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Absorption and Emission Spectra of Neodymium(III) and Europium(III) Complexes*

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The absorption and emission spectra of several complexes of neodymium(III) and europium(III) ions have been examined in order to obtain reliable information relating to coordination number, nature of bonding and symmetry around the lanthanide ion. It has been found that steric factors may force the polyhedron of coordination towards geometries less favourable by ligand–ligand repulsion. In general, no correlation has been found to exist between the low intensity of the hypersensitive transitions and high symmetry or low symmetry and high intensity. The results have pointed out the role of covalency in hypersensitivity.

Introduction

The rare earth complexes in which strong fluorescence has been observed have almost exclusively Sm^{3+}, Eu^{3+}, Tb^{3+} or Dy^{3+} as the central metal ion. Among these, the europium(III) complexes have been the subject of extensive studies 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 has been calculated. Thus, knowing the symmetry class at the cation site, the number of levels can be predicted. Alternatively, lanthanide(III) cations may be used to probe the symmetry of sites in crystals.

Metal ion fluorescence in europium(III) complexes originated mainly at the $^5D_0$ level and terminates prevalently at the $^7F_1$ and $^7F_2$ levels. Emission associated with transitions to the $^7F_0$, $^7F_3$ and $^7F_4$ levels is generally weak while that arising from transitions to the $^7F_5$ and $^7F_6$ levels is too weak to be observed. Transitions from the non-degenerate $^5D_0$ level to the various ^7F_J levels are useful for interpretation of the europium(III) site symmetries. The number of electric-dipole allowed ($\Delta J \leqslant 6$) and magnetic-dipole allowed ($\Delta J = 0, \pm 1$, except $J = 0 \rightarrow J' = 0$) transitions has in fact been predicted from group theory.

With the purpose of obtaining reliable information relating to coordination number, the nature of bonding and symmetry around the lanthanide(III) ion, a systematic study of the absorption and emission f–f spectra of lanthanide(III) complexes, lacking specific X-ray studies, has been undertaken in this laboratory. This work also concerns complexes the preparation and characterization of which has been reported previously. Conclusions on the cation environments were inferred by vibrational and electronic absorption spectra, molar conductivity and thermoanalytical measurements only.

Experimental

The following complexes were taken into account: $Ln(PU)_8X_3$ (**I**); $Ln(Eu)_8X_3$ (**II**); $Ln(PA)_4(ClO_4)_3$ (**III**); $Ln(pyO)_8X_3$ (**IV**); $Ln(2\text{-}AN)_2Cl\cdot 3H_2O$ (**V**); $Ln(pyO)_4(NCS)_3\cdot H_2O$ (**VI**); $Ln(biquO_2)_2(NCS)_3\cdot H_2O$ (**VII**); $Ln(PA)_3(NCS)_3$ (**VIII**); $Ln(PA)_3(NO_3)_3$ (**IX**); $Ln(DMU)_3(NO_3)_3\cdot 2H_2O$ (**X**); $Ln(DEU)_3(NO_3)_3\cdot 2H_2O$ (**XI**); $Ln(PU)_3(NO_3)_3\cdot 3H_2O$ (**XII**); $Ln(TMU)_3(NO_3)_3$ (**XIII**). The spectra of the complexes $Ln(HBpz_3)_3$ (**XIV**), synthesized following reference [1], are also reported. *Abbreviations:* PU = perhydropyrimidin-2-one; EU = imidazolin-2-one; PA = picolinamide; pyO = pyridine-N-oxide; 2-AN$^-$ = quinolinecarboxylato ion; biquO$_2$ = 2,2′-biquinolyl-N,N′-dioxide; DMU = N,N′-dimethylurea; DEU = N,N′-diethylurea; TMU = N,N,N′,N′-tetramethylurea; $HBpz_3^-$ = hydrotris(pyrazol-1-yl)borate ion; Ln = Nd, Eu, Ho; X = NO_3, ClO_4, Cl, NCS, PF_6, BF_4, CF_3SO_3.

Preparation of the Complexes

Complexes **I**, **II**, **X**, **XI**, **XII** and **XIII** were prepared following references [2] and [3]. Complexes **III**, **VIII** and **IX** were prepared following reference [4] and complexes **V** following reference [5]. Complexes **IV** were obtained by adding 8 mmol of pyO in 10 ml of anhydrous ethanol to a solution containing

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TABLE I. Emission Spectra of Europium(III) Complexes (nm).

Complex	$^5D_0 \rightarrow {}^7F_0$	$^5D_0 \rightarrow {}^7F_1$	$^5D_0 \rightarrow {}^7F_2$	$^5D_0 \rightarrow {}^7F_3$	$^5D_0 \rightarrow {}^7F_4$
$Eu(PU)_8(NO_3)_3$	579.5	588.3 593.3 593.9	612.7 617.0	651.5	692.7 693.8 697.2 698.5 701.6
$Eu(pyO)_8(BF_4)_3$	579.7	592.3 592.7	613.1 617.0 620.0	651.0	691.8 699.5
$Eu(HBpz_3)_3$	579.6	588.7 593.1	611.9 613.2 617.5	650.3	692.5 698.8
$Eu(2\text{-}AN)_2Cl \cdot 3H_2O$	579.8	587.8 589.6 594.8	612.3 617.2 622.5	651.7 657	689.0 692.6 694.4 700.3 702.5
$Eu(PA)_4(ClO_4)_3$	579.4	591.6 592.5 595.2	612.7 613.6 618.2	652.1 655	692.3 693.3 697.5 698.8 701.8
$Eu(biquO_2)_2(NCS)_3 \cdot H_2O$	579.8	590.6 591.9 595.0	612.2 613.4 617.2 618.0 620.7	650.6 656	691.8 692.6 695.3 696.1 699.2 702.2
$Eu(pyO)_4(NCS)_3 \cdot H_2O$	579.7	591.2 593.1 595.7	611.8 614.0 617.7 620.3	651.4 656	692.3 694.0 694.8 699.2 710.6
$Eu(PA)_3(NO_3)_3$	579.9	590.4 592.9 593.7	612.4 614.7 618.3	650.5 655.4	688.6 689.9 693.0 698.1 700.4
$Eu(DEU)_3(NO_3)_3 \cdot 2H_2O$	579.8	590.7[a] 593.5 595.0	614.5 617.2 618.1 620.0	650.8	690.6 694.0 695.2 699.7 700.6 702.5
$Eu(PU)_3(NO_3)_3 \cdot 3H_2O$	580.0	592.1 594.2	614.3 618.7	650.4 653.8	688.2 689.5 693.1 694.7 700.2

[a] The complex $Eu(TMU)_3(NO_3)_3$ exhibits a doublet at 591.2 and 592.6 nm and a line at 595.5 nm.

1 mmol of the lanthanide(III) cation in 10 ml of the same solvent and 10 ml of triethylorthoformate as dehydrating agent. The resulting solution was refluxed for 1 hr under dry nitrogen. After addition of dehydrated diethyl ether abundant precipitates formed on cooling the solution. The precipitates were rapidly filtered off, washed with anhydrous ethanol–diethyl ether mixture (1:5) and dried in vacuum at room temperature. The complexes are soluble in acetonitrile and alcohols where they act as 1:3 electrolytes. Complexes **VI** were prepared following reference [6]. Complexes **VII** were obtained by adding 2.5 mmol of $biquO_2$ dissolved in the minimum required volume of boiling anhydrous ethanol to 1

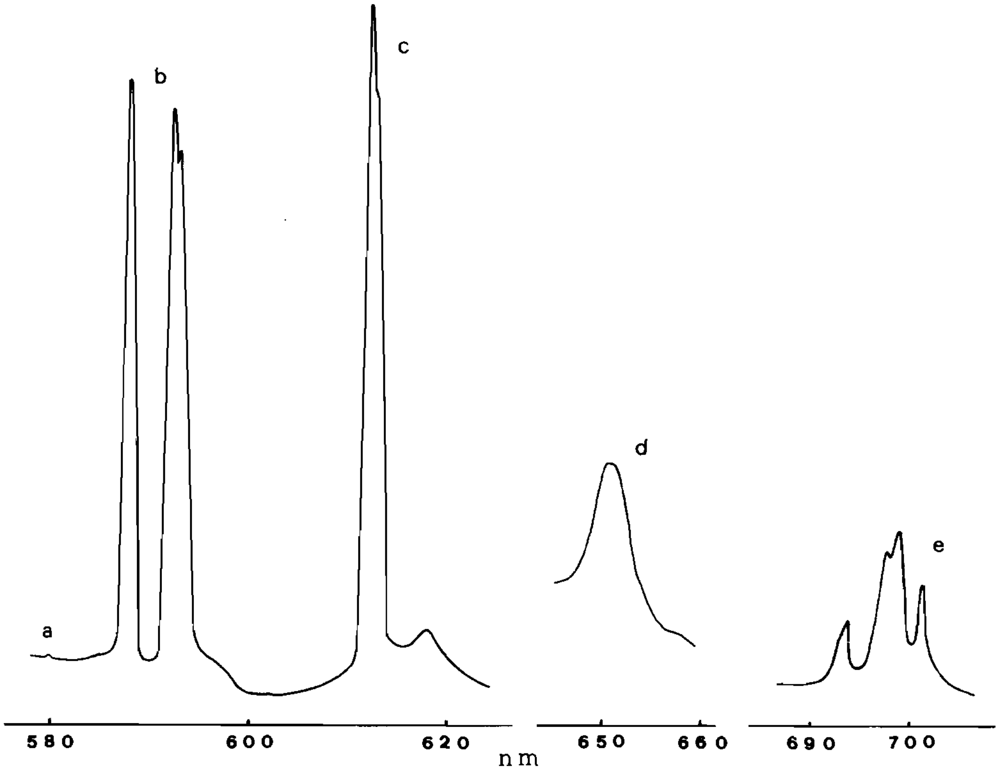

Fig. 1. Emission spectrum, from solid at 77 K, of $Eu(PU)_8(ClO_4)_3$. Excitation with 395 nm radiation. a) $^5D_0 \rightarrow {}^7F_0$; b) $^5D_0 \rightarrow {}^7F_1$; c) $^5D_0 \rightarrow {}^7F_2$; d) $^5D_0 \rightarrow {}^7F_3$; e) $^5D_0 \rightarrow {}^7F_4$.

mmol of the lanthanide(III) thiocyanate in 10 ml of the same solvent. The complexes precipitated slowly as crystalline powder on stirring the solution. The precipitates were filtered off, washed with anhydrous ethanol and dried in vacuum at room temperature. The complexes are soluble in acetonitrile where they behave as non-electrolytes.

Measurements

Electronic absorption spectra were measured with a Perkin-Elmer 330 spectrophotometer. The absorption intensity, presented as oscillator strengths, was calculated from the relationship:

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

where η is the refractive index of the solution and ϵ the molar extinction coefficient at the wavelength ν. The solid state absorption spectra were measured with the same instrument on solid compounds pasted with nujol and placed in a sandwich type quartz cell.

Metal ion fluorescence spectra were obtained by a Perkin-Elmer MPF-3L fluorescence spectrophotometer at room and liquid nitrogen temperatures by excitation of the europium(III) ion to the $^5L_6$ level or by intramolecular energy transfer from the excited ligand to the emitting states of the cation. The relative intensities of the $^5D_0 \rightarrow {}^7F_{0-4}$ transitions were obtained by direct planimetry of the spectra. Emission from the $^5D_1$ level was subtracted. The resolution was better than 7 cm^{-1}; when it was increased, there was no essential change in the spectra. For measurements either at room or liquid nitrogen temperature, the solution or the solid compound was placed in a quartz tube which was immersed in a Dewar flask filled (or not) with liquid nitrogen.

IR spectra were measured with a Perkin-Elmer 684 spectrophotometer on samples suspended in a KBr or CsBr matrix or mulled with mineral oil.

Other experimental procedures (electrolytic conductivity and thermal analysis measurements) were as described previously [7].

Results

Emission Spectra

The emission spectra of the europium(III) complexes are reported in Tables I, II and Figs. 1–8.

The emission spectra of the europium(III) complexes **I** and **II** are similar to one another and to the spectra of the corresponding trifluoromethanesulfonates [3], showing only insignificant differences

TABLE II. Partial Energy Level Diagram for Europium(III) Complexes (cm^{-1}).

Complex	${}^7F_0$	${}^7F_1$	${}^7F_2$	${}^7F_3$	${}^7F_4$	${}^5D_0$
$Eu(PU)_8(NO_3)_3$	0	258	935	1907	2820	17256
		401	1049		2843	
		418			2913	
					2940	
					3003	
$Eu(pyO)_8(BF_4)_3$	0	367	939	1889	2795	17250
		378	1043		2954	
			1121			
$Eu(HBpz_3)_3$	0	266	910	1875	2813	17253
		392	945		2943	
			1059			
$Eu(2\text{-}AN)_2Cl \cdot 3H_2O$	0	234	915	1903	2733	17247
		286	1045	2026	2809	
		435	1183		2846	
					2967	
					3012	
$Eu(PA)_4(ClO_4)_3$	0	356	938	1924	2814	17259
		381	962	1992	2835	
		458	1083		2922	
					2949	
					3010	
$Eu(biquO_2)_2(NCS)_3 \cdot H_2O$	0	315	912	1877	2792	17247
		352	944	2003	2809	
		452	1045		2865	
			1066		2881	
			1136		2945	
					3010	
$Eu(pyO)_4(NCS)_3 \cdot H_2O$	0	335	905	1898	2805	17250
		389	963	2006	2841	
		443	1061		2857	
			1129		2948	
					2997	
$Eu(PA)_3(NO_3)_3$	0	306	915	1871	2722	17244
		378	976	1986	2749	
		400	1071		2814	
					2919	
					2966	
$Eu(DEU)_3(NO_3)_3 \cdot 2H_2O$	0	318	974	1881	2767	17247
		398	1045		2838	
		440	1068		2863	
			1118		2955	
					2974	
$Eu(PU)_3(NO_3)_3 \cdot 3H_2O$	0	352	962	1866	2710	17241
		412	1078	1946	2738	
					2813	
					2846	
					2959	

in energy, number of components and relative intensity of the various transitions. Emission arises mainly from transitions originating at the ${}^5D_0$ level. Transitions originating at the ${}^5D_1$ level are not observed or are too weak for detailed study. These complexes show weak metal ion fluorescence even at liquid nitrogen temperature. In any case a band is observed in the region of the ${}^5D_0 \rightarrow {}^7F_0$ transition, but its intensity is so low that this transition can be taken as strictly forbidden. The ${}^5D_0 \rightarrow {}^7F_1$ is the most intense transition; it consists of two almost equal intensity components, one of which is split into two lines. This suggests that these two lines could originate from an E-component. The ${}^5D_0 \rightarrow {}^7F_2$ transition consists of a relatively intense band slightly split into two lines (E-component) and a much weaker one at lower frequencies. A unique, though broad band appears in the region of the ${}^5D_0$

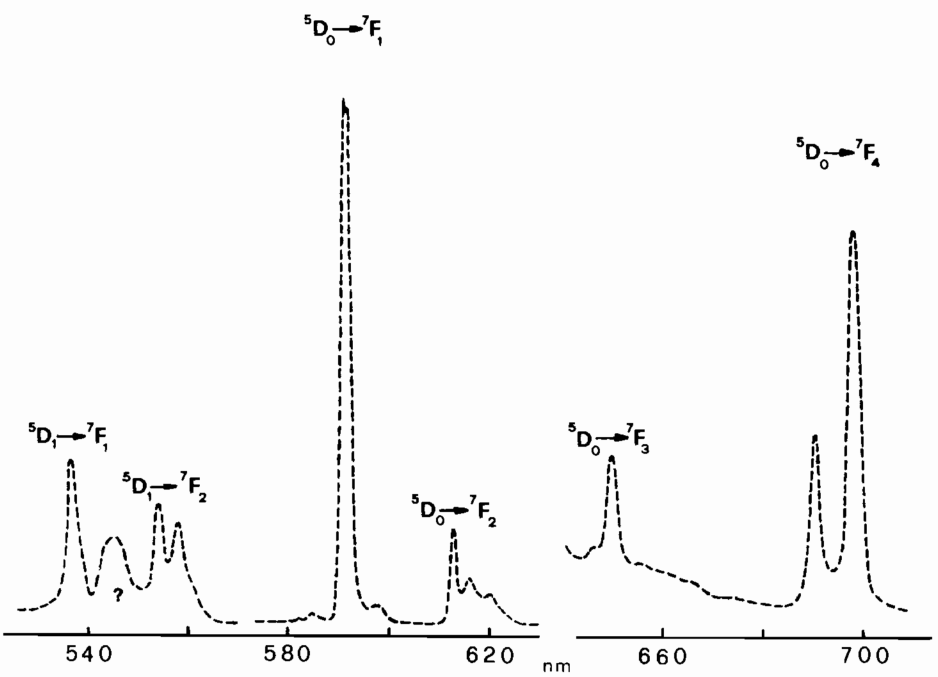

Fig. 2. Emission spectrum, from solid at 77 K, of $Eu(pyO)_8(BF_4)_3$. Excitation with 320 nm radiation.

→ $^7F_3$ transition while three bands, two of which are broad, appear in the region of the transition $^5D_0$ → $^7F_4$. On increasing the instrumental resolution, the broad bands appear clearly resolved into two components each. The emission spectrum of complex I is reported in Fig. 1 and Tables I and II.

It can be seen from Fig. 2 and Tables I, II that the spectra of the complexes $Eu(pyO)_8X_3$ are characterized by a unique band in the region of the $^5D_0$ → $^7F_1$ transition. Whereas in the spectra of the hexafluorophosphate, tetrafluoroborate, perchlorate and trifluoromethanesulfonate complexes this band is slightly split into two lines, it does not show any appreciable splitting in the spectrum of the nitrate complex [6]. The $^5D_0$ → $^7F_0$ transition is in all cases almost totally inactive, the spectra showing in the relative region no band or a very weak one. The $^5D_0$ → $^7F_2$ transition consists of three low-intensity components. Two very weak bands appear in the region of the $^5D_0$ → $^7F_4$ transition. The intensity of the strongest component is just that of the $^5D_0$ → $^7F_0$ transition. A single band arising from the $^5D_1$ → $^7F_1$ and two bands from the $^5D_1$ → $^7F_2$ transitions appear in the relative regions of the spectra.

In Fig. 3 and Tables I, II is reported the emission spectrum of the europium(III) complex V. The $^5D_0$ → $^7F_0$ transition can be taken as forbidden, the spectrum showing in the relative region a very weak band. Three components of the $^5D_0$ → $^7F_1$ transition and three components of the $^5D_0$ → $^7F_2$ transition are shown by the spectrum. Apart from the $^5D_0$ → $^7F_3$ transition which appears as a unique broad band, the $^5D_0$ → $^7F_4$ transition consists of three components, two of which split, at higher resolution, into two lines each. Emission arising from the $^5D_1$ level has been also observed. Two weak bands due to the $^5D_1$ → $^7F_1$ transition and three weak components of

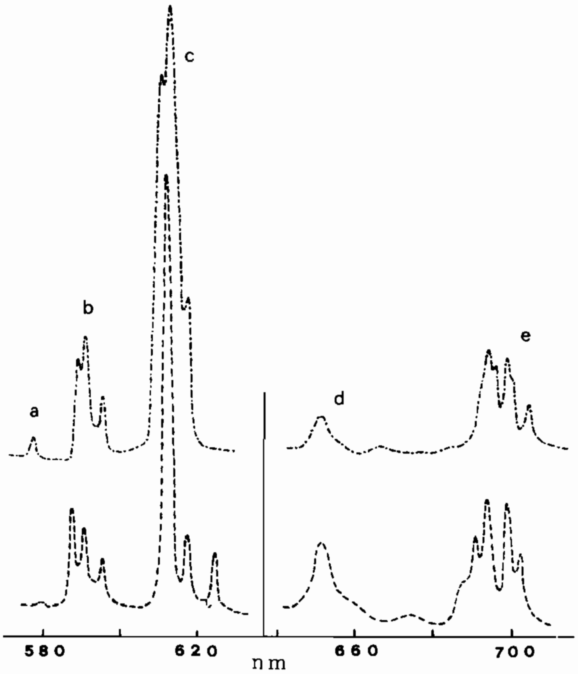

Fig. 3. Emission spectra, from solid at 77 K, of (— — —) $Eu(2\text{-}AN)_2Cl \cdot 3H_2O$, excitation with 340 nm radiation; (—·—·—) $Eu(PA)_4(ClO_4)_3$, excitation with 300 nm radiation. a) $^5D_0$ → $^7F_0$; b) $^5D_0$ → $^7F_1$; c) $^5D_0$ → $^7F_2$; d) $^5D_0$ → $^7F_3$; e) $^5D_0$ → $^7F_4$.

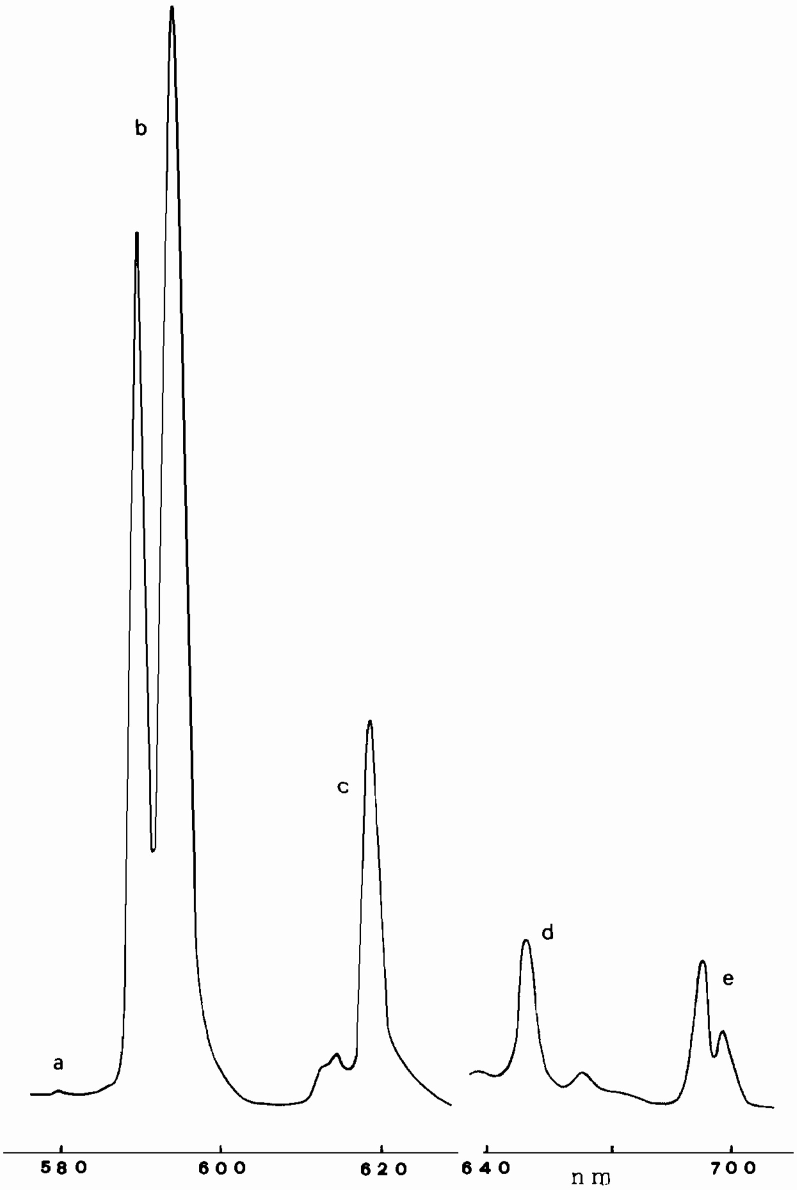

Fig. 4. Emission spectrum, from solid at 77 K, of Eu(HBpz$_3$)$_3$. Excitation with 330 nm radiation. a) $^5D_0 \rightarrow {}^7F_0$; b) $^5D_0 \rightarrow {}^7F_1$; c) $^5D_0 \rightarrow {}^7F_2$; d) $^5D_0 \rightarrow {}^7F_3$; e) $^5D_0 \rightarrow {}^7F_4$.

the $^5D_1 \rightarrow {}^7F_2$ transition appear in the spectrum of this complex. Emission occurs when the complex is excited with 340 nm radiation.

The europium(III) complex **XIV** is metal ion fluorescent when excited with 330 nm radiation. Emission arises mainly from transitions originating at the $^5D_0$ level and terminating at the $^7F_1$ and $^7F_2$ levels. Transitions from $^5D_0$ to $^7F_3$ and $^7F_4$ levels and from the $^5D_1$ to the various ^7F_J levels are of low intensity. The intensity of the $^5D_0 \rightarrow {}^7F_0$ transition is so low that it can be taken as strictly forbidden. The $^5D_0 \rightarrow {}^7F_1$ transition consists of two almost equal intensity components. One component of relatively low intensity (the intensity is less than 20% that of the most intense $^5D_0 \rightarrow {}^7F_1$ transition) and two much weaker ones at higher frequencies appear in the region of the $^5D_0 \rightarrow {}^7F_2$ transition. The intensity does not decrease significantly as the temperature is lowered, indicating that the origin of the most intense component is not vibronic. The transition $^5D_0 \rightarrow {}^7F_4$ shows two components of low intensity. Emission arising from the $^5D_1$ level is also observed. A broad band due to the $^5D_1 \rightarrow {}^7F_1$ transition and two bands accompanied by a much weaker one due to the transition $^5D_1 \rightarrow {}^7F_2$ appear in the relative regions of the spectrum. The emission spectrum is reported in Fig. 4 and Tables I, II.

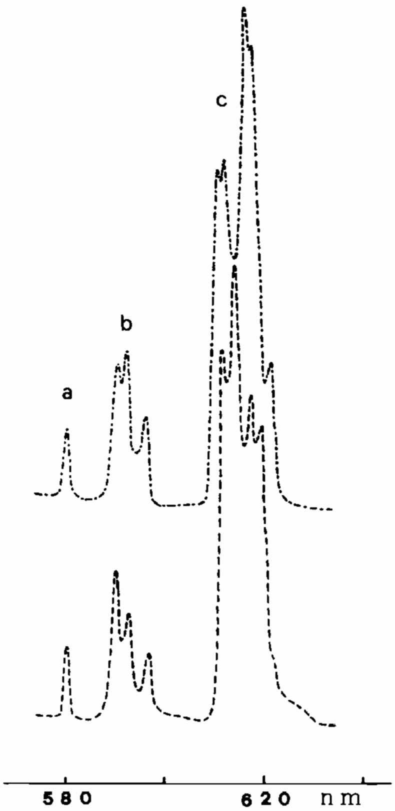

Fig. 5. Emission spectra, from solid at 77 K, of (– – –) $Eu(pyO)_4(NCS)_3 \cdot H_2O$, excitation with 320 nm radiation; (–·–·–) $Eu(biquO_2)_2(NCS)_3 \cdot H_2O$, excitation with 360 nm radiation. a) $^5D_0 \rightarrow {}^7F_0$; b) $^5D_0 \rightarrow {}^7F_1$; c) $^5D_0 \rightarrow {}^7F_2$.

The emission spectra of the europium(III) complexes **VI** and **VII** are reported in Fig. 5 and Tables I, II. Both spectra show a line of relatively high intensity arising from the $^5D_0 \rightarrow {}^7F_0$ transition. The spectrum of complex **VII** exhibits a band split into two lines in the region of the $^5D_0 \rightarrow {}^7F_1$ transition. A weaker but un-split component of this transition appears at lower frequencies. The $^5D_0 \rightarrow {}^7F_2$ transition consists of two high-intensity components which are split into two lines each. Three distinct components of the $^5D_0 \rightarrow {}^7F_1$ transition and four components of the transition $^5D_0 \rightarrow {}^7F_2$ appear in the spectrum of complex **VI**. Low-intensity components of this transition appear in both spectra at lower frequencies. The $^5D_0 \rightarrow {}^7F_3$ transition appears as two weak and broad bands. More than three poorly resolved bands arise from the $^5D_0 \rightarrow {}^7F_4$ transition; on increased instrumental resolution two bands appear split into two components each. Emission arising from transitions originating at the $^5D_1$ level is of low-intensity and consists of poorly resolved bands.

The emission spectrum of the europium(III) complex **III** is reported in Fig. 3 and Tables I, II. The complex is metal ion fluorescent at room and liquid nitrogen temperatures when excited with 300 nm radiation. The $^5D_0 \rightarrow {}^7F_0$ transition is weakly active; its intensity reaches just 4% that of the strongest $^5D_0 \rightarrow {}^7F_2$ transition. This consists of two components, one of which is split into two lines. The splitting is rather small and indicates that these lines could originate from an E-component. Similarly. the $^5D_0 \rightarrow {}^7F_1$ transition consists of two components, one of which is split into two lines. Two broad bands and a sharper one can be observed in the region of the $^5D_0 \rightarrow {}^7F_4$ transition. The resolution of the broad bands into two components each suggests that they originate from E-components. Two components of the $^5D_1 \rightarrow {}^7F_1$ transition and three components of the $^5D_1 \rightarrow {}^7F_2$ transition can be also observed in the relative regions.

The emission spectra of the europium(III) complexes **XI** and **XIII** are similar to one another. The spectrum of the complex **XI** is reported in Fig. 6 and Tables I, II. Both spectra show a weak and broad component of the $^5D_1 \rightarrow {}^7F_1$ transition and three weak components of the $^5D_1 \rightarrow {}^7F_2$ transition, one of which is broad. The $^5D_0 \rightarrow {}^7F_0$ transition is inactive, the spectra showing a line the intensity of which is just appreciable (~1% of the strongest $^5D_0 \rightarrow {}^7F_2$ transition). The transition $^5D_0 \rightarrow {}^7F_2$ consists of two components, one of which is clearly split into two lines while the other is broad. A much weaker component of this transition appears at higher frequencies. Three components of the transition $^5D_0 \rightarrow {}^7F_1$ can be observed in the relative region. The splitting of 42 cm^{-1} of the two almost equal intensity lines is not excessively high and can be reasonably assigned to an E-component. Apart from the $^5D_0 \rightarrow {}^7F_3$ transition that appears as a very weak and broad band, four components of the $^5D_0 \rightarrow {}^7F_4$ transition can be observed in the spectrum. Two components are split into two lines each, the third is broad while the component at higher frequencies is sharp, but much weaker.

A medium intensity line arising from the $^5D_0 \rightarrow {}^7F_0$ transition appears in the emission spectrum of the europium(III) complex **VIII**. The features of the transitions $^5D_0 \rightarrow {}^7F_{1-4}$ are similar to those of complexes **XI** and **XIII**; however, both E-components are less split while the lower-energy components of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions show a greater narrowness.

The emission spectrum of the europium complex **IX** in the region of the $^5D_0 \rightarrow {}^7F_2$ transition consists of a strong component accompanied by a much weaker one at higher frequencies. A third and broad component appears at lower frequencies (E-component). A sharp component and a stronger one split into two lines (E-component) can be associated with the transition $^5D_0 \rightarrow {}^7F_1$. The $^5D_0 \rightarrow {}^7F_0$ transition can be taken as forbidden, the spectrum showing only a weak line the intensity of which is less than

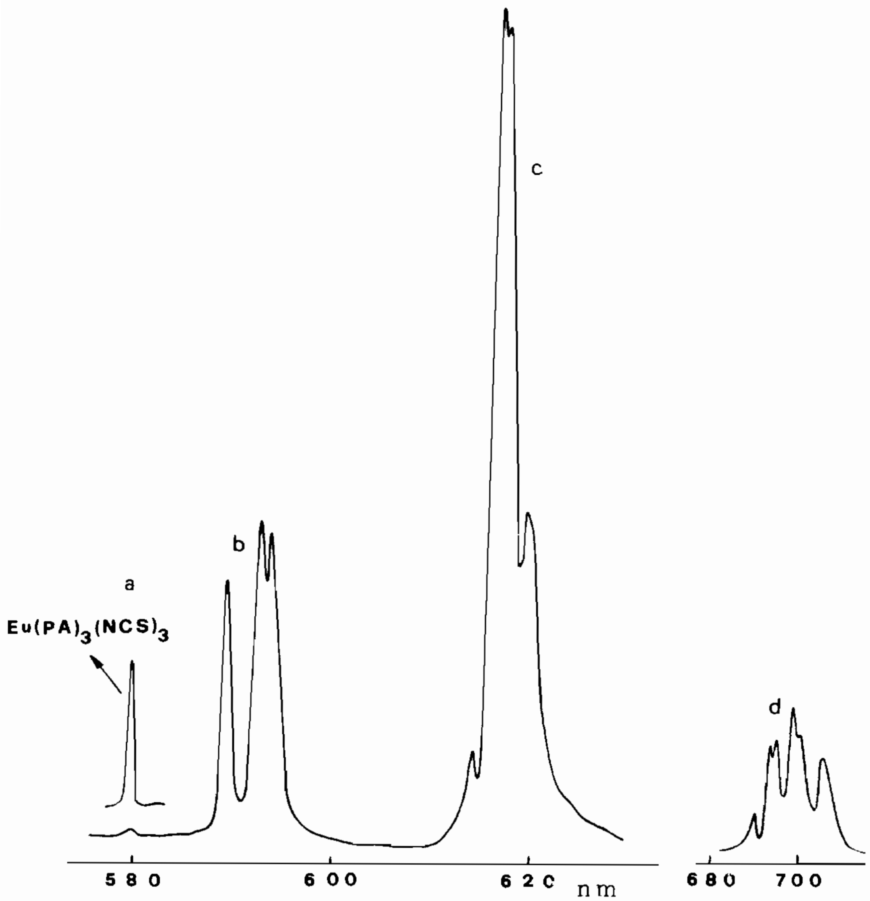

Fig. 6. Emission spectrum, from solid at 77 K, of $Eu(DEU)_3(NO_3)_3\cdot 2H_2O$; excitation with 385 nm radiation. a) $^5D_0 \rightarrow {}^7F_0$; b) $^5D_0 \rightarrow {}^7F_1$; c) $^5D_0 \rightarrow {}^7F_2$; d) $^5D_0 \rightarrow {}^7F_4$.

TABLE III. Basic Geometries and Symmetries Proposed for Europium(III) Complexes.

Complex	Apparent C.N.	Geometry	Symmetry	η^a
$Eu(biquO_2)_2(NCS)_3\cdot H_2O$	7	Monocapped octahedron	C_{3v}	4.20
$Eu(PU)_8(NO_3)_3$	8	Square antiprism	D_4	0.66
$Eu(EU)_8(ClO_4)_3$	8	Square antiprism	D_4	0.68
$Eu(pyO)_8(BF_4)_3$	8	Square antiprism	D_{4d}	0.30
$Eu(HBpz_3)_3$	8	Square antiprism	D_{4d}	0.24
$Eu(PA)_4(ClO_4)_3$	8	Dodecahedron	D_{2d}	3.07
$Eu(2\text{-}AN)_2Cl\cdot 3H_2O$	8	Dodecahedron	D_2	2.18
$Eu(pyO)_4(NCS)_3\cdot H_2O$	8	Bicapped trigonal prism	C_{2v}	3.70
$Eu(DEU)_3(NO_3)_3\cdot 2H_2O$	9	Tricapped trigonal prism	D_3	1.83
$Eu(PA)_3(NCS)_3$	9	Monocapped square antiprism	C_{4v}	2.65
$Eu(PU)_3(NO_3)_3\cdot 3H_2O$	10	Bicapped dodecahedron		2.04
$Eu(PA)_3(NO_3)_3$	10(?)	Bicapped dodecahedron(?)	S_4	2.78

$^a\eta = \dfrac{^5D_0 \rightarrow {}^7F_2}{^5D_0 \rightarrow {}^7F_1}$ (intensity ratio).

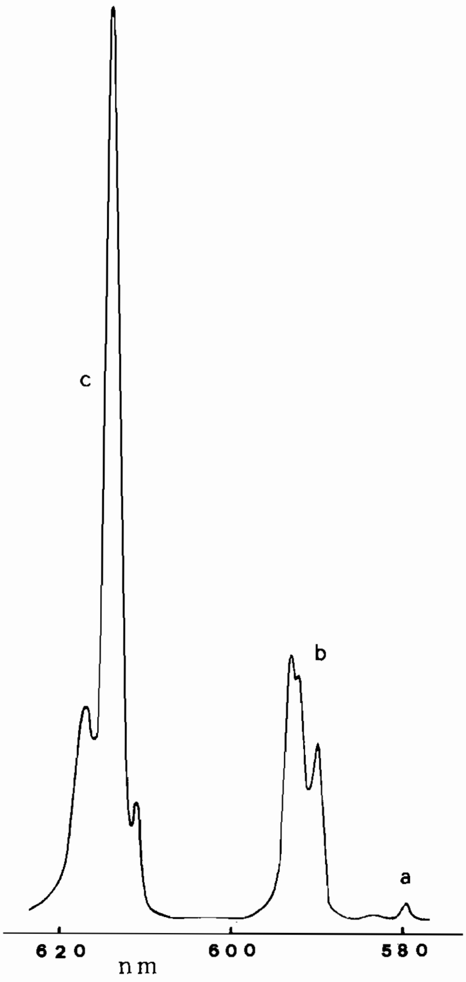

Fig. 7. Emission spectrum, from solid at 77 K, of Eu(PA)$_3$-(NO$_3$)$_3$; excitation with 305 nm radiation. a) $^5D_0 \rightarrow {}^7F_0$; b) $^5D_0 \rightarrow {}^7F_1$; c) $^5D_0 \rightarrow {}^7F_2$.

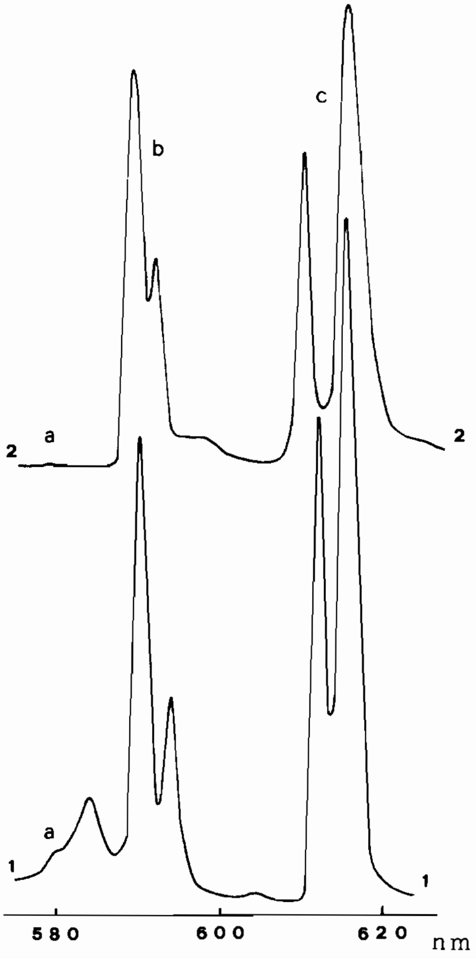

Fig. 8. Emission spectra, from solid at 77 K, of: 1) Eu-(NO$_3$)$_3$·6H$_2$O; 2) Eu(PU)$_3$(NO$_3$)$_3$·3H$_2$O. a) $^5D_0 \rightarrow {}^7F_0$; b) $^5D_0 \rightarrow {}^7F_1$; c) $^5D_0 \rightarrow {}^7F_2$.

2% of the strongest $^5D_0 \rightarrow {}^7F_2$ transition. The emission spectrum is reported in Fig. 7 and Tables I, II.

The emission spectra of europium(III) nitrate hexahydrate and of complex **XII** are reported in Fig. 8 and Tables I, II. The spectra are similar to one another. The transitions $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ consist of two components each. However, the stronger component of both transitions tends to split into two lines in complex **XII**. The transition $^5D_0 \rightarrow {}^7F_0$ is of low intensity and can be taken reasonably as forbidden.

Absorption Spectra

Absorption spectra of neodymium(III) complexes in the solid state are depicted in Figs. 9 and 10; absorption spectra of solid europium(III) complexes are depicted in Fig. 11. Spectral data are reported in Tables IV–VI. The spectroscopy in solution may be complicated by the presence of equilibria between two or more species due to solvolytic or dissociative effects. When this occurred in the case of the present complexes, measurements were performed in the presence of a large excess of ligand or, possibly, by changing the solvent. In all cases extreme caution was used. Measurements were taken into account only when the shape of the various bands and the relative absorbances of the non- and hypersensitive transitions obtained from the complexes in solution were found to be the same as or closely approximating to those obtained from the solid complexes.

The number of components that appear in the region of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ hypersensitive transitions in neodymium(III) complexes is, except in one case, higher than that predicted for the splitting for the half-integral J-values in cubic symmetries. The five principal bands observed for the octakis (pyridine-N-oxide) complexes indicate that the symmetry around the cation approximates to a cubic symmetry.

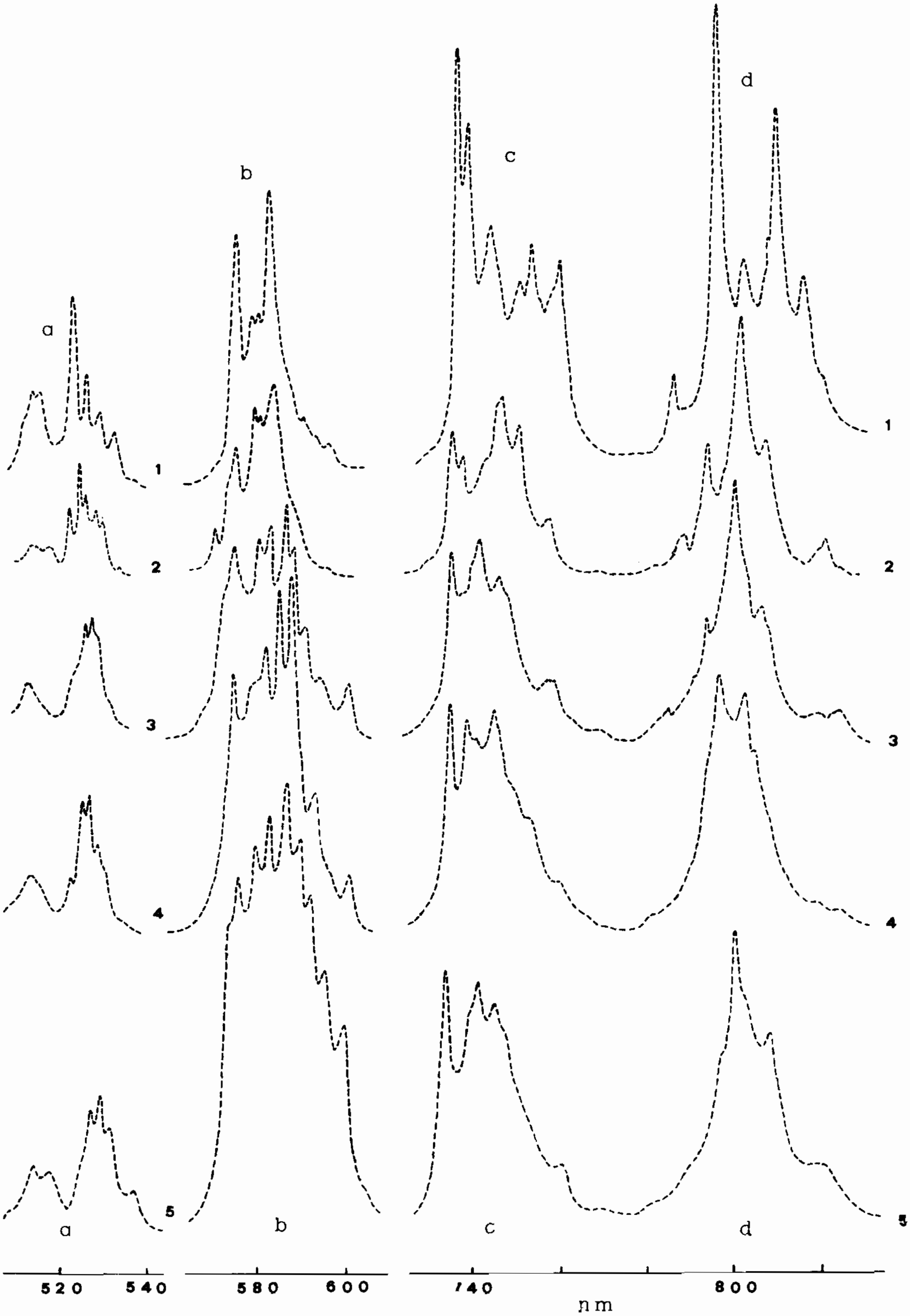

Fig. 9. Absorption spectra, from solid at room temperature, of neodymium(III) complexes: 1) $Nd(HBpz_3)_3$; 2) $Nd(PU)_8(NO_3)_3$; 3) $Nd(DEU)_3(NO_3)_3 \cdot 2H_2O$; 4) $Nd(PU)_3(NO_3)_3 \cdot 3H_2O$. 5) $Nd(TMU)_3(NO_3)_3$. a) $^4I_{9/2} \rightarrow {}^4G_{7/2}, {}^4G_{9/2}$; b) $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$; c) $^4I_{9/2} \rightarrow {}^4F_{7/2}, {}^4S_{3/2}$; d) $^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}$.

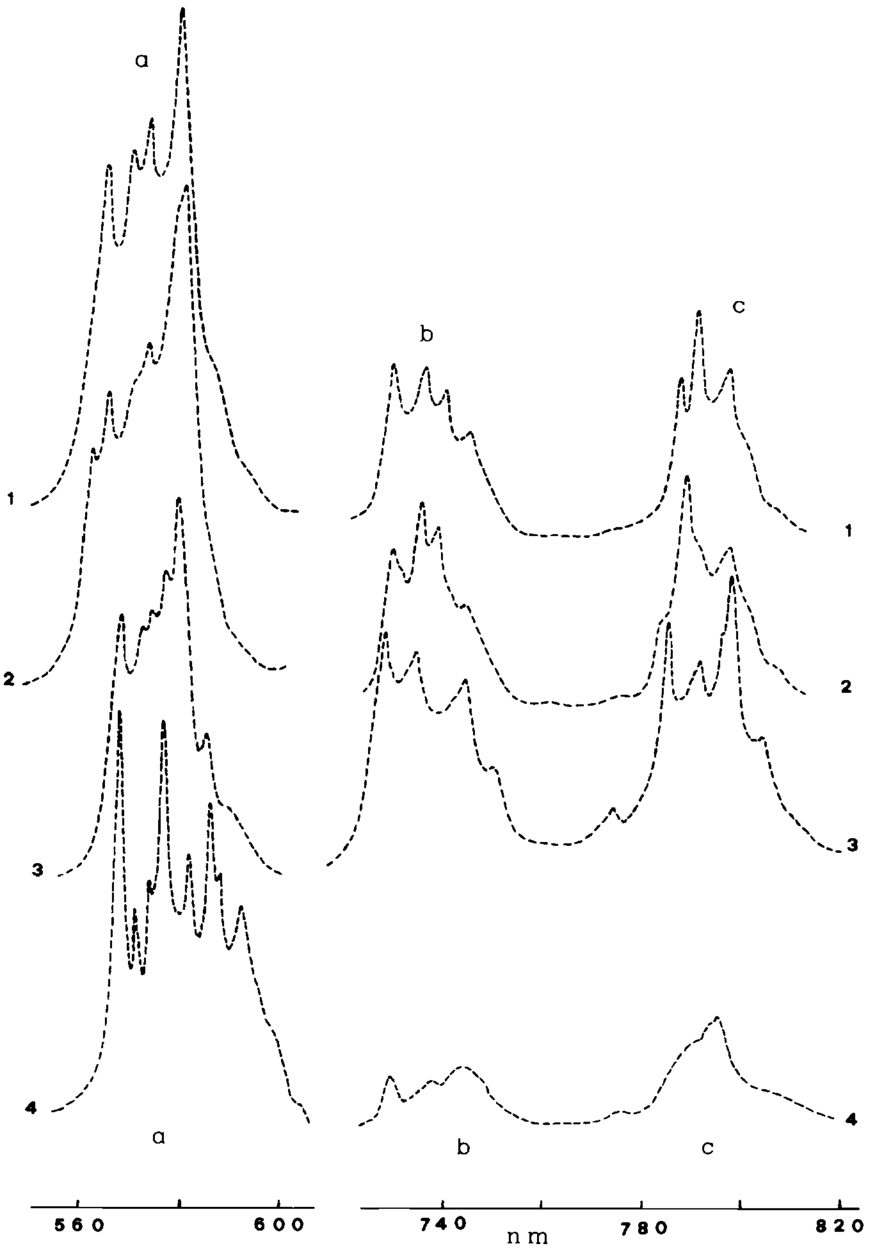

Fig. 10. Absorption spectra, from solid at room temperature, of neodymium(III) complexes: 1) $Nd(pyO)_8(NO_3)_3$; 2) $Nd(PA)_3(NO_3)_3$; 3) $Nd(2\text{-}AN)_2Cl\cdot 3H_2O$; 4) $Nd(biquO_2)_4(CF_3SO_3)_3$. a) $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$; b) $^4I_{9/2} \rightarrow {}^4F_{7/2}, {}^4S_{3/2}$; c) $^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}$.

Discussion

It has been found that PU, EU, 2-HAN and pyO act as neutral O-monodentate ligands and give rise, when perchlorate, trifluoromethanesulfonate, chloride or nitrate, is the counter ion, to species which, on the basis of their infrared and molar conductivity data, have been assumed to possess octacoordinated structures [2, 6, 8].

Eight-coordination is common in the structure of tripositive lanthanide complexes and is prevalently represented by the square antiprism (D_{4d}), the dodecahedron (D_{2d}) and the bicapped trigonal prism (C_{2v}). Less frequently encountered geometries are the cube, the hexagonal bipyramid and the tricapped trigonal antiprism. However, the geometrical distortions required to convert one structure into another are often small. Thus, by rotation of the upper set of sites around one fourfold axis relative to the lower one a square antiprism is produced by the cube.

The complexes **I** and **II** are characterized by the presence of uncoordinated anions and by f–f spectra that are practically unaffected by the anion

TABLE IV. Intensity, as Oscillator Strengths ($10^6 \times P$), of the Hypersensitive Transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ in Neodymium(III) Complexes in Acetonitrile–Ethanol (2:1) or Acetonitrile–Chloroform (3:1) Mixtures.

Complex	Solution	Solid[i]	References
$Nd(PU)_8X_3$[a]	11.57–12.48	0.90	This work, 2, 3
$Nd(EU)_8X_3$[b]	11.73–12.27	0.95	This work, 2, 3
$Nd(pyO)_8X_3$[c]	27.60–29.50[g]	3.20	This work, 7
$Nd(PA)_4X_3$[d]	27.40–28.05	3.00	This work, 3, 4
$Nd(biquO_2)_4X_3$[e]	52.65–53.84	4.90	This work, 20
$Nd(bipyO_2)_4X_3$[e]	59.10–59.50	5.30	This work, 7
$Nd(DMU)_3(NO_3)_3 \cdot 2H_2O$	24.85	1.25	This work, 2
$Nd(DEU)_3(NO_3)_3 \cdot 2H_2O$	25.97	1.40	This work, 2
$Nd(PU)_3(NO_3)_3 \cdot 3H_2O$	27.42	1.85	This work, 2
$Nd(TMU)_3(NO_3)_3$	31.50	2.30	This work, 2
$Nd(PA)_3(NO_3)_3$	32.70	2.70	This work, 4
$Nd(pyO)_4(NCS)_3 \cdot H_2O$	29.18	2.65	This work
$Nd(biquO_2)_2(NCS)_3 \cdot H_2O$	45.92	4.65	This work
$Nd(PA)_3(NCS)_3$	30.80	2.45	This work, 4
$Nd(2\text{-}AN)_2Cl \cdot 3H_2O$[f]	17.59	1.05	This work, 5
$Nd(HBpz_3)_3$	h	0.55	This work

[a] $X = ClO_4, NCS, NO_3, CF_3SO_3, Cl$. [b] $X = ClO_4, CF_3SO_3, PF_6, NO_3, NCS$. [c] $X = ClO_4, CF_3SO_3, NO_3, PF_6, BF_4$. [d] $X = ClO_4, CF_3SO_3, PF_6$. [e] $X = ClO_4, CF_3SO_3, BF_4$. [f] In DMSO. [g] The complexes probably undergo solvolysis. [h] Sparingly soluble in common solvents [1]. [i] Arbitrary values relative to the area, as average value, under the curves of the bands associated with the transitions $^4I_{9/2} \rightarrow {}^4F_{7/2}, {}^4S_{3/2}$ and $^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}$. For $Nd(NO_3)_3 \cdot 6H_2O$ the measured value is 2.18; this value indicates the relatively high contribution of the bidentate nitrates.

TABLE V. Intensity, as Oscillator Strength ($10^6 \times P$), of the Hypersensitive Transition $^7F_0 \rightarrow {}^5D_2$ in Europium(III) Complexes in Acetonitrile–Ethanol (2:1) or Acetonitrile–Chloroform (3:1) Mixtures.

Complex	$10^6 \times P$
$Eu(PU)_8X_3$[a]	<0.1
$Eu(PA)_3(NO_3)_3$	0.20
$Eu(TMU)_3(NO_3)_3$	0.17[d]
$Eu(PA)_4(ClO_4)_3$	0.18
$Eu(pyO)_8X_3$[b]	0.17–0.18
$Eu(biquO_2)_4X_3$[c]	0.29–0.30[e]
$Eu(bipyO_2)_4X_3$	0.40–0.38[e]
$Eu(pyO)_4(NCS)_3 \cdot H_2O$	0.22

[a] $X = ClO_4, Cl, NO_3, NCS, CF_3SO_3$. [b] $X = ClO_4, NO_3, CF_3SO_3, BF_4, PF_6$. The complexes probably undergo solvolysis. [c] $X = ClO_4, CF_3SO_3$. See also reference 20. [d] $\eta = 2.45$. [e] $10^6 \times P$ for $Eu(biquO_2)_2(NCS)_3 \cdot H_2O$ is 0.26 and for $Eu(bipyO_2)_2(NCS)_3 \cdot H_2O$ is 0.34.

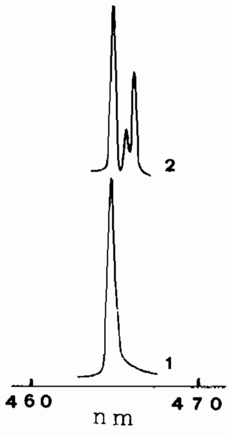

Fig. 11. Absorption spectra, from solid at room temperature, of europium(III) complexes: 1) $Eu(bipyO_2)_4(CF_3SO_3)_3$; 2) $Eu(biquO_2)_4(CF_3SO_3)_3$.

present [2, 3]. The emission spectra of the europium(III) complexes can be reasonably interpreted in terms of square antiprismatic geometry and almost perfect D_4 site symmetry. If the europium(III) ion is placed in non-centrosymmetric ligand fields not only magnetic-dipole but also electric-dipole transitions are allowed. For the cation having 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 should appear in the spectra. The band appearing in the region of the $^5D_0 \rightarrow {}^7F_2$ transition is thus assigned to the transition $^5D_0 \rightarrow {}^7F_2(E)$ and the two components of the $^5D_0 \rightarrow {}^7F_1$ transition to the

TABLE VI. Intensity, as Oscillator Strength ($10^6 \times P$), of the Hypersensitive Transition $^5I_8 \rightarrow {}^6G_6$ in Holmium(III) Complexes in Acetonitrile–Ethanol (2:1) or Acetonitrile–Chloroform (3:1) Mixtures.

Complex	Solution	Solid[e]	References
$Ho(PU)_8X_3$[a]	14.20–15.38	1.45	This work, 2, 3
$Ho(PU)_3(NO_3)_3 \cdot 3H_2O$	31.08	2.50	This work, 2
$Ho(TMU)_3(NO_3)_3$	37.54	2.85	This work, 2
$Ho(DEU)_3(NO_3)_3 \cdot 2H_2O$	28.65	2.10	This work, 2
$Ho(pyO)_8X_3$[b]	33.25–36.68[d]	4.65	This work, 7
$Ho(bipyO_2)_4X_3$[c]	110.27	7.75	This work, 7
$Ho(biquO_2)_4X_3$[c]	98.74	7.10	This work

[a] X = ClO_4, Cl, NO_3, CF_3SO_3. [b] X = NO_3, CF_3SO_3, ClO_4. [c] X = CF_3SO_3, ClO_4. [d] The complexes probably undergo solvolysis. [e] Arbitrary values relative to the area, as average value, under the curves of the bands associated with the transitions $^5I_8 \rightarrow {}^5F_4$, $^5S_2$ and $^5I_8 \rightarrow {}^5F_5$.

transitions $^5D_0 \rightarrow {}^7F_1(A_2)$ and $^5D_0 \rightarrow {}^7F_1(E)$. The three bands that appear in the region of the $^5D_0 \rightarrow {}^7F_4$ transition can be associated with the transitions to the A_2 and both the E-components.

The complexes $Ln(pyO)_8X_3$, where X = Cl, Br, I or ClO_4, have been previously described in terms of square antiprismatic geometry and D_{4d} weakly distorted to D_{2d} symmetry [9]. A geometry intermediate between the cube and the square antiprism has been indicated by the X-ray study of the complex $La(pyO)_8(ClO_4)_3$ [10] and by the emission spectrum of the complex $Eu(pyO)_8(NO_3)_3$ [6]. The complexes $Eu(pyO)_8(BF_4)_3$ and $Eu(pyO)_8(PF_6)_3$ have now been prepared and their emission spectra examined to investigate the possible influence of the anion on the emission spectra of the europium(III) ion. It has been found that the spectra of the hexafluorophosphate, tetrafluoroborate and trifluoromethanesulfonate complexes are practically superimposable on one another. All complexes are strongly metal ion fluorescent when excited with near ultraviolet radiations. Emission arises mainly from transitions originating at the $^5D_0$ level, but bands associated with the various $^5D_1 \rightarrow {}^7F_J$ transitions can also be observed. These spectral patterns are those expected from the europium(III) ion located at a site that is a centre of symmetry in the crystal lattice. In this case, the only possible transition that originates at the $^5D_0$ excited state and is accompanied by emission of radiation is the magnetic-dipole allowed $^5D_0 \rightarrow {}^7F_1$ transition. No band associated with the electric-dipole allowed transitions $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_2$ should appear in the spectra. The $^5D_0$ level cannot be split while the $^7F_1$ level is triply degenerate and can be split under the field of the various symmetries. A field possessing cubic symmetry permits triple degeneration and does not cause splitting. According to the magnetic-dipole selection rules, the $^5D_0 \rightarrow {}^7F_1$, $^5D_1 \rightarrow {}^7F_0$ and $^5D_1 \rightarrow {}^7F_1$ transitions must consist of a single component each while the transition $^5D_1 \rightarrow {}^7F_2$ must consist of two components. Tetragonal and trigonal fields cause splitting of the $^7F_1$ level into two sublevels while lower symmetry fields cause splitting into three sublevels. If the environment has square antiprismatic geometry and D_{4d} symmetry no band should be observed in the regions of the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_2$ transitions. Since the $^7F_1$ level splits into two sublevels, two components of the $^5D_0 \rightarrow {}^7F_1$ transition ($^5D_0 \rightarrow {}^7F_1(A_2)$ and $^5D_0 \rightarrow {}^7F_1(E_3)$) should appear in the spectra. The spectrum of the octakis(pyridine-N-oxide)europium(III) tetrafluoroborate, hexafluorophosphate and trifluoromethanesulfonate complexes suggests that the polyhedron approximates to the square antiprism (D_{4d}) rather than to the cube. The broadness or splitting of the bands associated with the $^5D_1 \rightarrow {}^7F_{1,2}$ transitions and the appearance in the region of the transition $^5D_0 \rightarrow {}^7F_2$ of a line non-vibronic in origin indicate deviation from the idealized polyhedron (SAP).

Ligands PU, EU and pyO form complexes with lanthanide(III) cations which are characterized by the same coordination polyhedron attained by eight molecules of ligand. The polyhedron may approximate to the cube if pyO is the ligand or to the square antiprism if PU (EU) is the ligand. It should be noted that, since pyO is bulkier than PU (EU), the polyhedron is forced towards less favourable geometries (cube) by ligand–ligand repulsions.

The 2-quinolinecarboxylic acid may form neutral, cationic and mixed species with lanthanide(III) cations [5, 11, 12]. Complexes V are an example of mixed complexes with the acid acting as bidentate in the anionic form. A coordination number higher than eight is incompatible with the stoichiometries of the complexes. Most likely, these consist of octacoordinated structures attained by two N,O-bidentate 2-quinolinecarboxylato ions, one chlorine and three molecules of water. D_2 site symmetry for the europium(III) ion is suggested by the emission spectrum of the europium complex. For the europium(III) ion having D_2 site symmetry both the $^5D_0 \rightarrow {}^7F_1$ magnetic-dipole and $^5D_0 \rightarrow {}^7F_2$ electric-dipole allowed transitions consist of three components each (B_1, B_2, and B_3) which should of course appear in the spectra. This acid may form with lanthanide(III) salts species where the acid acts as O-monodentate ligand in the neutral form [5, 11]. The europium(III) compounds strongly fluoresce when excited with 365 nm radiation. Eight-coordination and square antiprismatic geometries have been assigned to these species on the basis of IR and f–f spectra, molar conductivity and thermal analysis measurements [5, 11]. Deviation from the basic D_{4d} towards the D_2 form of the square antiprism has been indicated by the emission spectra. The emission spectra of these compounds are similar one to another, independently of the anion present, and are similar to the emission spectrum of the europium(III) complex **XIV**, showing only small and insignificant differences in the energies and relative intensities of the various transitions (Tables I, II).

The ligand $HBpz_3^-$ forms lanthanide(III) complexes having stoichiometry $Ln(HBpz_3)_3$. Although $HBpz_3^-$ is potentially a tridentate ligand, complexes **XIV** consist, most likely, of octacoordinated structures. In fact the emission spectrum of the europium(III) complex is in good agreement with square antiprismatic geometry and D_{4d} symmetry. Deviation from the basic D_{4d} symmetry is, however, suggested by the appearance of lines of appreciable intensity in the region of the transition $^5D_0 \rightarrow {}^7F_2$ and by the broadness of one component of the $^5D_0 \rightarrow {}^7F_1$ transition.

Among lanthanide(III) complexes having octacoordinated structures, complexes **III** need consideration. Synthetic and spectroscopic data indicate that these complexes consist of octacoordinated structures attained by four bidentate PA molecules and surrounded by the three anions. The emission spectrum of the europium(III) complex agrees with D_{2d} site symmetry and dodecahedral geometry. The two bands appearing in the region of the $^5D_0 \rightarrow {}^7F_1$ transition are assigned to the transitions $^5D_0 \rightarrow {}^7F_1(A_2)$ and $^5D_0 \rightarrow {}^7F_1(E)$ and the components of the transition $^5D_0 \rightarrow {}^7F_2$ to the $^5D_0 \rightarrow {}^7F_2(B_2)$ and $^5D_0 \rightarrow {}^7F_2(E)$ transitions. The relative activity of the $^5D_0 \rightarrow {}^7F_0$ transition is consistent with deviation from D_{2d} towards C_{nv}, n = 3, 4, symmetries.

Complexes **VI** and **VII** have apparent coordination numbers eight and seven, respectively. Seven-coordination in tripositive lanthanide complexes is represented almost exclusively by the pentagonal bipyramid (D_{5h}), the monocapped octahedron (C_{3v}) and the monocapped trigonal prism (C_{2v}). Dehydration of complexes **VI** occurs at a relatively high temperature (~130 °C) whilst complexes **VII** lose their water molecule at 70 °C and the f–f spectra do not undergo any significant change. The water molecule can therefore be assumed to be of the inner-sphere type only in the case of complexes **VI**. The emission spectra of both the europium(III) complexes show a band associated with the $^5D_0 \rightarrow {}^7F_0$ transition. The exhibition of this band agrees with the following site symmetries: C_n, C_s, $C_{n'v}$ (n = 2, 3, 4, 6; n' = 1, 2, 3, 4, 6). We may consider C_{3v} symmetry and monocapped octahedron as the most consistent for the europium(III) complex **VII**. The split component arising from the $^5D_0 \rightarrow {}^7F_1$ transition is, therefore, assigned to transitions to an E-component and the un-split component to transition to A_2. Similarly, the two split bands appearing in the region of the $^5D_0 \rightarrow {}^7F_2$ transition are assigned to transitions to both the E-components. The component at 620.7 nm is associated with the transition to A_1. It is worth noting, however, that the energy difference between the monocapped octahedron and the monocapped trigonal prism is small. These two geometries depend in fact on the capping ligand entering a triangular or a tetragonal face of the trigonal prism giving rise to C_{3v} or C_{2v} symmetry respectively. The splitting of the high-intensity components of both the transitions $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ in the spectrum of the europium(III) complex **VI** is too high to be attributed to an E-component and suggests C_{2v} site symmetry for the europium(III) ion. This is in accord with the analytical, molar conductivity, thermal analysis and IR spectral data which indicate eight-coordination for this complex. Most likely, five oxygen and three nitrogen atoms form a bicapped trigonal prism.

An interesting case is represented by the complexes **XI**, **VIII** and **XIII**. Since DEU and TMU act as O-monodentate ligands and the nitrato groups as bidentate, the coordination number depends on the number of molecules of water in the inner-sphere of coordination. A nona-coordinated structure attained by three molecules of DEU and three bidentate nitrato groups can be assigned to the europium complex **XI** by the study of proper emission spectrum. This is essentially similar to that of the europium(III) complex **XIII**. The europium(III) ion in this complex has a C.N. of nine with the three nitrates symmetrically coordinated in a bidentate fashion and three O-monodentate TMU molecules. The polyhedron conforms, however, to neither of the common geometries for nine-coordination [13]. Monocapped square antiprism (C_{4v}) and tricapped trigonal prism (D_{3h}) are polyhedra encountered for lanthanide(III) complexes having nona-coordinated structures. C_{4v} symmetry is excluded by the emission spectra. These suggest that the coordination polyhedra of both the complexes approximate to the tricapped trigonal prism and D_3 site symmetry for the europium(III) ion. The rather high splitting observed for the E-components of the $^5D_0 \rightarrow {}^7F_1$

and $^5D_0 \rightarrow {}^7F_2$ transitions indicates a comparatively high deviation from a regular D_3 symmetry. D_3 symmetry allows the transitions $^5D_0 \rightarrow {}^7F_4(3E)$ and $^5D_0 \rightarrow {}^7F_4(A_2)$ and the transitions $^5D_0 \rightarrow {}^7F_2$-(2E), $^5D_0 \rightarrow {}^7F_1(E)$ and $^5D_0 \rightarrow {}^7F_1(A_2)$ while D_{3h} symmetry allows the magnetic-dipole $^5D_0 \rightarrow {}^7F_1(A_2')$, $^5D_0 \rightarrow {}^7F_1(E'')$ and the electric-dipole $^5D_0 \rightarrow {}^7F_2(E')$, $^5D_0 \rightarrow {}^7F_4(A_2'')$ and $^5D_0 \rightarrow {}^7F_4(2E')$ transitions. Replacement of the bidentate nitrates by PA and of the monodentate TMU by NCS causes the coordination polyhedron approximating to the monocapped square antiprism with activation of the $^5D_0 \rightarrow {}^7F_0$ transition (Fig. 6).

The emission spectrum of the europium(III) complex **IX** clearly indicates a higher site symmetry for the europium(III) ion than C_{1h}, C_n and $C_{n'v}$ with $n \geqslant 1$ and $n' \geqslant 2$. On the other hand, the most frequently encountered symmetries that generate an E-component for the $^5D_0 \rightarrow {}^7F_1$ transition are D_4, S_4, D_{3h}, D_3 and D_{2d}. Symmetries D_4, D_3, D_{3h} and D_{2d} do not agree, however, with the features of the $^5D_0 \rightarrow {}^7F_2$ transition. D_4 symmetry allows in fact only the transition $^5D_0 \rightarrow {}^7F_2(E)$ while D_3 symmetry allows both the transitions $^5D_0 \rightarrow {}^7F_2(2E)$. On the other hand, S_4 symmetry allows transitions to E and 2B components while D_{3h} symmetry allows the transition $^5D_0 \rightarrow {}^7F_2(E')$ (electric-dipole) alone and D_{2d} symmetry the transitions $^5D_0 \rightarrow {}^7F_2(B_2)$ and $^5D_0 \rightarrow {}^7F_2(E)$. The three components of the $^5D_0 \rightarrow {}^7F_2$ transition that appear in the spectrum of the complex **IX** suggests S_4 symmetry. In this case, these components can be associated with the transitions $^5D_0 \rightarrow {}^7F_2(E)$ and $^5D_0 \rightarrow {}^7F_2(2B)$. However, both vibrational and electronic spectra are inadequate to indicate the coordination number of this complex; it may be in fact ten or higher, depending on the number of nitrato groups mono- and bidentate to the cation.

Lanthanide(III) nitrates hexahydrate have been found to possess deca-coordinated structures. A complete structural analysis of the praseodymium nitrate showed that the structure can be rationally described in terms of a bicapped dodecahedron with coordination sites occupied by three bidentate nitrates and four molecules of water [14]. The emission spectra of the complexes $Eu(PU)_3(NO_3)_3 \cdot 3H_2O$ (**XII**) and $Eu(PU)_4(NO_3)_3 \cdot 2H_2O$ are similar one to another and to the spectrum of the europium(III) nitrate hexahydrate. This indicates that the coordination polyhedron remains essentially unchanged upon replacement of three (four) molecules of water by three (four) molecules of PU. No one or only one molecule of water is thus in the coordination sphere of the cation. This is in accord with thermoanalytical measurements. Dehydration of the complexes $Ln(PU)_3(NO_3)_3 \cdot 3H_2O$ occurs in fact through two consecutive endothermic processes between 70 and 160 ℃ whilst only one process of dehydration is observed in the TG and DTA curves of the $Ln(PU)_4(NO_3)_3 \cdot 2H_2O$ complexes at 80 ℃.

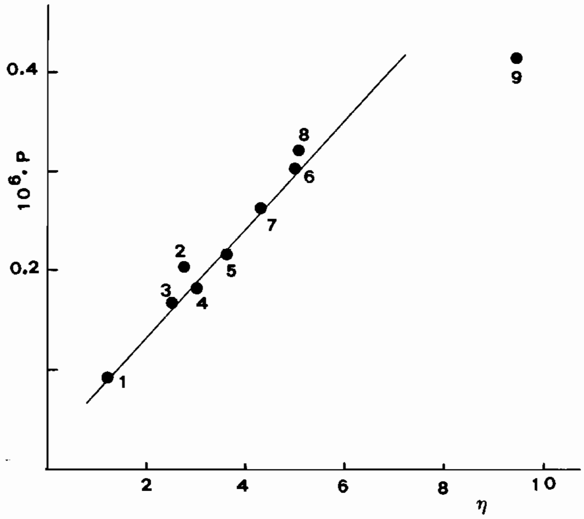

Fig. 12. Europium(III) complexes. Plot of $10^6 \times P$ *vs.* η: 1) $Eu(PU)_8X_3$; 2) $Eu(PA)_3(NO_3)_3$; 3) $Eu(TMU)_3(NO_3)_3$; 4) $Eu(PA)_4(ClO_4)_3$; 5) $Eu(pyO)_4(NCS)_3 \cdot H_2O$; 6) $Eu(biquO_2)_4X_3$; 7) $Eu(biquO_2)_2(NCS)_3 \cdot H_2O$; 8) $Eu(bipyO_2)_2(NCS)_3 \cdot H_2O$; 9) $Eu(bipyO_2)_4(BF_4)_3$.

In Table III are reported the basic geometries and symmetries proposed for the present europium(III) complexes.

The intensity ratios $\eta = {}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ obtained for complexes where the europium(III) ion lies in a non-centrosymmetric ligand field increase in the order: DEU < PU = EU < TMU < PA < $biquO_2$ < $bipyO_2$, reaching rather uncommon values for the $bipyO_2$ complexes. If excitation of the ligand occurs, the emission intensity depends on the probability that the emitting levels in the cation have to receive energy from the ligand. These complexes are metal ion fluorescent by energy transfer from the excited ligand. The efficiency of the intramolecular energy transfer is expected to increase with covalency. This corresponds to an increase, among the various transitions that occur between low J-values, in the $^5D_0 \rightarrow {}^7F_2$ transition probability.

It can be seen from Tables III and V and Fig. 12 that the ratio $\eta/10^6 \times P$ for europium(III) complexes remains approximately constant.

Absorption Spectra

Unlike the d–d bands, the f–f absorption bands show normally weak perturbation due to complexation. Shift of the barycentre, usually to the low wavenumbers, splitting due to the crystal fields and increase in the intensity of certain transitions (the so-called hypersensitive transitions) with respect to the aquo-ions, are effects that can be observed on complex formation. A correlation has been found to exist between the intensity of the hypersensitive transitions and the nephelauxetic effect, the basicity and number of the coordinated ligand.

Jørgensen and Judd [15] came to the conclusion that hypersensitivity may be due to inhomogeneity of the dielectric surrounding the cation while Judd [16] assigned the hypersensitivity to the changes in the symmetry of the lanthanide ion environment. Mason *et al.* [17] developed a model based on a dynamic coupling mechanism involving the mutual perturbation of the metal ion and ligand while Henrie *et al.* [18] proposed a covalent model of hypersensitivity. A vibronic mechanism has also been invoked as the source of hypersensitivity [19].

It is found in the case of the present complexes that the intensity of the hypersensitive transitions increases in the order: $HBpz_3^-$ < DMU < DEU < EU = Pu < TMU < PA < pyO < $biquO_2$ < $bipyO_2$. This series results from the combination of some partial series obtained from homogeneous complexes in the solid state. The values reported in column 3 of Tables IV, VI refer to the area under the band of the hypersensitive transition(s) relative to the area, as average value, under the bands of two (or more) non-hypersensitive transitions; these have shown for all complexes intensity changes of less than 30% with respect to the aquo-ions. This series corresponds, on the other hand, to that established by the absorption spectra, apart from the inversion concerning the octakis (pyridine-N-oxide) and the tetrakis(picolinamide) complexes, most likely due to a solvolytic effect. In general, no correlation exists between high intensity and low symmetry or high symmetry and low intensity. The emission spectra of the europium complexes **IV** and **XIV** support the attribution of the same polyhedron of coordination and high site symmetries for the europium(III) ion. By contrast, the intensity of the hypersensitive transitions increases drastically from $HBpz_2^-$ to pyO complexes. Similarly, the same basic structure can be assigned to the complexes **XI** and **XIII** while the intensity of the hypersensitive ones increases from DEU to TMU complexes. Changes in symmetry may contribute but are not determining for hypersensitivity, at least in the case of the present complexes. The reason is most likely an increased electron density on the donor atoms with partial transfer to the lanthanide ion. Interpretation of NMR and Mössbauer spectral data indicates that the lanthanide–ligand bond has generally a predominant ionic character, thus assigning only a limited role to covalency. However, the high and rather uncommon values measured for the hypersensitive transitions in complexes with amine-N-oxides [20, 7] and the increase in both the $^5D_0 \rightarrow {}^7F_2$ (expressed as intensity ratio η) and $^7F_0 \rightarrow {}^5D_2$ transition intensities (Fig. 12) may be considered as an indication of the role of covalency. As the number of coordinated ligand molecules increases and the cation–ligand distance is shortened, the intensity of the hypersensitive transitions increases. The perchlorate, thiocyanate and nitrate complexes of large cations with PA have C.N. of eight, nine and ten (likely), respectively. Apart from symmetry arguments, the intensity of the hypersensitives increases in the same order. Moreover, $biquO_2$ ligand is more basic than $bipyO_2$ while a drop in symmetry occurs from the $bipyO_2$ to the $biquO_2$ complexes [20]. However, the intensity of the hypersensitive transitions increases from $biquO_2$ to $bipyO_2$ complexes. Since $biquO_2$ is bulkier than $bipyO_2$, a reasonable explanation is connected with the greater steric hindrance of the $biquO_2$ molecule which causes the Ln–O bonds distance to lengthen and the intensity of the hypersensitives to decrease.

TABLE VII. Metal–Ligand Stretching Frequencies and Force Constants.

Complex	ν(Ln–O) (cm^{-1})	f(Ln–O) (mdyne/Å)
$Eu(DEU)_3(NO_3)_3 \cdot 2H_2O$	327	0.911
$Eu(PU)_8(ClO_4)_3$	325	0.900
$Eu(PU)_3(NO_3)_3 \cdot 3H_2O$	335	0.956
$Eu(TMU)_3(NO_3)_3$	353	1.061
$Eu(biquO_2)_4(ClO_4)_3$	352	1.055
$Eu(bipyO_2)_4(CF_3SO_3)_3$	357	1.086
$Eu(pyO)_8(NO_3)_3$	308	0.808
$Eu(pyO)_4(NCS)_3 \cdot H_2O$	350	1.043
$Eu(biquO)_2(NCS)_3 \cdot H_2O$	355	1.073

The energy of the Ln–ligand stretching vibrations can be assumed as a direct measure of the bond strength. Normally, the assignment of the Ln–ligand stretching modes is based upon the appearance of new bands in the far-infrared region of the spectra. However, one must point out that this assumption is not necessarily valid since ligand vibrations may be activated on complex formation by symmetry changes. Nevertheless, when the energy of the new bands depends on the metal ions this correlation can be reasonably accepted. IR data concerning the Ln–ligand stretching vibrations are reported in Table VII.

It can be seen from Figs. 9–11 that complexes having the same C.N. do not show any similarity in the band shapes of the hypersensitive transitions. Similarity can be observed, as expected, between complexes for which the emission spectra suggest the same basic site symmetry for the lanthanide(III) ion. In this regard, the different spectral patterns of the complexes $Eu(bipyO_2)_4(ClO_4)_3$ and $Eu(biquO_2)_4(ClO_4)_3$ in the region of the hypersensitive transition $^7F_0 \rightarrow {}^5D_2$ are meaningful. Three peaks appear in the spectrum of the biquO_2 complex whereas a unique, though asymmetric band is exhibited by the bipyO_2 complex [20].

References

1 K. W. Bagnall, A. C. Tempest, J. Takats and A. P. Masino, *Inorg. Nucl. Chem. Lett., 12,* 555 (1976).
2 A. Seminara, A. Musumeci and A. Chisari, *J. Inorg. Nucl. Chem., 40,* 269 (1978).
3 A. Seminara and E. Rizzarelli, *Inorg. Chim. Acta, 40,* 249 (1980).
4 G. Condorelli, A. Seminara and A. Musumeci, *J. Inorg. Nucl. Chem., 36,* 3763 (1974).
5 A. Musumeci, A. Chisari and A. Seminara, *Boll. Acc. Gioenia, (Catania), Serie IV, vol. XIV,* 41.
6 A. Musumeci and A. Seminara, *Inorg. Chim. Acta, 54,* L81 (1981).
7 A. Musumeci, R. P. Bonomo, V. Cucinotta and A. Seminara, *Inorg. Chim. Acta, 59,* 133 (1982).
8 S. Calogero, A. Seminara and U. Russo, *Gazzetta Chim. Ital., 109,* 45 (1979).
9 E. Butter and W. Seifert, *Z. anorg. allg. Chemie, 368,* 133 (1969).
10 A. R. Al-Karaghouli and J. S. Wood, *Inorg. Chem., 18,* 1177 (1979).
11 A. Musumeci, *Inorg. Chim. Acta, 53,* L249 (1981).
12 A. Seminara and A. Musumeci, *J. Inorg. Nucl. Chem., 39,* 599 (1977).
13 Chung Chieh, G. E. Toogood, T. D. Boyle and C. M. Burgess, *Acta Cryst., B32,* 1008 (1976).
14 I. M. Rumanova, G. F. Volodina and N. V. Belov, *Crystallography (Soviet Phys.), 9,* 545 (1965).
15 C. K. Jørgensen and B. R. Judd, *Mol. Phys., 8,* 281 (1964).
16 B. R. Judd, *J. Chem. Phys., 44,* 839 (1966).
17 S. F. Mason, R. D. Peacock and B. Stewart, *Mol. Phys., 30,* 1829 (1975).
18 D. E. Henrie, R. L. Fellows and G. R. Choppin, *Coord. Chem. Rev., 18,* 199 (1976).
19 I. Richman, R. A. Satten and E. Y. Wong, *J. Chem. Phys., 39,* 1833 (1963);
W. F. Krupke, *Phys. Rev. A, 145,* 325 (1966).
20 A. Seminara, A. Musumeci and A. Chisari, *Inorg. Chim. Acta, 82,* 173 (1984).