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Crystal Structure and Emission Spectrum of Tris(nitrato)-1,4,7,10-tetraoza-cyclododecane–Europium(III)*

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The crystal and molecular structure of the title compound was determined from single crystal X-ray diffraction. The complex crystallizes in the monoclinic space group $P2_1/c$, *with* $Z = 4$. *Lattice parameters are:* $a = 12.121(3)$, $b = 8.556(2)$, $c = 15.269(4)$ Å *and* $\beta = 91.86(2)°$. *The structure was solved by Patterson and Fourier techniques and refined by least-squares to a final conventional* R *value of 0.079. The europium(III) ion is 10-coordinate, being bonded to three bidentate nitrate groups and to the four oxygen atoms of the crown ether. The Eu–O distances are in the range 2.41–2.57 Å (average: 2.49(5) Å). The nitrate groups are planar with N–O bond lengths between 1.21 and 1.29 Å. The coordination polyhedron of Eu(III) is discussed. The effective ionic radius of the 10-coordinate Eu(III) ion is 1.178 Å.*

The emission spectrum at 77 K is presented and discussed. Unusual splittings of two components of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ *transitions are interpreted as arising from Fermi-type resonances with vibrational levels.*

Introduction

Complexes between lanthanoid salts and crown ethers are attracting considerable interest [1–2]. In previous parts of this series, we have shown that these ligands may be used to force the rare earth ion to adopt any coordination number between 7 and 12, provided a suitable choice of the counterion and of the polyether is done [3]. In the structural part of our work, we particularly focus on complexes in which the Ln(III) ion possesses a high coordination number (10, 11 or 12), since data for such compounds are still scarce [4]. We also perform a detailed analysis of their emission spectra to investigate the information about the idealized symmetry of their coordination polyhedra to be gained from such data [5–6].

In this communication, we present the single-crystal X-ray diffraction structure of the title compound, a 1:1 complex between europium trinitrate and 12-crown-4 ether. We also discuss its emission spectrum and, especially, an unusual splitting of two components of the $^5D_0 \rightarrow {}^7F_2$ transition.

Experimental

The complex was synthesized as described previously [7]; recrystallization in nitromethane yielded crystals which were suitable for X-ray analysis. The emission spectra were measured at 77 K on finely powdered samples [8]. Selective excitations to the $^5D_0$, $^5D_1$ and $^5D_2$ electronic levels were performed by means of a dye laser (579.9 nm, 100 mW) or an Ar laser (528.7 nm, 50 mW or 465.5 nm, 50 mW). The lutetium complex doped with 1.5% europium was crystallized from a solution containing 1.5% europium nitrate; the Eu-content of the microcrystals was determined by fluorimetry, after hydrolysis of the complex in D_2O.

Crystal data: $EuC_8H_{16}N_3O_{13}$, Monoclinic, space group $P2_1/c$, $a = 12.121(3)$, $b = 8.556(2)$, $c = 15.269(4)$ Å, $\beta = 91.86(2)°$, $U = 1582.7(7)$ Å^3, $Z = 4$, $D_c = 2.16$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 40.4 cm^{-1}, $F(000) = 1008$, M = 514.2.

Initial photographs showed frequent twinned crystals (with a′ = a, b′ = –b), but an intensity check on the crystal used for data collection showed only a low intensity due to the second component. This crystal was therefore accepted for data collection. Data were collected with a Syntex $P2_1$ four circle diffractometer. Maximum 2θ was 50°, with scan

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*Part 12 of the series 'Complexes of Lanthanoid Salts with Macrocyclic Ligands'. For Part 11, see [5].

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0020-1693/82/0000-0000/$02.75

TABLE I. Atomic Coordinates ($\times 10^4$) with Standard Deviations in Parentheses and Temperature Factors ($\times 10^3$) in the Form $\exp(-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}\,h\,k\,a^*b^* + \ldots)$.

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu	2550.6(6)	1845.9(8)	−493.1(4)	33.3(10)	28.4(10)	26.0(10)	−0.3(3)	−2.7(3)	−0.2(3)
O(1)	1311(8)	740(12)	621(7)	38(6)	36(6)	39(6)	0(5)	1(5)	6(5)
O(2)	3488(8)	1141(12)	918(7)	38(6)	37(6)	40(6)	2(5)	−5(5)	4(5)
O(3)	3662(9)	4020(12)	247(7)	48(6)	37(6)	42(6)	−4(5)	−13(5)	−4(5)
O(4)	1470(9)	3820(12)	414(8)	45(6)	27(5)	57(7)	−2(5)	5(5)	−8(5)
O(11)	2509(8)	−979(12)	−673(7)	41(6)	31(6)	47(6)	6(5)	9(5)	0(5)
O(12)	2543(11)	323(14)	−1894(7)	80(9)	52(7)	30(6)	0(6)	−8(6)	−7(5)
O(13)	2536(14)	−2214(15)	−1921(9)	122(14)	48(7)	68(10)	−2(9)	6(9)	−40(7)
O(21)	1573(9)	3647(13)	−1538(8)	39(6)	42(6)	55(7)	−1(5)	0(5)	8(5)
O(22)	627(9)	1690(13)	−1087(8)	37(6)	42(7)	65(8)	−9(5)	−6(6)	7(6)
O(23)	−109(11)	3310(16)	−2026(9)	45(7)	72(9)	59(8)	12(6)	−14(6)	8(7)
O(31)	3816(9)	3133(13)	−1535(7)	37(6)	53(7)	36(6)	13(5)	−1(5)	7(5)
O(32)	4449(10)	1243(14)	−767(8)	48(7)	47(7)	49(7)	−2(6)	4(5)	22(6)
O(33)	5481(10)	2440(18)	−1731(9)	44(7)	80(9)	72(9)	7(7)	9(7)	2(8)
N(1)	2518(11)	−1004(16)	−1514(9)	40(7)	45(8)	54(8)	5(6)	−4(6)	−19(7)
N(2)	684(11)	2880(16)	−1549(9)	44(7)	48(8)	34(7)	8(6)	1(6)	−7(6)
N(3)	4619(10)	2238(19)	−1347(10)	14(6)	71(10)	58(9)	0(6)	3(6)	−31(8)
C(1)	1880(13)	−193(19)	1295(11)	42(9)	42(9)	45(9)	−21(7)	−1(7)	15(7)
C(2)	2865(15)	692(21)	1665(10)	63(11)	54(10)	25(8)	15(9)	3(7)	4(7)
C(3)	4460(14)	2067(21)	1149(12)	36(9)	61(11)	48(10)	9(8)	−7(8)	4(8)
C(4)	4157(13)	3726(21)	1104(11)	35(8)	52(10)	49(10)	−1(8)	−16(7)	−13(8)
C(5)	3017(16)	5431(19)	120(14)	66(12)	24(8)	82(14)	2(8)	−10(10)	−9(9)
C(6)	1940(15)	5323(20)	615(13)	48(10)	42(9)	71(13)	5(8)	9(9)	−9(9)
C(7)	746(16)	3290(22)	1087(11)	57(11)	64(12)	36(9)	−8(9)	10(8)	−6(8)
C(8)	395(14)	1633(19)	880(11)	42(9)	39(9)	39(9)	−2(7)	8(7)	0(7)
H(11)	1402	−431	1753						
H(12)	2132	−1153	1042						
H(21)	2648	1569	1986						
H(22)	3314	22	2044						
H(31)	4735	1775	1742						
H(32)	5055	1828	767						
H(41)	3651	3979	1556						
H(42)	4803	4385	1205						
H(51)	3459	6334	327						
H(52)	2864	5614	−493						
H(61)	2096	5437	1241						
H(62)	1443	6153	448						
H(71)	1111	3373	1653						
H(72)	111	3995	1097						
H(81)	81	1171	1388						
H(82)	−159	1639	419						

Isotropic temperature factors for H atoms: 0.076

range ±1° (2θ) around the $K_{\alpha_1} - K_{\alpha_2}$ angles, scan speed 3–29° mn^{-1}, depending on the intensity of a 2s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 300 reflections, and showed slight changes during data collection; the data were rescaled to correct for this. Unit cell dimensions and standard deviations were obtained by least-squares fit to 15 high angle reflections. 2643 observed reflections ($I/\sigma(I) > 3.0$) were used in refinement, and corrected for Lorentz, polarization and absorption effects, the last with ABSCOR [9], maximum and minimum transmission factors were 0.77 and 0.48. The crystal dimensions were 0.13 × 0.33 × 0.47 mm. Systematic absences *hol*, $l = 2n$, *oko*, $k = 2n$ indicate space group $P2_1/c$.

The heavy atom was located by Patterson techniques and the light atoms were then found on successive Fourier syntheses. Hydrogen atoms were inserted at calculated positions with fixed isotropic temperature factors, B = 5.0 Å^2, and were not refined. Final refinement was by least squares methods, in large blocks. A weighting scheme of the form W = X*Y was used, where X = 1.0 or 35.0/F for

TABLE II. Bond Lengths and Angles with Standard Deviations in Parentheses.

Eu–O(1)	2.493(10)	Eu–O(12)	2.504(11)
Eu–O(2)	2.477(10)	Eu–O(21)	2.491(11)
Eu–O(3)	2.540(11)	Eu–O(22)	2.478(12)
Eu–O(4)	2.570(11)	Eu–O(31)	2.501(11)
Eu–O(11)	2.433(11)	Eu–O(32)	2.408(12)
O(1)–C(1)	1.46(2)	C(1)–O(1)–C(8)	117.1(12)
O(1)–C(8)	1.41(2)	O(1)–C(1)–C(2)	110.0(13)
C(1)–C(2)	1.51(2)	C(1)–C(2)–O(2)	105.4(12)
C(2)–O(2)	1.44(2)	C(2)–O(2)–C(3)	113.2(12)
O(2)–C(3)	1.45(2)	O(2)–C(3)–C(4)	108.4(13)
C(3)–C(4)	1.47(3)	C(3)–C(4)–O(3)	107.9(14)
C(4)–O(3)	1.44(2)	C(4)–O(3)–C(5)	118.2(13)
O(3)–C(5)	1.45(2)	O(3)–C(5)–C(6)	110.4(14)
C(5)–C(6)	1.53(3)	C(5)–C(6)–O(4)	106.7(14)
C(6)–O(4)	1.44(2)	C(6)–O(4)–C(7)	112.1(13)
O(4)–C(7)	1.45(2)	O(4)–C(7)–C(8)	108.6(14)
C(7)–C(8)	1.51(2)	C(7)–C(8)–O(1)	110.3(14)
N(1)–O(11)	1.29(2)	O(11)–N(1)–O(12)	116.1(13)
N(1)–O(12)	1.28(2)	O(11)–N(1)–O(13)	122.0(14)
N(1)–O(13)	1.21(2)	O(12)–N(1)–O(13)	122.0(14)
N(2)–O(21)	1.26(2)	O(21)–N(2)–O(22)	118.9(13)
N(2)–O(22)	1.24(2)	O(21)–N(2)–O(23)	119.7(13)
N(2)–O(23)	1.24(2)	O(22)–N(2)–O(23)	121.3(14)
N(3)–O(31)	1.26(2)	O(31)–N(3)–O(32)	115.4(12)
N(3)–O(32)	1.25(2)	O(31)–N(3)–O(33)	117.9(15)
N(3)–O(33)	1.23(2)	O(32)–N(3)–O(33)	126.7(14)

$F > 35.0$, and $Y = 1.0$ or $0.4/(\sin\theta/\lambda)$ for $\sin\theta/\lambda > 0.4$. This was shown to be satisfactory by a weight analysis. The twinning problems encountered during data collection may account for the relatively poor final *R*-value: 0.079. The largest peaks on a final difference Fourier synthesis lay on the line through Eu parallel to *a*, and they may also be due to twin effects. Computing was with the X-Ray system [10], on a Burroughs B6700 computer. Scattering and anomalous dispersion factors were taken from [11]. Final atomic coordinates are given in Table I and bond lengths and angles in Table II. A listing of the structure factors is available upon request.

Results and Discussion

The crystals contain isolated $Eu(NO_3)_3\cdot$(12-crown-4) molecules (Fig. 1) with no prominent intermolecular interactions between them. The Eu(III) ion is coordinated by all four crown ether oxygen atoms and by the oxygen atoms of three bidentate nitrate groups. The mean Eu–O distance is 2.49(5) Å, the Eu–O(NO_3) distances being slightly shorter, 2.47(4) Å, than the Eu–O(ether) distances, 2.52(4) Å. These compare with a mean bond-length of 2.48(4) in $[Eu(NO_3)_5]^{2-}$ [12] and of 2.56(9) Å in the 11-coordinate complex $Eu(NO_3)_3\cdot C_{10}H_{20}O_5$ [5]. The polyether is of course too small to encircle the Eu(III) ion. It sits to one side of the metal atom with the 'lone pairs' of the oxygen atoms directed towards the metal ion, as in the 1:1 complex between europium nitrate and 15-crown-5 ether. However, the smaller size of the 12-membered ring allows it to sit closer to the metal ion: the Eu–O(ether) distance is, on average, 0.11 Å shorter than the corresponding distances for the 15-membered polyether. The arrangement of the ten coordinating oxygen atoms around the reare earth ion is rather irregular; it can be described as a 1:5:4 arrangement (Fig. 2). The base plane contains the four oxygen atoms of the polyether (standard deviation: 0.37 Å). The next plane contains five of the six nitrate oxygen atoms (standard deviation: 0.29 Å) and it is capped by the last of these. The (5) plane is distorted because O(11)

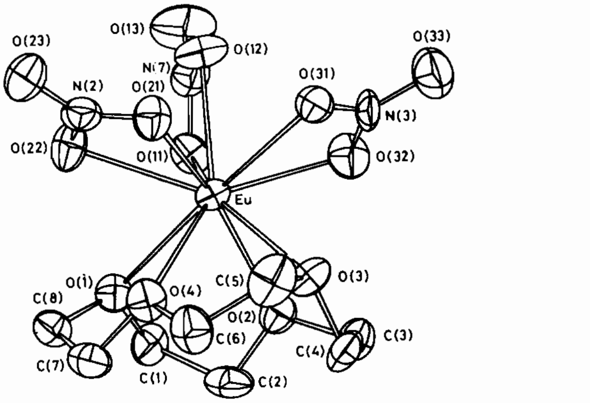

Fig. 1. View of the complex molecule $Eu(NO_3)_3\cdot C_8H_{16}O_4$, with thermal ellipsoids and the numbering of the atoms.

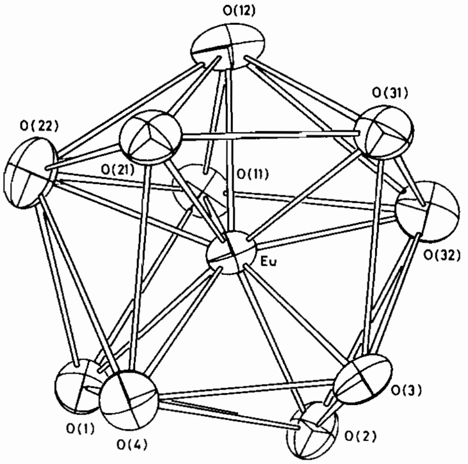

Fig. 2. Coordination polyhedron of $Eu(NO_3)_3\cdot C_8H_{16}O_4$, showing the 1:5:4 arrangement.

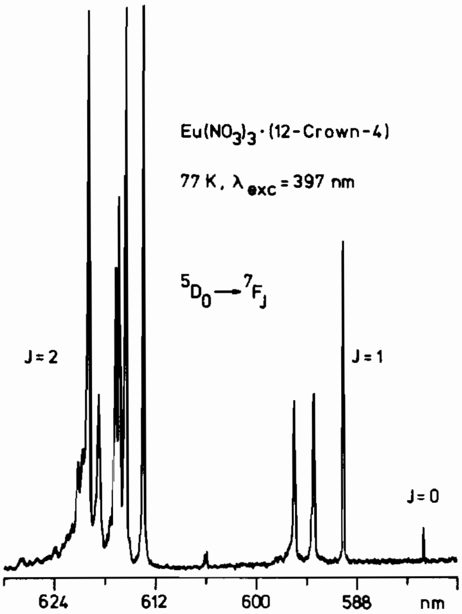

Fig. 3. Part of the emission spectrum of a powdered sample of $Eu(NO_3)_3 \cdot C_8H_{16}O_4$, at 77 K, with λ_{exc} = 397 nm. The bandpass used was 0.8 Å.

is lifted somewhat out of it by the short distance between it and the capping atom O(12). We have tried to compare the coordination polyhedron to one of the three ideal polyhedra for ten coordination [13]. The best fit [14] is with the bicapped dodecahedron of D_2 symmetry, but the overall deviation, $\bar{\epsilon}$/Eu–O = 0.093, remains relatively large. A similar result was obtained with $[Eu(NO_3)_5]^{2-}$ (deviation: 0.078) [15].

The effective ionic radius of the 10-coordinate Eu(III) ion, calculated according to [16], with $r_{O(NO_3)}$ = 1.314 Å and $r_{O(ether)}$ = 1.310 Å [5], amounts to 1.178 Å, a value close to that found by Shannon [16], 1.180 Å, and identical to the value calculated for the pentanitrate ion. The ionic radius is therefore little affected by the presence of a neutral ligand in the coordination sphere, which imposes a relatively large steric constraint.

The nitrate groups are planar; the local symmetry of $N(1)O_3^-$ is C_{2v}, $N(2)O_3^-$ almost retains the D_{3h} symmetry of an ionic nitrate, whereas $N(3)O_3^-$ is more severely distorted. The dimensions of these are normal: a slight tendency is apparent for N–O(terminal) to be shorter than N–O(coordinating) and for the O(1)–N(i)–O(2) angle to be smaller than the two angles involving the non-coordinating oxygen atom.

The cyclic polyether adopts a conformation which tends to equalize all the Eu–O(ether) distances. The four O–C–C–O torsion angles are very nearly synclinal (66, 65, 59, and 58°) and smaller than in the uncoordinated 12-crown-4 ether (75°) [17]. Syn-

TABLE III. Electronic Levels and Sub-levels of $Eu(NO_3)_3 \cdot C_8H_{16}O_4$ in cm^{-1}; $^5D_0$ and ^7F_J Levels from the Emission Spectra at 77 K (Corrected Values, ±4 cm^{-1}); Other Levels from the Excitation Spectrum at 77 K (±100 cm^{-1}). For the ^7F_J Levels, the Barycentre is Indicated between Parentheses. Origin: $^7F_0$ = 0 cm^{-1}.

Assignment	$\tilde{\nu}$ (cm^{-1})
$^5D_4$	27,500
$^5G_{5,6}$	26,500
$^5L_6$	25,200
$^5D_3$	24,000
$^5D_2$	21,400
$^5D_0$	17,244
$^7F_6$ (5,062)	5,214
	5,164
	5,144
	5,079
	5,014
	4,914
	4,904
$^7F_5$ (3,889)	3,949
	3,909
	3,899
	3,859
	3,829
$^7F_4$ (2,748)	3,034
	2,989
	2,974
	2,663
	2,652
	2,629
	2,609
	2,599
	2,584
$^7F_3$ (1,869)	1,929
	1,864
	1,814
$^7F_2$ (1,027)	1,115
	1,082
	1,034
	1,029
	1,021
	1,016
	1,002
	998
	942
$^7F_1$ (369)	447
	381
	280

TABLE IV. IR Spectrum of $Eu(NO_3)_3 \cdot C_8H_{16}O_4$ (±2 cm^{-1}, Polyethylene Pellet and Nujol Mull) and Vibronic Transitions (±4 cm^{-1}) from the Emission Spectrum at 77 K Calculated as $\tilde{\nu}(v) = \tilde{\nu}(obs) - \tilde{\nu}(^5D_0 \rightarrow {}^7F_0)$. The Spectra of Anhydrous $Eu(NO_3)_3$ and of the Ligand Alone Along with their Assignments are Reported in [19] and [7], Respectively.

$\tilde{\nu}$ (IR)	$\tilde{\nu}$ (v)	$\tilde{\nu}$ (IR)	$\tilde{\nu}$ (v)	$\tilde{\nu}$ (IR)	$\tilde{\nu}$ (v)
85		795		1,286	
101		815		1,302	
145		820		1,315	1,314
176		869		1,347	
186		899		1,361	
207		921		1,368	
221		932	933	1,379	
230			984	1,410	
265			989	1,421	
278		1,004		1,460	
315		1,021		1,500	
327		1,029		1,720	
360		1,034		1,735	
381	388	1,039		1,752	
406		1,047	1,044	1,771	
475	458	1,071	1,074	2,280	
509		1.097	1,094	2,310	
534		1,110		2,490	
575			1,124	2,520	2,520
598		1,131	1,134		2,545
			1,146		
710		1,160	1,159		2,560
728			1,179	2,670	
743			1,214		2,704
746		1,236		[a]	2,989
752		1,248		[a]	3,034
778		1,269			

[a] The C–H region is obscured by the Nujol in the IR spectrum.

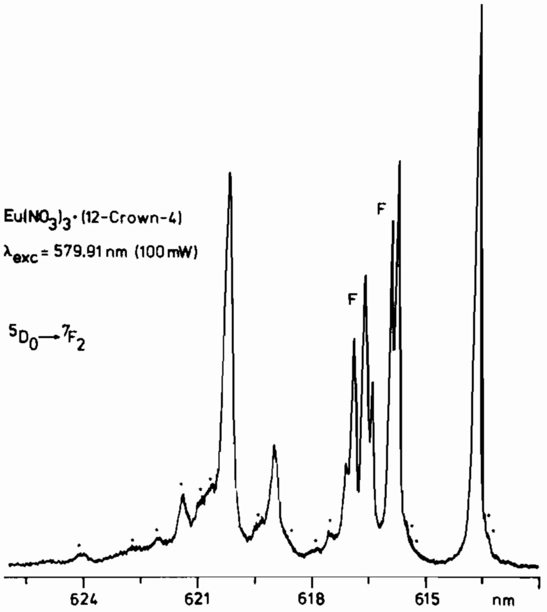

Fig. 4. Expanded view of the $^5D_0 \rightarrow {}^7F_2$ transition of $Eu(NO_3)_3 \cdot C_8H_{16}O_4$ at 77 K, with λ_{exc} = 579.91 nm (100 mW) and recorded with a bandpass of 0.2 Å. Stars denote transitions assigned to vibronic processes. The two multiplets labelled F are assumed to arise from Fermi-type resonances (see text).

clinal O–C–C–O angles have also been observed in many related polyethers [18] [5]. There are some deviations from the energetically favourable *trans* arrangement around the C–O bonds: two conformations are synclinal, two are anticlinal and four are antiperiplanar. Mean C–O and C–C distances, 1.44(1) and 1.51(3) Å, respectively, as well as mean C–O–C and C–C–O angles, 115(3) and 108(2)°, respectively, are within experimental errors of the corresponding data for the uncomplexed ligand. However, the inversion centre of the crystalline ligand is not retained in the complex, as already suggested by vibrational data [7].

Part of the emission spectrum at 77 K is displayed in Fig. 3 and the energies of the electronic levels and sublevels are reported in Table III*. The fluorescence arises mainly from the $^5D_0$ level (75%) and from the $^5D_1$ level (25%). Transitions from the latter occur as broad and featureless bands between 515 and 580 nm. There is only one sharp $^5D_0 \rightarrow {}^7F_0$ transition, with a width at half height of 2.5 cm^{-1}, indicating the presence of only one site for the Eu(III) ion, which is consistent with the crystal structure discussed above. The integrated and corrected relative intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions are 5, 100, 550, and 120% for J = 0, 1, 2, and 4, respectively, reflecting the low site symmetry (C_1) of the metal ion. Vibronic lines can be observed among the transitions from the $^5D_0$ level; they are listed in Table IV along with the vibrational frequencies measured by IR spectroscopy. The hypersensitive transition to the $^7F_2$ level has more than (2J + 1) components: it consists of 23 lines, of which 14 can be assigned to vibronic transitions (Table IV). The remaining nine lines are assigned to electronic transitions. Selective excitations to the $^5D_0$, $^5D_1$ or $^5D_2$ levels result in identical spectra in which all the 23 lines have the same relative intensities. Similarly, a sample of the corresponding isostructural lutetium complex [7] doped with 1.5% of europium ions displays the same spectrum. A closer scrutiny of these nine lines reveals they may be described as three singlets, one doublet and one quartet (Fig. 4). Upon raising the temperature to 300 K each multiplet coalesces into a broad singlet. A possible explanation

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*A listing of the 67 observed transitions is available upon request.

for the additional splitting of two sub-levels of the electronic $^7F_2$ state is that Fermi-type resonances [20] occur between them and vibrational states. Indeed, with respect to the energy of the $^5D_0$ level, the 615 to 618 nm spectral range corresponds to wavenumbers between *ca.* 985 and 1065 cm^{-1} and in this spectral range the complex possesses six sharp IR absorptions at 1004, 1021, 1029, 1034, 1039, and 1047 cm^{-1} arising from both nitrate and ligand vibrations. Both the IR absorption bands and the components of the $^5D_0 \rightarrow {}^7F_2$ transitions have widths at half height of about 5 cm^{-1}. It should be emphasized that the invoked phenomenon is different from the cooperative vibronic process recently proposed to explain the nature of the coupling which leads to non-radiative relaxation and vibronic transitions in systems involving trivalent rare earth ions and water molecules [21]. Some theoretical evidences for the possible existence of extra bands, different from phonon sidebands, in the absorption spectra of transition metal ions have been presented by S. Brawer [22]. In a model calculation this author considers a two-level system interacting linearly with the phonon modes; in the isolated complex limit, when the phonon band is very narrow, which corresponds indeed to our case, the absorption spectrum is predicted to consist of two sharp and intense bands.

If our explanation is correct, the extra splitting should either be modified or disappear upon changing slightly the energy of the interacting levels. This effectively happens when the nitrate ions are replaced by chloride ions in $EuCl_3 \cdot$(12-crown-4). The IR spectrum of this compound displays five bands in the spectral range of interest, arising from ligand vibrations, which are broader than the IR absorptions of the nitrate complex. The $^5D_0 \rightarrow {}^7F_2$ transition of its emission spectrum, at 77 K, consists of ten components, five of which can be assigned to vibronic transitions. However, due to the fairly large differences in the chemical bonding of these two complexes, their entire emission spectra are quite different. We are currently designing experiments with isotopically substituted substances in order to elucidate further the unusual splittings in the emission spectrum of $Eu(NO_3)_3 \cdot$(12-crown-4).

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