Lanthanide Complexes with N-oxides. Complexes with Pyridine 1-Oxide, 2,2′-Bipyridine 1,1′-Dioxide and 2,2′,2″-Terpyridine 1,1′, 1″-Trioxide

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Several complexes of lanthanide(III) thiocyanates, nitrates, perchlorates and trifluoromethanesulphonates with pyridine 1-oxide (pyO), 2,2′-bipyridine 1,1′-dioxide (bipyO_2) and 2,2′,2″-terpyridine 1,1′, 1″-trioxide (terpyO_3) have been prepared and characterized. The complexes achieve preferentially the eight-coordination; nine- and ten-coordination have been also observed. Complexation of lanthanide(III) cations with these ligands occurs also in aqueous solution. Information on the electron-donating power of the ligands and geometry of the complexes has been obtained from the absorption and emission f–f spectra. Correlation between Sinha's parameter and hypersensitivity has been observed. The intensity of the hypersensitive transitions increases in the order: pyO < terpyO_3 < bipyO_2 reaching very high and uncommon values for the bipyO_2 complexes. The emission spectra of the octakis(pyO) complexes suggest a rather high symmetry for the electrostatic field surrounding the cation. A drop in site symmetry occurs on passing from the pyO to the bipyO_2 and terpyO_3 complexes. Exceptionally high values for the intensity ratios $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ in europium(III) complexes and $^5D_4 \rightarrow {}^7F_5/{}^5D_4 \rightarrow {}^7F_6$ in terbium(III) complexes have been determined.

Introduction

Ternary complexes of lanthanide(III) cations formed by mono- or polydentate anions and neutral ligands are of a great interest because they provide cases in which the cation is highly coordinated. In addition, the use of lanthanide salts with weakly or non-coordinating anions allows the cation to achieve full-ligand coordination and minimize the effects of the anion coordination on the properties of the complexes.

Amine N-oxides normally behave as strongly basic ligands towards lanthanide cations and give rise to compounds with well-defined stoichiometry. However, the number of the reported complexes is relatively scanty [1–3]. Coordination occurs through the oxygen atoms and seven-membered chelate rings form in some cases. Stable complexes can be formed with poly-oxygen donor molecules if the ligand molecule adopts suitable geometry or yields polymeric species. In the case of bipyO_2 and terpyO_3 the free molecule cannot be planar both for steric interaction of the oxygen atoms and for repulsion of the lone electron pairs. Useful information concerning the nature of the chromophoric group and the geometry of the lanthanide complexes can be obtained by the study of the absorption and emission f–f spectra. However, lanthanide(III) complexes in which strong emission has been observed have, almost exclusively, Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+} as central ions. Among these the europium(III) complexes have been the subject of very extensive studies in preference to other lanthanide(III) cations since the low J-values give rise to a smaller number of closely spaced energy levels. The number of levels in which a state of a given J will be split for each of the thirty-two crystallographic point groups have been calculated; thus, knowing the symmetry class at the cation site, the number of levels can be readily predicted. Alternatively, lanthanide(III) cations may be used to probe the symmetry of sites in crystals.

As part of a systematic investigation of the complexes of lanthanide salts having weakly or non-coordinating anions, the synthesis and f–f spectra of the complexes of lanthanide(III) nitrates, thiocyanates, perchlorates and trifluoromethanesulphonates with the following N-oxide ligands: pyridine 1-oxide (pyO), 2,2′-bipyridine 1,1′-dioxide (bipyO_2) and 2,2′,2″-terpyridine 1,1′,1″-trioxide (terpyO_3) are reported here.

Experimental

Materials

PyO was distilled at reduced pressure (~10^{-2} mmHg); terpyO_3 was prepared as previously described [4]. Lanthanide(III) trifluoromethanesulphonates were prepared according to previous procedure [5];

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they were heated at 130 °C for 1 h at reduced pressure ($\sim 10^{-2}$ mmHg) and immediately dissolved in the appropriate anhydrous solvent. As a starting material for the preparation of the perchlorate complexes, anhydrous perchlorate complexes with DMSO were employed. 15 ml of triethylorthoformate, as dehydrating agent, were added to the alcoholic or acetonitrile solution containing the lanthanide(III) nitrate or thiocyanate (1 mmol); the resulting solution was refluxed for 3 h.

Synthesis of the Complexes with pyO

The octakis(pyO) lanthanide(III) nitrate complexes and the tetrakis and tris(pyO) lanthanide(III) thiocyanate complexes were prepared by mixing 1 mmol of the hydrated nitrate or thiocyanate in 10 ml of anhydrous ethanol with 8 or 5 mmol of pyO, respectively, in 10 ml of the same solvent. The solution was refluxed for 30 min under dry nitrogen and slowly concentrated. 50 ml of anhydrous diethylether were successively added to the solution vigorously stirred. When necessary, the solution was further refluxed and concentrated. Abundant precipitates formed on cooling the solution; they were rapidly filtered off, washed with small amounts of ethanol–diethylether mixture (1:5) and dried *in vacuo* at room temperature. The method is essentially that described in reference 3. The tris(pyO) lanthanide(III) nitrate complexes were prepared following the procedure described for the synthesis of the octakis complexes but mixing the reagents in the 1:3 molar ratio.

Octakis(pyO) lanthanide(III) perchlorate and trifluoromethanesulphonate complexes were prepared according to previous procedures [5, 6].

Synthesis of the Complexes with bipyO$_2$

The bis(bipyO$_2$) lanthanide(III) nitrate and thiocyanate complexes were obtained by adding 2.5 mmol of bipyO$_2$ in 50 ml of boiling anhydrous ethanol to 1 mmol of the appropriate lanthanide salt in 10 ml of the same solvent. The complexes precipitated slowly as crystalline powder on stirring the solution; sometimes, successive small amounts of anhydrous diethylether were added to promote crystallization. The precipitates were filtered off, washed with anhydrous ethanol–diethylether mixture (1:1) and dried *in vacuo* at room temperature.

Tetrakis(bipyO$_2$) lanthanide(III) perchlorate and trifluoromethanesulphonate complexes were prepared according to previous procedures [5, 7].

Synthesis of the Complexes with terpyO$_3$

1 mmol of the appropriate lanthanide(III) salt in 20 ml of anhydrous ethanol was added to a suspension of 1.5 mmol (nitrate) or 4 mmol (perchlorate, trifluoromethanesulphonate) of terpyO$_3$ in a mixture of ethanol–tetrahydrofuran (2:1) (150–300 ml) vigorously stirred. Microcrystalline products slowly formed on boiling the solution. When necessary, small amounts of anhydrous diethylether were added to promote crystallization. The precipitates were filtered off, washed with anhydrous ethanol and dried *in vacuo* at room temperature. The method is essentially that described for the preparation of the terpyO$_3$ complexes with europium(III) nitrate and perchlorate [2].

Measurements

IR spectra were obtained from KBr pellets and nujol mulls by a Perkin-Elmer 577 spectrophotometer. Electronic absorption spectra were recorded with an Optica 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. The absorption intensity, presented as oscillator strengths, was calculated from the expression: $P = 4.31 \times 10^{-9}\, [9\eta/(\eta^2 + 2)^2] \int \epsilon(\nu) d\nu$ where η is the refractive index of the solution and ϵ the molar extinction coefficient at the wavelength ν. Electrolytic conductivity was measured employing an Amel 951 conductivity bridge at 25 ± 0.1 °C. Thermal analysis was performed with a Mettler vacuum thermoanalyzer in dynamic nitrogen atmosphere at the 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 or aqueous solution by exciting with near ultraviolet radiations at room and liquid nitrogen temperatures. The resolution was better than 10 cm^{-1}.

Results and Discussion

The series of complexes we obtained can be represented by the general formula $LnL_mX_3 \cdot nH_2O$ where X = NO_3, NCS, ClO_4, CF_3SO_3, $m \leqslant 8$, n = 0–4. Spectroscopic data clearly indicated that complexes of lanthanide(III) cations with these ligands also form in water although, at present, attempts to isolate these complexes were unsuccessful.

Octakis(pyO) lanthanide(III) complexes form easily when the anion is Cl, Br, I, ClO_4, CF_3SO_3, NO_3 [1, 3, 5, 6]; on the contrary,we could only prepare complexes containing four or three molecules of pyO when the anion was NCS. These complexes are hygroscopic and highly soluble in ethanol and acetonitrile. The thiocyanate complexes behave in these solvents as non-electrolytes. Molar conductivity measured for the octakis(pyO) nitrate complexes indicates lower than 1:3 electrolytic behaviour. Since the three nitrate groups are undoubtedly ionic in the solid, this trend arises from replacement of pyO inner-sphere molecules by nitrate groups. The octakis(pyO) lanthanide(III) perchlorate and trifluoromethanesulphonate complexes are 1:3 electrolytes [5].

Tetrakis(bipyO$_2$) lanthanide(III) nitrate complexes having highly coordinated environments have been reported [8]. As in the case of the lanthanide nitrate complexes with phenO [9], we obtained bis(bipyO$_2$) nitrate and thiocyanate complexes in preference to species more rich in ligand. Molar conductivity measured for these complexes indicates non-electrolytic behaviour; however, the complexes of the heavy nitrates behave as 1:1 electrolytes.

The tris(terpyO$_3$) complexes of the lanthanide(III) perchlorates and trifluoromethanesulphonates behave as 1:3 electrolytes. The complexes of the lanthanide(III) nitrates from lanthanum to terbium are non-electrolytes, whereas the 1:1 electrolytic behaviour shown by the nitrate complexes from dysprosium to lutetium suggests ionization of one nitrate group.

IR Spectra

Ligand modes

The IR spectra of the complexes show the shift of the NO stretching mode from 1265 (pyO), 1267 and 1260 (bipyO$_2$) or 1258 and 1245 (terpyO$_3$) cm^{-1} to 1240–1220 cm^{-1}. This shift is associated with coordination of the ligand to the lanthanide(III) cation through the oxygen atoms. However, three peaks associated with this mode may appear in the spectra of the bipyO$_2$ and terpyO$_3$ complexes. This effect arises from non-coplanarity of the two or three oxygen atoms in the bipyO$_2$ and terpyO$_3$ molecules owing to the distorted conformation that these molecules are constrained to assume on forming chelates or polymeric species. Steric consideration suggests that, on forming complexes, the pyridine N-oxide rings must be suitably twisted out of the molecular plane. The NO bending mode shown around 860 cm^{-1} and the pyridine ring modes shown in the 1600–1400 cm^{-1} region are slightly affected on complex formation showing only 5–10 cm^{-1} shifts. The shift of the ν(NO) mode, measured with respect to the barycentre of the band group, increases in the order: pyO < terpyO$_3$ < bipyO$_2$. This trend is in line with f–f spectra and reflects the electron-donating power of these ligands.

Anion modes

The exhibition of two un-split and strong bands at 1095 and 620 cm^{-1} (ν_3 and ν_4, T_d symmetry) in the spectra of the perchlorate complexes and of three un-split and strong bands at 1280–1275 cm^{-1} ($\nu_4(E)$), 1038–1035 cm^{-1} ($\nu_1(A_1)$) and 645–642 cm^{-1} ($\nu_3(A_1)$) (C_{3v} symmetry –SO$_3$ group) in the spectra of the trifluoromethanesulphonate complexes is consistent with the presence in these complexes of ionic perchlorate and trifluoromethanesulphonate groups only [5].

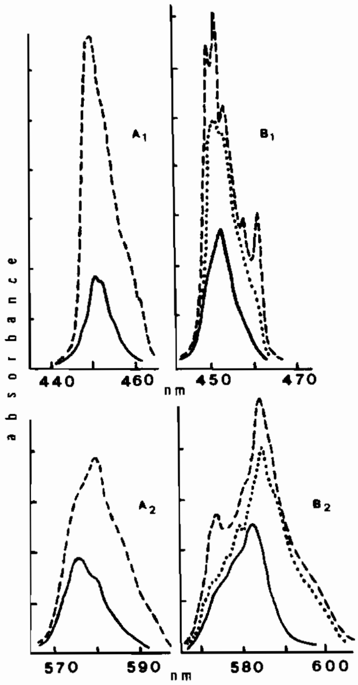

Fig. 1. The hypersensitive transitions $^5I_8 \rightarrow {}^5G_6$ in Ho^{3+} ion and $^4I_{9/2} \rightarrow {}^4G_{5/2}$ in Nd^{3+} ion (A in water, B in acetonitrile). A$_1$: (———) Ho(NO$_3$)$_3$·5H$_2$O; (– – –) Ho(NO$_3$)$_3$·5H$_2$O + bipyO$_2$ (excess). A$_2$: (———) Nd(NO$_3$)$_3$·5H$_2$O; (– – –) Nd(NO$_3$)$_3$·5H$_2$O + bipyO$_2$ (excess). B$_1$: (———) Ho(NO$_3$)$_3$·5H$_2$O; (……) Ho(terpyO$_3$)(NO$_3$)$_3$·H$_2$O; (– – –) Ho(bipyO$_2$)$_2$(NO$_3$)$_3$. B$_2$: (———) Nd(NO$_3$)$_3$·5H$_2$O; (……) Nd(terpyO$_3$)(NO$_3$)$_3$·H$_2$O; (– – –) Nd(bipyO$_2$)$_2$(NO$_3$)$_3$.

Only bands assigned to ionic (D_{3h} symmetry) nitrate groups appear in the spectra of the octakis (pyO) nitrate complexes; on the other hand, only bands assigned to coordinated nitrate groups appear in the spectra of the tris(pyO) nitrate complexes. In the spectra of most of the nitrate complexes with bipyO$_2$ only bands associated with coordinated nitrate groups appear; however, the spectra of the complexes of the heavy cations show bands arising both from D_{3h} and C_{2v} symmetries. Two groups of nitrate complexes with terpyO$_3$ can be also distinguished with the aid of the IR spectra. In this case, however, the presence of both ionic and coordinated nitrate groups concerns the complexes from disprosium to lutetium nitrates.

The thiocyanate complexes show the CN stretching mode of the NCS group normally split into two components appearing around 2060 and 2040 cm^{-1}. The splitting is, however, consistent with crystalline

TABLE I. Selected Analytical Data, Electrolytic Conductivity and Thermal Decomposition Temperatures of Lanthanide(III) Complexes with N-oxides. In parentheses the calcd. values.

Complex	Ln	%C	%H	%N	%Ln	Λ_M[c]	t_i °C
$Ln(pyO)_8(NO_3)_3$[a]	Ce	43.78(44.20)	3.81(3.71)	14.07(14.18)	12.45(12.89)	290	185
(Ln = La–Ho)	Gd			13.75(13.96)	13.65(14.24)	308	180
$Ln(pyO)_4(NCS)_3 \cdot 2H_2O$	Pr	38.03(37.76)	3.35(3.31)	13.12(13.41)	19.53(19.26)	28	205
(Ln = La–Tb)	Tb	35.93(36.85)	3.41(3.23)	12.78(13.08)	21.80(21.20)	31	200
$Ln(pyO)_3(NCS)_3 \cdot 2H_2O$	Ho			12.64(12.73)	24.69(24.97)	20	210
(Ln = Ho–Tm)	Tm	31.68(32.53)	3.02(2.89)	12.31(12.65)	25.26(25.42)	25	190
$Ln(bipyO_2)_2(NO_3)_3$	Pr	33.71(34.15)	2.21(2.29)	14.01(13.94)	20.50(20.04)	28	260
(Ln = La–Tm)	Gd			13.48(13.63)	21.62(21.85)	22	255
	Tm	33.57(32.84)	2.09(2.21)	13.17(13.41)	23.57(23.10)	192	240
$Ln(bipyO_2)_2(NCS)_3 \cdot nH_2O$	La	38.40(39.04)	2.62(2.56)	13.48(13.86)	19.40(19.63)	25	230
(Ln = La–Eu, n = 1;	Nd			13.52(13.75)	20.10(20.24)	22	240
Ln = Gd–Er, n = 2)	Er	37.11(36.64)	2.53(2.67)	12.80(13.01)	22.34(22.19)	30	220
$Ln(terpyO_3)_3(ClO_4)_3 \cdot 2H_2O$[b]	La	40.50(41.03)	2.97(2.83)	9.36(9.57)	10.70(10.55)	395	280
(Ln = La–Tb)	Nd			9.60(9.53)	11.15(10.91)	403	290
	Tb	39.68(40.42)	2.60(2.79)	9.31(9.43)	12.10(11.89)	375	280
$Ln(terpyO_3)(NO_3)_3 \cdot H_2O$[b]	Nd	28.13(28.61)	2.27(2.08)	13.51(13.35)	22.74(22.92)	18	260
(Ln = La–Ho)	Ho	26.80(27.71)	2.12(2.01)	12.46(12.93)	24.62(25.37)	104	240
$Ln(terpyO_3)_3(CF_3SO_3)_3 \cdot 2H_2O$	Pr	39.05(39.27)	2.62(2.54)	8.61(8.59)	9.48(9.60)	385	300
(Ln = La–Tb)	Dy	38.15(38.70)	2.65(2.50)	8.18(8.46)	11.07(10.91)	395	280

[a] See also reference 3. [b] See also reference 2. [c] Ohm^{-1} cm^2 M^{-1}, in acetonitrile, at 25 ± 0.1 °C; c = 0.8–1.3 × 10^{-3} M.

perturbations. The frequencies of this and of the NCS bending mode (480–470 cm^{-1}) are in the range of values expected for N-coordination of the thiocyanate groups.

Electronic Spectra

The f–f transition bands show normally, unlike the d–d ones, weak perturbation due to complexation. Increase in the intensity, shift of the barycentre and splitting of certain bands due to the crystal field with respect to the aquo-ions are effects that can be observed on complex formation. The nephelauxetic effect and the hypersensitivity of certain transitions have been correlated with covalency. The nephelauxetic parameter β, defined as:

$$\beta = \frac{1}{n} \sum^{n=1} \nu^i_{com.}/\nu^i_{aqu.}$$

and the Sinha's covalency parameter δ, defined as: $\delta = 100\,(1 - \beta)/\beta$ [10], have been indicated as semiempirical estimates of covalency. However, the actual correlation between Sinha's parameter and covalency has been debated because of some contrasting results. Indeed, with respect to the aquo-ions, the spectra of most of the complexes here reported show remarkable and rather uncommon enhancements in the band shape and intensity of the hypersensitive transitions. Some spectra are depicted in Fig. 1. Spectral data are reported in Table II. All the

TABLE II. Intensity, as Oscillator Strengths (10^6 P), of the hypersensitive transitions ${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ in Nd^{3+} Ion and ${}^5I_8 \rightarrow {}^5G_6$ in Ho^{3+} Ion.

Complex	10^6 P		σ[d]
	CH_3CN	H_2O	kK
$Nd(pyO)_8(NO_3)_3$	27.56	14.74[a]	17.14
$Nd(pyO)_8(ClO_4)_3$	29.42		
$Nd(bipyO_2)_2(NO_3)_3$	53.71[b]	51.02[a]	
$Nd(bipyO_2)_4(ClO_4)_3$	59.05[b]		17.09
$Nd(terpyO_3)(NO_3)_3 \cdot H_2O$	[c]		
$Nd(terpyO_3)_3(ClO_4)_3 \cdot 2H_2O$	43.80[b]		17.11
$Ho(pyO)_8(NO_3)_3$	33.25	16.37[a]	22.06
$Ho(pyO)_8(ClO_4)_3$	36.48		
$Ho(bipyO_2)_2(NO_3)_3$	83.78[b]	88.31[a]	22.02
$Ho(bipyO_2)_4(ClO_4)_3$	110.27[b]		
$Ho(terpyO_3)(NO_3)_3 \cdot H_2O$	65.73[b]		
$Nd(NO_3)_3 \cdot 5H_2O$	25.86	8.12	17.18
$Ho(NO_3)_3 \cdot 5H_2O$	26.13	5.08	22.11

[a] By addition of large excess of the ligand. [b] Saturated solution, at 25 °C. [c] Poorly soluble. [d] Barycentre of the band group, in acetonitrile.

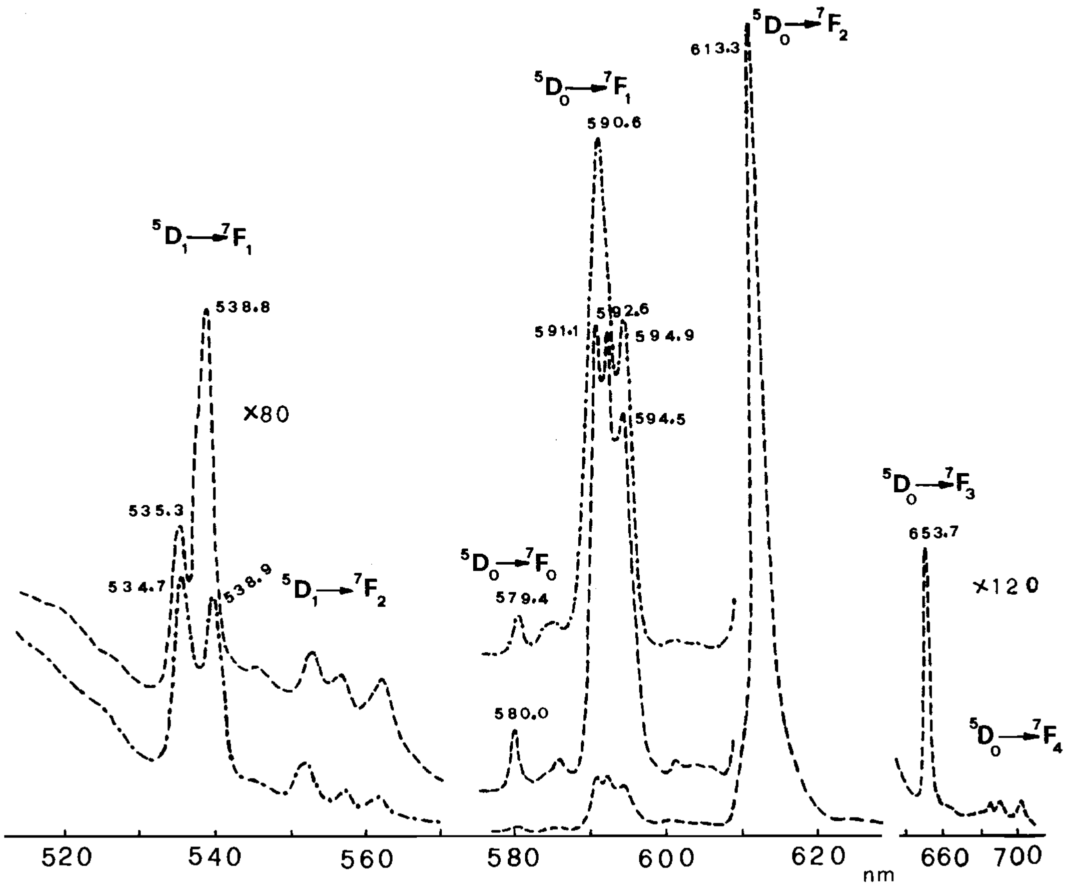

Fig. 2. Emission spectra, from solid at 77 K, of: (– – –) $Eu(bipyO_2)_2(NO_3)_3$; (–·–) $Eu(bipyO_2)_4(ClO_4)_3$; excitation with 320 nm radiation.

octakis (pyO), the tetrakis ($bipyO_2$) and the tris-($terpyO_3$) perchlorate and trifluoromethanesulphonate complexes have well-defined environments of the type LnO_8 and LnO_9. This group of complexes is characterized by the presence of uncoordinated anions and by f–f spectra which are unaffected by the anion present. The intensity of the hypersensitive transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}$ in Nd^{3+} and $^5I_8 \rightarrow {}^5G_6$ in Ho^{3+} ions increases in the order: pyO < $terpyO_3$ < $bipyO_2$ reaching very high and uncommon values for the $bipyO_2$ complexes. Likely, this chelating, although non-coplanar molecule represents an example of exceptionally high electron-donating power ligands toward lanthanide(III) cations. Steric effects certainly contribute to determine the relatively low intensity values measured for the complexes with $terpyO_3$. Both $bipyO_2$ and $terpyO_3$ molecules form, on complexation, seven-membered chelate rings; however, $terpyO_3$ is constrained to assume highly distorted conformation and, probably, forms polymeric structures. This trend is the same as observed for octahedral complexes of these ligands with d-transition metals for which the lowest values of Dq are those measured for the $terpyO_3$ complexes and attributed to the formation of highly distorted pseudooctahedral structures [11].

As regards the δ parameter, the values measured for these complexes are positive in any case (for Ho^{3+} smaller than unity) and increase, for systems where the anion is certainly uncoordinated, in the order: pyO < $terpyO_3$ < $bipyO_2$. This series is the same as found on the basis of the intensity enhancements and correlates the nephelauxetic effect with hypersensitivity although, in accordance with Sinha [12], the absolute value of this parameter is not of decisive importance.

Marked enhancements of the band shape and intensity of the hypersensitive transitions occurring by addition of excess of the ligand to the cation in water show the ability of these ligands to coordinate with lanthanide(III) cations also in aqueous solution. The low intensity values generally measured for these systems can be associated with instability of the complexes in water.

The emission spectra of some complexes are reported in Figs. 2–4 and Table III.

There is little doubt both from synthetic and spectral data that the octakis(pyO) lanthanide(III)

TABLE III. Partial Energy Level Scheme for Some Europium(III) and Terbium(III) Complexes with N-oxides. The values refer to the barycentre of the band (cm^{-1}).

Complex	Level									η^d
	$^7F_0$	$^7F_1$	$^7F_2$	$^7F_3$	$^7F_4$	$^7F_5$	$^7F_6$	$^5D_0$	$^5D_4$	
$Eu(pyO)_8(NO_3)_3$	0	379[b]	1015	1884*	2907			17262[b]		0.31
$Eu(bipyO_2)_2(NO_3)_3$	0	366	938	1939	[a]			17241		6.85
$Eu(bipyO_2)_2(NCS)_3 \cdot H_2O$	0	378	961	1937*	[a]			17256		4.74
$Eu(bipyO_2)_4(ClO_4)_3$	0	367	955	1932	2875*			17259		10.62
$Eu(terpyO_3)(NO_3)_3 \cdot H_2O$[c]	0	367	1044	1895	2641*			17265		3.52
$Eu(terpyO_3)_3\ (ClO_4)_3 \cdot 2H_2O$[c]	0	355	889	1924	[a]			17250		4.45
$Tb(pyO)_8(NO_3)_3$	5640	5407	4968	4292	3558	2115	0		20400	1.15
$Tb(bipyO_2)_2(NO_3)_3$	[a]	5181	4849	4298	3331	2055	0		20367	2.35
$Tb(bipyO_2)_4(ClO_4)_3$	5546*	5213	4877	4285	3391	2095	0		20427	2.10
$Tb(terpyO_3)(NO_3)_3 \cdot H_2O$	5395*	5012*	4910*	4285	3339	2039	0		20354	1.42

*±10. [a] Very weak. [b] The position of the $^5D_1$ state is obtained from both the emission and absorption spectra and is located at 19004 cm^{-1}. The barycentres of the bands associated with the transitions $^5D_1 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_1$ lie at 18625 and 16883 cm^{-1}, respectively. Combining these values, the 379 cm^{-1} value for the $^7F_1$ state and the 17262 cm^{-1} value for the $^5D_0$ state were obtained. [c] From ref. 2. [d] See text.

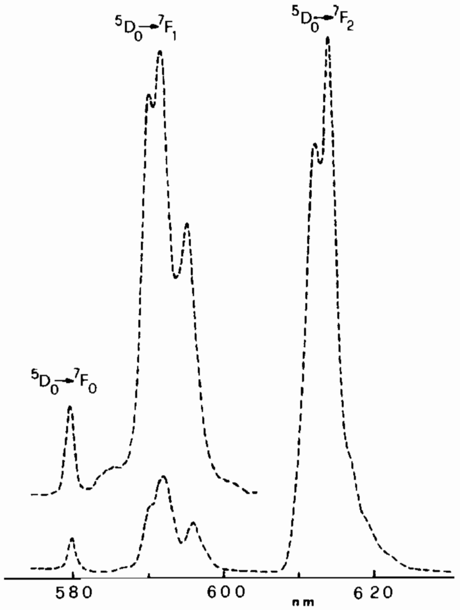

Fig. 3. Emission spectrum of $Eu(bipyO_2)_2(NCS)_3 \cdot H_2O$, from solid at 77 K; excitation with 330 nm radiation.

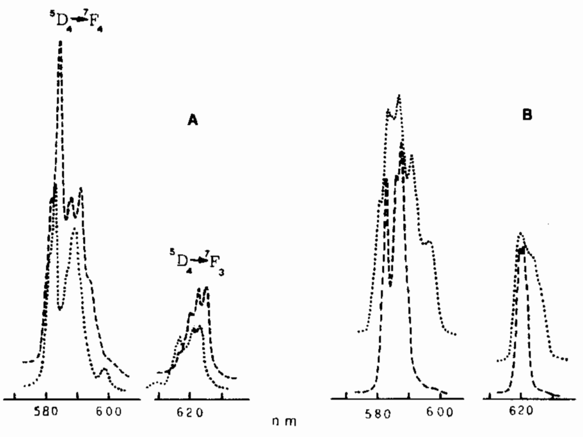

Fig. 4. Emission spectra, from solid at 77 K, of: A (– – –) $Tb(bipyO_2)_2(NO_3)_3$; (.....) $Tb(bipyO_2)_4(ClO_4)_3$. B (– – –) $Tb(pyO)_8(NO_3)_3$; (.....) $Tb(terpyO_3)(NO_3)_3 \cdot H_2O$. $TerpyO_3$ and $bipyO_2$ complexes excited with 320 nm radiation; pyO complexes excited with 365 nm radiation.

nitrate complexes consist of the octacoordinated ion $[Ln(pyO)_8]^{3+}$ surrounded by the three nitrate ions. The dominant geometries for eight-coordination are the square antiprism (D_{4d}), the tetragonal dodecahedron (D_{2d}) and the bicapped trigonal prism (C_{2v}); much less represented are the cube and other geometries. The octakis(pyO) lanthanum(III) and neodymium(III) perchlorate complexes have been described in terms of square antiprismatic geometry; however, a geometry intermediate between a cube and a square antiprism is stabilized in a second modification [13]. Samarium(III) ion has three fluorescing levels close to the triplet state and several final states which can be manifoldly split under the field of the various symmetries. The emission spectrum of the complex $Sm(pyO)_8(NO_3)_3$ obtained from the solid at 77 K and excited with 365 nm radiation shows that the number of components of the transitions $^4G_{5/2} \rightarrow {}^6H_{5/2,7/2,9/2}$ is rather low and consistent with a high symmetry for the electrostatic field surrounding the cation [3]. In this connection, the emission spectrum of the corresponding europium(III) complex is more indicative. The spectrum shows only one intense component of the $^5D_0 \rightarrow {}^7F_1$ transition and four much weaker components of the $^5D_0 \rightarrow {}^7F_2$ transition, the intensity of which decreases by about 50% on lowering the temperature from 300 to 77 K. The $^5D_0 \rightarrow {}^7F_0$ transition is forbidden; no line appears in fact in the relative region [3]. The spectrum is essentially the same as observed for systems having ascertained cubic symmetry [14, 15]. Only a field possessing a cubic symmetry does not cause splitting of the $^7F_1$ state. However, the slight broadening of the band associated with the $^5D_0 \rightarrow {}^7F_1$ transition, the exhibition in this region of a second, though very weak, component and the appearance of discrete lines in the region of the $^5D_0 \rightarrow {}^7F_2$ transition indicate that, probably, a geometry intermediate between the cube and the square antiprism is stabilized also in this case [3].

Samarium(III), europium(III) and terbium(III) complexes with $bipyO_2$ show strong emission when excited with near ultraviolet radiation. Emission arises due to the ligand to cation energy transfer and mainly from the $^4G_{5/2}$, $^5D_0$ and $^5D_4$ excited states, respectively.

Synthetic and spectroscopic data suggest that the complex $Eu(bipyO_2)_2(NO_3)_3$ consists of the decacoordinated EuO_{10} entity acquired by three bidentate nitrate groups and two bidentate $bipyO_2$ molecules. The emission spectrum, from the solid at 77 K and excited with 320 nm radiation, shows two almost equal intensity lines in the region of the $^5D_0 \rightarrow {}^7F_1$ transition (Fig. 2). A second, but weaker line appearing at lower frequencies can be associated also with this transition. A very intense line is shown in the region of the $^5D_0 \rightarrow {}^7F_2$ transition; it is, however, slightly broadened because of the exhibition of other two very weak components. A line appears in the region of the $^5D_0 \rightarrow {}^7F_0$ transition, the intensity of which is less than 0.3% of the $^5D_0 \rightarrow {}^7F_2$ transition but about 4% of the $^5D_0 \rightarrow {}^7F_1$ transition, indicating that this transition cannot be taken as strictly forbidden. The $^5D_0 \rightarrow {}^7F_3$ transition consists of a unique, though broad, component while three weak components of the $^5D_0 \rightarrow {}^7F_4$ transition appear in the relative region. Emission arises also from the $^5D_1$ level. Two weak and broad components of the $^5D_1 \rightarrow {}^7F_1$ transition and three weak components of the $^5D_1 \rightarrow {}^7F_2$ transition appear in the regions 530–545 and 550–565 nm, respectively. The almost exclusive geometries for ten-coordination are the bicapped square antiprism (D_{4d}) and the bicapped dodecahedron (D_2 or C_{2v}). The appearance of three lines in the region of the $^5D_0 \rightarrow {}^7F_1$ transition and three ones in the region of the $^5D_0 \rightarrow {}^7F_2$ transition agrees with a bicapped dodecahedral geometry and D_2 site symmetry for the europium(III) ion. The emission spectrum of the complex $Eu(bipyO_2)_4(ClO_4)_3$ differs only in some details from the emission spectrum of the corresponding nitrate complex. The perchlorate complex consists of the chromophore EuO_8 formed by four bidentate $bipyO_2$ molecules and exhibits a spectrum which is essentially the same as shown by the corresponding tetrakis($bipyO_2$) trifluoromethanesulphonate complex for which a distorted D_4 site symmetry was suggested [5].

For the cation in non-centrosymmetric ligand field not only magnetic-dipole but also electric-dipole transitions are allowed. For the europium(III) ion in D_4 site symmetry one component of the $^5D_0 \rightarrow {}^7F_2$ transition and two components of the $^5D_0 \rightarrow {}^7F_1$ transition are allowed; for the cation in D_{2d} site symmetry two components of each transition are allowed and should be, of course, observed in the spectrum. D_4 site symmetry for the europium(III) ion in this complex is suggested by the emission spectrum. An exceptionally high value for the intensity ratio $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ has been measured for both complexes.

The emission spectrum of the complex $Eu(bipyO_2)_2(NCS)_3 \cdot H_2O$ shows a line at 579.5 nm associated with the $^5D_0 \rightarrow {}^7F_0$ transition (Fig. 3). The exhibition of this line agrees with the following site symmetries: C_n, C_s, $C_{n'v}$ ($n = 2, 3, 4, 6$; $n' = 1, 2, 3, 4, 6$) [16]. The $^5D_0 \rightarrow {}^7F_1$ transition consists of a component at 595.5 nm and two more intense ones at 590.2 and 591.6 nm. Two lines at 612.5 and 614.5 and two shoulders at lower frequencies arise from the $^5D_0 \rightarrow {}^7F_2$ transition. The emission spectrum does not change on dehydrating the complex; moreover, dehydration occurs at low temperature (~50 °C) indicating the presence of free water molecules only. On the basis of these results, seven-coordination can be suggested for this complex. We may consider the C_{2v} site symmetry as the most consistent for the europium(III) ion in this complex, corresponding to a capped trigonal prism. On the other hand, the energy difference between this model and the capped octahedron (C_{3v}) is small. These two geometries depend on the capping ligand entering a triangular or a tetragonal face of the trigonal prism giving rise to a C_{3v} or C_{2v} geometry.

The emission spectra obtained from aqueous solutions containing the europium(III) ion and large excess of $bipyO_2$ or pyO show that complexes form also in water. The spectrum of the $bipyO_2$–europium system resembles those obtained from the solid complexes $Eu(bipyO_2)_4X_3$, $X = ClO_4, CF_3SO_3$ [5]. This indicates that the tetrakis($bipyO_2$) complex is stable also in aqueous solution. The emission spectrum of the pyO–europium system in water differs remarkably from that of the solid octakis(pyO) complex, even when large excess of pyO is used, indicating different environment.

The emission spectra of the complexes $Eu(terpyO_3)(NO_3)_3 \cdot H_2O$ and $Eu(terpyO_3)_3(ClO_4)_3 \cdot 2H_2O$ have been discussed previously [2] and interpreted in terms of monocapped square antiprismatic and tricapped trigonal prismatic geometries, respectively.

Terbium(III) complexes with these ligands show strong emission when excited with 320–340 nm radiations at 77 K. Tb^{3+} ion has one emitting level below 22.000 cm^{-1} ($^5D_4$) and, like the Eu^{3+} ion although in the reverse order, seven final states ($^7F_{6-0}$). These states, except J = 0 in any case and J = 1 in cubic symmetry, are split under the field of the various symmetries and the number of lines associated with each transition that occurs between the $^5D_4$ and the lowest final states is normally high. The $^5D_4 \rightarrow {}^7F_6$ and the $^5D_4 \rightarrow {}^7F_5$ transitions are generally the most populated transitions; however, the $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ transitions, although much less intense, may appear in the spectra clearly resolved into their components.

The emission spectra of some terbium(III) complexes with these ligands, relatively to the regions where the $^5D_4 \rightarrow {}^7F_{4,3}$ transitions are expected, are reported in Fig. 4. In cubic field the $^7F_4$ and $^7F_3$ states split into four and three levels respectively while in lower symmetries the number of levels increases from six to nine and from five to seven, respectively. The number of components of the $^5D_4 \rightarrow {}^7F_{4,3}$ transitions that appear in the spectra of the octakis(pyO) complexes is rather small, indicating a high symmetry for the electrostatic field surrounding the cation. This number increases on passing from the pyO to the $bipyO_2$ ad $terpyO_3$ complexes with terbium(III) nitrate and from the perchlorate to the nitrate complexes and is consistent with a generalized lowering in the symmetry at the cation site. As in the case of the corresponding europium(III) complexes, the bis($bipyO_2$) nitrate and the tetrakis($bipyO_2$) perchlorate complexes exhibit spectra which differ from one another only in the number of the lines observed in the region of the $^5D_4 \rightarrow {}^7F_4$ transition which increases for the nitrate complex.

Conclusions

Although various series of complexes, depending on several factors, can be obtained, these molecules have demonstrated to behave as strongly basic ligands toward lanthanide(III) cations giving rise to well-defined stoichiometry compounds and full-ligand species also in aqueous solution. Lanthanide(III) nitrates and thiocyanates, however, preferentially form bis($bipyO_2$) and mono($terpyO_3$) species in non-aqueous solvents.

The intensity of the hypersensitive transitions and the nephelauxetic effect measured for complexes of these ligands in which the anionic groups are certainly uncoordinated show actual correlation, both increasing in the order: pyO < $terpyO_3$ < $bipyO_2$. Lack of planarity in $terpyO_3$ molecule, constrained by steric and electrostatic repulsive effects to assume distorted conformation, contributes to determine the relatively low values measured both for the intensity of the hypersensitive transitions and for the nephelauxetic effect. The three oxygen atoms make this molecule less adaptable around the cation than the $bipyO_2$ molecule causing an increase in the molecular distortion and a lengthening of the cation–ligand bond distance. A generalized lowering in the site symmetry is observed on passing from the pyO to the $bipyO_2$ and $terpyO_3$ complexes.

The intensity ratio values $\eta_{Eu} = {}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ and $\eta_{Tb} = {}^5D_4 \rightarrow {}^7F_5/{}^5D_4 \rightarrow {}^7F_6$ obtained from the europium and terbium complexes, respectively, increase in the order: pyO < $terpyO_3$ < $bipyO_2$. If excitation of the ligand occurs, the emission intensity depends on the probability of the fluorescing levels in the ions receiving energy from the ligand. On the other hand, the efficiency of the intramolecular energy transfer increases with covalency. This corresponds, among the various transitions that occur between the low J-values in these tripositive cations, to an increase in the $^5D_0 \rightarrow {}^7F_2$ (Eu^{3+}) and $^5D_4 \rightarrow {}^7F_5$ (Tb^{3+}) transitions probability.

The intensity ratios η_{Eu} and η_{Tb} increase in the same order found for the intensity enhancements, reflecting the electron-donating power of these ligands; the values measured for the $bipyO_2$ complexes are in all cases very high and uncommon.

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