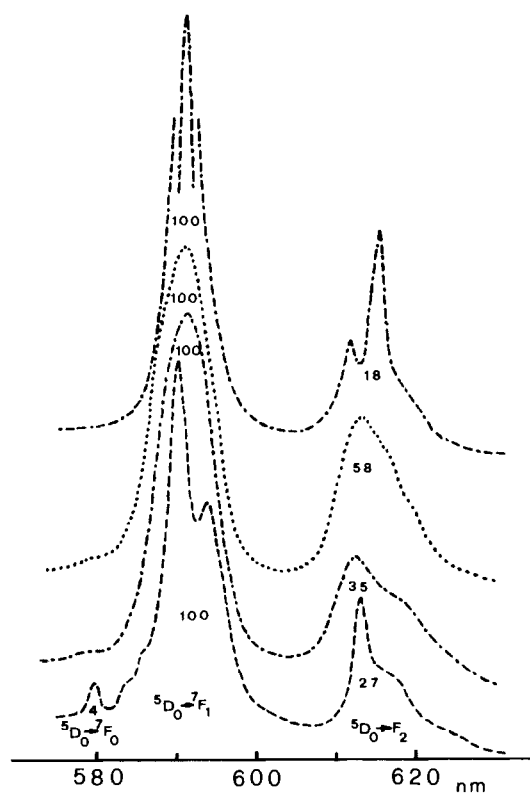


Fig. 2. Fluorescence spectra of europium trifluoromethanesulfonate at 77 K: (---) solid state; (---) in ethanol; (····) in acetonitrile; (---) in acetonitrile by addition of $\text{CF}_3\text{SO}_3\text{H}$ ($c_{\text{CF}_3\text{SO}_3^-} = 4.0$ M). Attribution and relative intensity of the various emission bands are also in the figure (%).

$^7\text{F}_0$ transitions. The spectrum does not show any pronounced change on passing from the aqueous to the ethanolic and acetonitrile solutions. The emission spectrum of the solid europium trifluoromethanesulfonate enneahydrate shows a weak line at 580.5 nm assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition. Two components of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition appear at 591.5 and 595.0 nm (Fig. 2). The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition consists of a line at 613.8 nm and two weaker components at 617 and 624 nm. This spectral pattern suggests D_{3h} distorted towards C_{4v} site symmetry for the europium ion. The addition of $\text{CF}_3\text{SO}_3\text{H}$ to the europium trifluoromethanesulfonate in acetonitrile causes an increase in the intensity of both the $^5\text{D}_0 \rightarrow ^7\text{F}_{1,2}$ transitions and a significant modification of the spectral pattern. The splitting of the $^7\text{F}_1$ level is reduced drastically, the spectrum showing only an intense line at 591.7 nm arising from the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition. The $^7\text{F}_2$ level is triply split but poorly populated; the intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is only a 18% of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition. The $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition is strictly forbidden the spectrum showing no line in the relative region. This spectral pattern suggests D_{4d} distorted towards D_{2d} site sym-

metry for the europium(III) ion. All these changes, however, do not necessarily arise from a penetration of trifluoromethanesulfonate groups into the inner-sphere of the cation, rather from the action on the ion of an increased electric field produced by high electrolytic concentration and from a lowering of the coordination number from nine to eight, thus forming, so as suggested by Karraker for the corresponding chlorides and perchlorates in aqueous solutions [9], the entity $[\text{Ln}(\text{OH}_2)_8]^{3+}$.

The Complexes

The complexes with PU and EU are scarcely soluble in common organic solvents; they melt before thermal decomposition begins around 200 °C. Molar conductivity values in nitromethane-ethanol mixture (9:1) vary between 210 and 250 $\text{ohm}^{-1} \text{cm}^2 \text{M}^{-1}$ ($c = 1-2 \times 10^{-3} \text{M}$) indicating 1:3 electrolytic behaviour. The IR spectra resemble those of other lanthanide(III) complexes with these ligands for which, from the shifts of the bands amide I, amide II and amide III, which arise from intense mixing of CO, CN and NH modes, a Ln-O bonding was postulated [12].

The complexes with pyO, bipyO₂, PA and phen are soluble in acetonitrile, alcohols and nitromethane. The molar conductivity values in acetonitrile vary between 290 and 350 $\text{ohm}^{-1} \text{cm}^2 \text{M}^{-1}$ (Table I) and correspond to 1:3 electrolytes. Coordination of pyO and bipyO₂ through the NO oxygen atom is clearly demonstrated by the shift of the NO stretching mode from 1265 (pyO) or 1260 (bipyO₂) cm^{-1} to 1230–1225 cm^{-1} ; this mode is in most cases mixed with -CF₃ modes and appears as a strong and broad band at 1235 cm^{-1} . The bending NO mode at 845 cm^{-1} is slightly affected whereas the pyridine ring stretching mode at 1460 cm^{-1} shifts to 1480–1475 cm^{-1} upon complexation. The coordination of PA can be determined by the shifts of the amide and pyridine residue bands. The occurred shifts are similar to those previously observed for other complexes of lanthanides with PA, pyridine and pyridinecarboxamide metal complexes [13, 14] and attributed to cation-ligand bonds through the carbonyl oxygen and the pyridine nitrogen atoms. The IR spectra of the phen complexes show the shift of the ring stretching modes at 1430, 1495 and 1505 cm^{-1} to higher frequencies (5–15 cm^{-1}); also the ring breathing mode at 1025 cm^{-1} shifts about 10 cm^{-1} to higher frequencies whereas the CH out-of-plane bending mode at 855 cm^{-1} shifts 5–8 cm^{-1} to lower frequencies. These spectral changes are a clear indication of the pyridine nitrogen atoms involved in bonding with metal ions.

In all cases three un-split and strong bands appear at 1280–1285, 1038–1035 and 645–642 cm^{-1} assigned to stretching and bending modes of the -SO₃ group. This spectral pattern indicates that only C_{3v}

symmetry (ionic) trifluoromethanesulfonate groups act in all these complexes.

Both absorption and reflectance f-f spectra show changes in the band shape and intensity of the hypersensitive transitions with respect to the aquo-ions which indicate environmental changes. If the shape of the band changes significantly, the intensity, however, increases only a 40% (Nd) or 120% (Ho) that of the aquo-ion upon complexation with PU and EU (Table II). Symmetry and covalency are both factors which can affect, also remarkably, the hypersensitive transitions. The Mössbauer spectra of the europium(III) complexes with PU and EU have shown that the lanthanide-oxygen bond as a predominant ionic character assigning to the covalency only a limited role [15]; on the other hand, the emission spectra (see later) indicate high site symmetry for the europium(III) ion in both complexes. Other complexes having the same chromophore ([LnO₈]) and high symmetry (complexes with pyO and bipyO₂) exhibit oscillator strength values which are remarkably greater than the aquo-ion reaching the uncommon values of 57.9 for Nd³⁺ ion and 113 for Ho³⁺ ion (bipyO₂) complexes). Such an increase in the intensity has been previously observed for the tris 2,2,6,6-tetramethyl-3,5-heptanedionates in the vapor phase [16] and likely arises from an exceptional donating ability of these chelating molecules. Since all these complexes have the same chromophore and high symmetry, an increase in the s-electron density corresponds to an increase in the intensity of the transition.

The fluorescence spectra at 77 K of some complexes of the europium trifluoromethanesulfonate in the solid state are depicted in Fig. 3. Spectral data are reported in Table III.

The emission spectra of the PU and EU complexes were obtained by excitation to the ⁵L₆ level. The

TABLE III. Partial Energy Level Scheme for Europium Complexes. The values refer to the baricenter of the band group (in cm^{-1} , ±7).

Level	Ligand				
	PU	pyO	bipyO ₂	PA	phen
⁵ D ₂	21505	21524	21533	21496	21492
⁵ D ₁	19003	19025	18986		
⁵ D ₀	17271	17253	17265	17259	17247
⁷ F ₄		2895 ^a	2845 ^a		2879
⁷ F ₃	1898	1904	1939	1910 ^a	1921 ^a
⁷ F ₂	944	1024	962	1052	960
⁷ F ₁	368	365	373	390	355
⁷ F ₀	0	0	0	0	0

^a±10.

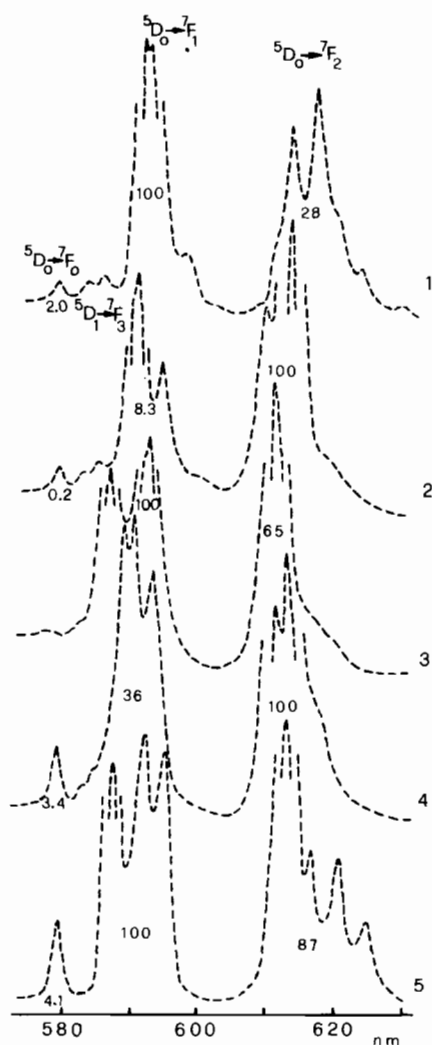


Fig. 3. Fluorescence spectra at 77 K of solid complexes of europium trifluoromethanesulfonate: 1. $\text{Eu}(\text{pyO})_8(\text{CF}_3\text{SO}_3)_3$; 2. $\text{Eu}(\text{bipyO}_2)_4(\text{CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$; 3. $\text{Eu}(\text{PU})_8(\text{CF}_3\text{SO}_3)_3$; 4. $\text{Eu}(\text{PA})_4(\text{CF}_3\text{SO}_3)_3 \cdot 2\text{H}_2\text{O}$; 5. $\text{Eu}(\text{phen})_2(\text{CF}_3\text{SO}_3)_3 \cdot 4\text{H}_2\text{O}$. Attribution and relative intensity (%) of the various emission bands are also in the figure.

cation fluoresces almost exclusively from the $^5\text{D}_0$ excited state; bands associated with the various $^5\text{D}_1 \rightarrow ^7\text{F}_{0-4}$ transitions are very weak. The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition consists of two components; the first appears at 588.5 nm as a line, the second is slightly split into two lines at 593.6 nm and 594.2 nm, this splitting indicating that they could originate from an E-component. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition consists of a line at 612.5 nm and two very weak components at 616 and 621 nm. The $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition can be taken as forbidden, the spectra showing only a very weak line at 579.0 nm. The $^5\text{D}_0 \rightarrow ^7\text{F}_{3,4}$ transitions appear as weak and poorly resolved bands and thus are poorly indicative. This spectral pattern well agrees with a

square antiprismatic geometry with the cation in an almost perfect D_4 site symmetry.

Fluorescence of the pyO, bipyO₂, PA and phen europium complexes arises from ligand to cation energy transfer and mainly from the $^5\text{D}_0$ level; only the bipyO₂ complex shows bands of appreciable intensity associated with the various $^5\text{D}_1 \rightarrow ^7\text{F}_{0-4}$ transitions.

The emission spectrum of the solid octakis pyO europium complex excited with 320 nm radiation shows three weak lines at 579.6, 584.5 and 587.0 nm; the first is assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition and the others to the $^5\text{D}_1 \rightarrow ^7\text{F}_3$ transition. The intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition is about 2% of the most intense $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition and cannot be taken as strictly forbidden. The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition consists of a relatively intense line at 592.4 nm and a weak one at 596.6 nm. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition consists of three components at 614.0, 617.5 and 620.0 nm, however, the intensity is less than 30% of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition. Two weak lines appear at 624.0 and 629.0 nm; the former can be associated also with the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, the latter arises from the $^5\text{D}_1 \rightarrow ^7\text{F}_4$ transition. One broad band centered at 651.5 nm and a broad one at 691 together with a doublet at 698.0 and 699.0 nm (E-component) are assigned respectively to the $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions. Weak bands arising from the $^5\text{D}_1 \rightarrow ^7\text{F}_{1,2}$ transitions are also visible in the spectrum; the former appears as a single but broad line at 536.9 nm, the latter as a triplet at 555.0, 558.2 and 560.0 nm. The complex $\text{Eu}(\text{pyO})_8(\text{ClO}_4)_3$ has been described in terms of square antiprismatic geometry with the cation in D_{4d} weakly distorted to D_{2d} site symmetry [16]. From crystallographic data distortion of the polyhedron towards a cube rather than a dodecahedron has been indicated [17]. The fluorescence spectrum of the complex $\text{Eu}(\text{pyO})_8(\text{CF}_3\text{SO}_3)_3$, by the multiplicity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition and the intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition, indicates C_{2v} distortion rather than D_{2d} .

The emission spectrum of the solid complex $\text{Eu}(\text{PA})_4(\text{CF}_3\text{SO}_3)_3 \cdot 2\text{H}_2\text{O}$ at 77 K and excited with 300 nm radiation shows a weak line at 579.4 nm associated with the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition. The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition consists of two components; the first appears split into two lines at 591.5 and 592.3 nm (E), the second appears at 594.8 nm. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition also consists of two components; the former is slightly split into two lines at 612.3 and 613.3 nm and probably arises from transition to an E-component, the latter is weaker and appears at 620 nm. Bands arising from the various $^5\text{D}_0 \rightarrow ^7\text{F}_{3,4}$ and $^5\text{D}_1 \rightarrow ^7\text{F}_j$ transitions appear also in the spectrum, but all are very weak and poorly resolved. The chelation of the PA molecule to the cation leads to the formation of the $[\text{LnO}_4\text{N}_4]$ chromophore. The emission spectrum indicates C_{4v} site symmetry for the

europium(III) ion in this complex, but it is not possible from the spectroscopic data alone to exclude the C_4 one.

The solid bis(1,10-phenanthroline) europium tris trifluoromethanesulfonate tetrahydrate when excited with 340 nm radiation exhibits an emission spectrum at 77 K which is rich with lines arising from the various $^5D_0 \rightarrow ^7F_J$ transitions. Three lines appear in the region of the $^5D_0 \rightarrow ^7F_1$ transition at 588.5, 593.0 and 596.0 nm. An intense line at 612.0 nm and three weaker lines at 616.5, 620.2 and 624.8 nm appear in the region of the $^5D_0 \rightarrow ^7F_2$ transition. The $^5D_0 \rightarrow ^7F_0$ transition appears to be allowed showing a line at 579.8 nm. This spectral pattern suggests C_{2v} site symmetry for the europium ion in this complex. Unfortunately the $^5D_0 \rightarrow ^7F_{3,4}$ transitions are not indicative; both appear in fact as weak and poorly resolved bands.

The emission spectrum at 77 K of the solid $\text{Eu}(\text{bipyO}_2)_4(\text{CF}_3\text{SO}_3)_3$ complex excited with 315 nm radiation shows a broad line at 591.5 nm and a weaker one at 595.0 nm, both associated with the $^5D_0 \rightarrow ^7F_1$ transition. A relatively weak line at 612.4 nm and a very intense line at 613.8 nm arise from the $^5D_0 \rightarrow ^7F_2$ transition; a weak component of this transition appears at 618.0 nm. A line is exhibited at 579.2 nm arising from the $^5D_0 \rightarrow ^7F_0$ transition; its intensity is less than 0.2% of the $^5D_0 \rightarrow ^7F_2$ transition but about 2.5% of the $^5D_0 \rightarrow ^7F_1$ transition and it is arbitrary to take it as strictly forbidden. Fluorescence arises also from the 5D_1 level. Two medium intensity lines appear at 536.0 and 538.8 nm as components of the $^5D_1 \rightarrow ^7F_1$ transition; two weak lines at 552.0 and 561.0 nm and a weak and broad line at 556.8 nm are associated with the $^5D_1 \rightarrow ^7F_2$ transition. There is little doubt both from synthetic and spectroscopic data that this complex consists in the solid state of the $[\text{EuO}_8]$ chromophore acquired through four bidentate bipyO_2 molecules. The emission spectrum well agrees with a square antiprismatic geometry with the europium(III) ion in D_4 distorted towards C_{4v} site symmetry. Steric considerations suggest that the chelation of this molecule requires the two pyridine N-oxide rings suitably twisted out of the molecular plane giving rise to a *gauche* conformation. The dissolution of this complex in methanol or acetonitrile causes the conversion $D_4 \rightarrow C_{4v}$. A relatively intense line appears at 579.5 nm indicating that the $^5D_0 \rightarrow ^7F_0$ transition is allowed. Two lines, one broad at 590.5 nm and one sharp at 594.2 nm arise from the $^5D_0 \rightarrow ^7F_1$ transition; the former is assigned to the doubly degenerate E-component, the latter to the non-degenerate A_2 -component. The $^5D_0 \rightarrow ^7F_2$ transition also consists of two components; the first is split into two lines appearing at 611.3 and 612.4 nm (E-component), the second appears as a weak line at 616.7 nm. In any case the intensity ratio $\eta = ^5D_0 \rightarrow ^7F_2 / ^5D_0 \rightarrow ^7F_1$ remains exceptionally high, although

the intensity of the various transitions increases with temperature.

Conclusion

All results indicate that the $\text{Ln}^{3+}/\text{CF}_3\text{SO}_3^-$ interactions are of the outer-sphere type only and that coordination of trifluoromethanesulfonate groups with lanthanides does not occur. Coordination with tin has been previously observed [19]. On this ground 8-coordinated arrangements of the $[\text{LnO}_8]$, $[\text{LnO}_4\text{N}_4]$ and $[\text{LnN}_8]$ types can be suggested for the complexes in the solid state.

It is found that the intensity of the hypersensitive transitions in neodymium and holmium complexes increases in the order: $\text{PU} \approx \text{EU} < \text{phen} < \text{pyO} < \text{PA} < \text{bipyO}_2$, which differs, as regards the place of the pyO ligand, from that established from the η values: $\text{pyO} < \text{PU} \approx \text{EU} < \text{phen} < \text{PA} < \text{bipyO}_2$. It is expected that the more covalent the complex the more efficient the intramolecular energy transfer from the ligand to the cation; on the other hand, it has been found also that, among the various transitions occurring between low J-values in europium(III) ion, the $^5D_0 \rightarrow ^7F_2$ transition is more sensitive to environmental changes than the $^5D_0 \rightarrow ^7F_1$ one. The anomaly represented by the low η value measured for the pyO complex likely arises from the fact that the $^5D_0 \rightarrow ^7F_2$ transition, is, in this case, forbidden by the D_{4d} selection rules.

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References

- 1 T. Gramstad, *Tidsskr. Kjemi, Bergves. Metall.*, **19**, 30 (1959).
- 2 A. Engelbrecht and B. M. Rode, *Monatsh. Chem.*, **103**, 1315 (1972).
- 3 H. W. Quinn and D. N. Glew, *Can. J. Chem.*, **40**, 1103 (1962).
- 4 W. Featherstone and A. J. S. Sorrie, *J. Chem. Soc.*, 5235 (1964).
- 5 G. S. Lewandos, D. K. Gregston and F. R. Nelson, *J. Organometal. Chem.*, **118**, 363 (1976).
- 6 K. F. Thom, *U. S. Patent*, **3**, 296, 725 (1973).
- 7 J. Massaux and G. Duyckaerts, *Anal. Chim. Acta*, **73**, 416 (1974).
- 8 M. M. Kopečni and D. J. M. Petkovic, *Thermochim. Acta*, **25**, 241 (1978).

- 9 D. G. Karkaker, *Inorg. Chem.*, **7**, 473 (1968).
- 10 H. Burger, K. Burczyk and A. Blaschette, *Monatsh. Chem.*, **101**, 102 (1970).
- 11 (a) J. A. A. Ketelaar, *Physica*, **4**, 619 (1937); (b) L. Helmholtz, *J. Am. Chem. Soc.*, **61**, 1544 (1939).
- 12 A. Seminara, A. Musumeci and A. Chisari, *J. Inorg. Nucl. Chem.*, **40**, 269 (1978).
- 13 G. Condorelli, A. Seminara and A. Musumeci, *J. Inorg. Nucl. Chem.*, **36**, 3763 (1974).
- 14 K. Yamasaki and M. Sekizaki, *Bull. Chem. Soc. Japan*, **38**, 2206 (1965).
- 15 S. Calogero, A. Seminara and U. Russo, *Gazzetta Chimica*, **109**, 45 (1979).
- 16 D. M. Gruen, C. V. DeKock and R. L. McBeth, 'Lanthanide/Actinide Chemistry', *Advances in Chemistry Series, Am. Chem. Soc.*, **71** (1967).
- 17 E. Butter and W. Seifert, *Z. anorg. allg. Chem.*, **368**, 133 (1969).
- 18 A. R. Al-Karaghoulis and J. S. Wood, *Chem. Comm.*, 516 (1972).
- 19 R. J. Batchelor, J. N. R. Ruddick, J. R. Sams and F. Aubke, *Inorg. Chem.*, **16**, 1414 (1977).