Crystal Structures and Luminescence Spectra of Ten-co-ordinate Lanthanide(III) Complexes (Ln = Ce, Sm, Eu or Tb) with 2,6-Bis(benzimidazol-2-yl)pyridine†

Shuangxi Wang,*[a,b] **Ying Zhu,**[c] **Yuxin Cui,**[b] **Liufang Wang***[b] **and Qinhui Luo**[a]
[a] *Co-ordination Chemistry Institute, Nanjing University, Nanjing 210008, China*
[b] *National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China*
[c] *Instrumental Analysis and Research Center, Lanzhou University, Lanzhou 730000, China*

The complexes $[LnL_2(NO_3)_2]NO_3{\cdot}n MeOH$ [L = 2,6-bis(benzimidazol-2-yl)pyridine, Ln = Ce **1**, $n = 3$; Ln = Eu **3** or Tb **4**, $n = 2$] have been characterized by single-crystal X-ray diffraction, IR and ^1H NMR spectroscopy and molar conductivity. They are ten-co-ordinate with six nitrogen atoms from two tridentate L ligands and four oxygen atoms from two bidentate nitrates, crystallizing in the triclinic system, space group $P\bar{1}$, $Z = 2$: **1**, $a = 10.907(1)$, $b = 14.498(1)$, $c = 16.187(2)$ Å, $\alpha = 63.02(1)$, $\beta = 75.54(1)$, $\gamma = 74.54(1)°$; **3**, $a = 10.864(8)$, $b = 14.57(1)$, $c = 15.95(1)$ Å, $\alpha = 116.92(8)$, $\beta = 90.46(8)$, $\gamma = 106.32(8)°$; **4**, $a = 10.847(1)$, $b = 14.567(2)$, $c = 15.847(2)$ Å, $\alpha = 117.25(1)$, $\beta = 90.39(1)$, $\gamma = 106.37(1)°$. The luminescence spectra of complexes **2** (Ln = Sm), **3** and **4** were recorded at room temperature in the solid state, and the quantum yields measured in methanol solution were in the order Eu > Tb > Sm. In the luminescence spectrum of complex **3**, the electric dipole transitions $^5D_0 \longrightarrow {}^7F_2$ and $^5D_0 \longrightarrow {}^7F_4$ are more intense than is the magnetic dipole transition $^5D_0 \longrightarrow {}^7F_1$, and the latter comprises three bands, suggesting a low C_1 symmetry for the Eu^{3+} ion, consistent with the crystallographic results.

There is currently increasing interest in luminescent lanthanide complexes because they can be used as probes and labels for a variety of chemical and biological applications. For example, luminescence spectroscopic measurements in co-ordination chemistry have been used to determine the symmetry, dissociation constants, number of bonded water molecules, metal–metal distances, number of distinct metal environments and bonding nature of the ligands.[1,2] Europium(III) ion is particularly suitable because its luminescence spectra display a high sensitivity to the co-ordination environment. In addition, it has similar chemical and physical properties to Ca^{2+} which is of biological importance, and easily substitutes the latter in complex biological systems. Thus, the analysis of the luminescence spectra of Eu^{3+} at such sites may enable the structure and chemical properties of Ca^{2+} in complex biological systems to be elucidated.[3–5]

To obtain luminescent lanthanide complexes it is necessary to bind lanthanide cations with chromophoric ligands, which are able to absorb energy and then transfer it effectively to the cation or shield the lanthanide ion from interaction with solvent (water) molecules which leads to deactivation of the luminescent excited state.[6,7] The potentially tridentate planar compound 2,6-bis(benzimidazol-2-yl)pyridine (L), can meet these requirements. Its complexes with Sm^{III}, Eu^{III} and Tb^{III} exhibit strong luminescence.[8a] To understand the relationship between the structure and the luminescence spectra of the complexes, we here report the crystal structures of complexes of Ce^{III}, Eu^{III} and Tb^{III} with L (preliminary results for the first have been published [8b]) and discuss their luminescent properties.

Experimental

The compound 2,6-bis(benzimidazol-2-yl)pyridine was prepared according to the literature method.[9] Hydrated lanthanide nitrates were prepared by dissolving the respective oxides (99.99%) in 50% nitric acid. The other chemicals were analytical reagent grade.

Preparation of $[LnL_2(NO_3)_2]NO_3$ (Ln = Ce **1**, Sm **2**, Eu **3** *or* Tb **4**).—The complexes were prepared using a slight modification of the method described previously.[8a] To a solution of L (20 mmol) in Me_2CO (40 cm^3) was added dropwise a solution of hydrated lanthanide(III) nitrate (10 mmol) in Me_2CO (10 cm^3) with stirring at room temperature. A precipitate formed in a few minutes. After stirring for several hours the product was filtered off, washed several times with Me_2CO and Et_2O and dried for 24 h in a vacuum desiccator at constant 60 °C to remove crystal water. Complex **1** (Found: C, 47.70; H, 2.75; Ce, 14.45; N, 18.90. $C_{38}H_{26}CeN_{13}O_9$ requires C, 48.10; H, 2.75; Ce, 14.80; N, 19.20%): IR (cm^{-1}) 1503s, 1391vs, 1302s [$\nu(NO_3^-)$]; Λ_M: 121 Ω^{-1} cm^2 mol^{-1}. Complex **2** (Found: C, 47.25; H, 2.70; N, 18.55; Sm, 15.15. $C_{38}H_{26}N_{13}O_9Sm$ requires C, 47.60; H, 2.70; N, 19.00; Sm, 15.55%): IR (cm^{-1}) 1496s, 1495vs, 1288s [$\nu(NO_3^-)$]; Λ_M: 96 Ω^{-1} cm^2 mol^{-1}. Complex **3** (Found: C, 47.30; H, 2.70; Eu, 15.35; N, 19.05. $C_{38}H_{26}EuN_{13}O_9$ requires C, 47.50; H, 2.70; Eu, 15.85; N, 18.95%): IR (cm^{-1}) 1496s, 1382vs, 1288s [$\nu(NO_3^-)$]; Λ_M: 90 Ω^{-1} cm^2 mol^{-1}. Complex **4** (Found: C, 47.00; H, 2.70; N, 18.70; Tb, 16.10. $C_{38}H_{26}N_{13}O_9Tb$ requires C, 47.15; H, 2.70; N, 18.80; Tb, 16.45%): IR (cm^{-1}) 1495s, 1384vs, 1285s [$\nu(NO_3^-)$]; Λ_M: 98 Ω^{-1} cm^2 mol^{-1}.

Physical Measurements.—Microanalyses (C, H, N) were performed on a Carlo-Erba 1106 elemental analyser. Metal contents were determined by titration with ethylenediaminetetraacetate. The IR spectra were recorded on a Nicolet-170 SX FT-IR spectrophotometer as KBr discs in the range 4000–200 cm^{-1}, ^1H NMR spectra using a Bruker AM 400 spectrometer. Electrolytic conductivity was measured using a DDS-II A molar conductometer using methanol as solvent at 25 °C. The luminescence spectra were measured on a Hitachi 850 fluorescence spectrophotometer. Luminescence quantum yields were obtained according to the literature method [10] on the same instrument using a 0.5 mol dm^{-3} H_2SO_4 solution of quinine

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

sulfate as a standard ($\Phi = 0.55$) and corrected using the formula $\Phi_{corr} = \Phi_{uncorr} n^2_{MeOH}/n^2_{H_2O}$ where n_{MeOH} and n_{H_2O} refer to refractive indexes of methanol and water solutions, respectively.

Crystal Structure Determinations.—Single crystals of complexes **1**, **3** and **4** were obtained by slow evaporation of a methanol solution of $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Ce, Eu or Tb) and L. Since the crystals lose solvent and collapse to a powder upon standing in air, they were sealed in Lindemann capillaries containing mother-liquor. The crystal data sets were collected on an Enraf–Nonius CAD4 diffractometer. The unit-cell dimensions were determined by centring 25 reflections with $18 < \theta < 32$ (Ce), $8 < \theta < 15$ (Eu) and $19 < \theta < 36°$ (Tb) and refined by least squares. Graphite-monochromated Cu-Kα radiation (λ = 1.541 84 Å) for Ce and Tb and Mo-Kα radiation (λ = 0.710 69 Å) for Eu were used. Intensities were measured with a ω–2θ scan mode, scan width $(0.5 + 0.35 \tan \theta)°$ for Eu and $(0.55 + 0.15 \tan \theta)°$ for Ce and Tb and a variable scan rate. Details of the data collections and processing are presented in Table 1. The three standard reflections monitored periodically during data collection showed small fluctuations of intensities for **3** which were corrected. The data were corrected for Lorentz and polarization effects. An absorption correction was applied using ψ-scan data.[11]

Solution and refinement. The structures were solved by direct methods and successive Fourier-difference syntheses and refined by full-matrix least-squares methods. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma$ for Ce and Tb and $1/\sigma^2(F)$ for Eu. Almost all hydrogen atoms except for some of those of the solvent molecules (CH_3OH) for complexes **1** and **4** were located from difference electron-density maps and refined with an overall isotropic thermal parameter. The hydrogen atoms for the europium complex were generated geometrically and included isotropically in the structure-factor calculations but not refined. The largest peaks in the final Fourier-difference maps for complexes **1** and **4** showed peaks less than 0.69 and 1.174 e Å^{-3} respectively, 2.37 e Å^{-3} for **3** in the vicinity of the Eu atom.

Atomic scattering factors were taken from ref. 12. All calculations for complexes **1** and **4** were performed on a PDP 11/44 computer using the SDP package,[13] while for complex **3** a VAX-11 785 computer and the TEXSAN program package[14] were employed.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Crystal structures.—The three structures **1**, **3** and **4** consist of discrete $[LnL_2(NO_3)_2]^+$ (Ln = Ce, Eu or Tb) complex cations, unco-ordinated nitrate anions and three methanol molecules for Ce and two for Eu and Tb. The final atomic positional coordinates are listed in Table 2, selected bond distances and angles in Table 3. Fig. 1 shows a perspective view of the $[EuL_2(NO_3)_2]^+$ cation with atom numbering. The three complexes are ten-co-ordinated, by six nitrogen atoms from two tridentate ligands and four oxygen atoms from the two bidentate nitrate groups. In complex **1**, the shortest cerium to ligand bond length is to the nitrate group [2.552(2) Å], the longest is to the L ligand [2.699(3) Å]. The Ce–N distances (average 2.645 Å) are shorter than those reported (average 2.673 Å) for a macrocyclic hexaimine cerium complex,[15] and the Ce–O(nitrate) distances (average 2.616 Å) are also shorter than the Ce–O(nitrate) distances (average 2.692 Å). In **3** the Eu–N distances vary between 2.51(1) and 2.633(8) Å and are similar to those reported (2.57–2.61 Å) for a complex with the similar ligand 2,2′:6′,2″-terpyridine (terpy),[16] but longer than those (average 2.542 Å) in a complex with 2,6-bis(1-methylbenzimidazol-2-yl)pyridine.[17] In **4** the Tb–N distances vary between 2.500(4) and 2.590(3) Å. The Eu–O and Tb–O distances range from 2.477(8) to 2.604(8) Å and from 2.461(3) to 2.591(4) Å respectively. In complexes **1**, **3** and **4** the Ln–N (pyridine nitrogen) distances are longer than the Ln–N (benzimidazole nitrogen) distances, as observed in the complex of L with Mn^{II},[18] which is in contrast with the fact that the co-ordination ability of the pyridine nitrogen is stronger than that of the benzimidazole nitrogen. This may arise from the geometric requirements of the ligand, because the bonding distance between the metal and co-ordinating atom depends not only on the nature of the latter, but also on the geometric requirements of the ligand. It is also worth pointing out that the bidentate nitrate groups in **1**, **3** and **4** are asymmetrically co-ordinated, the two Ln–O distances being significantly different due to the crowded metal co-ordination spheres.

The co-ordination polyhedron about Ce is best described as a sphenocorona [or tetradecahedron, Fig. 2(*a*)] characterized

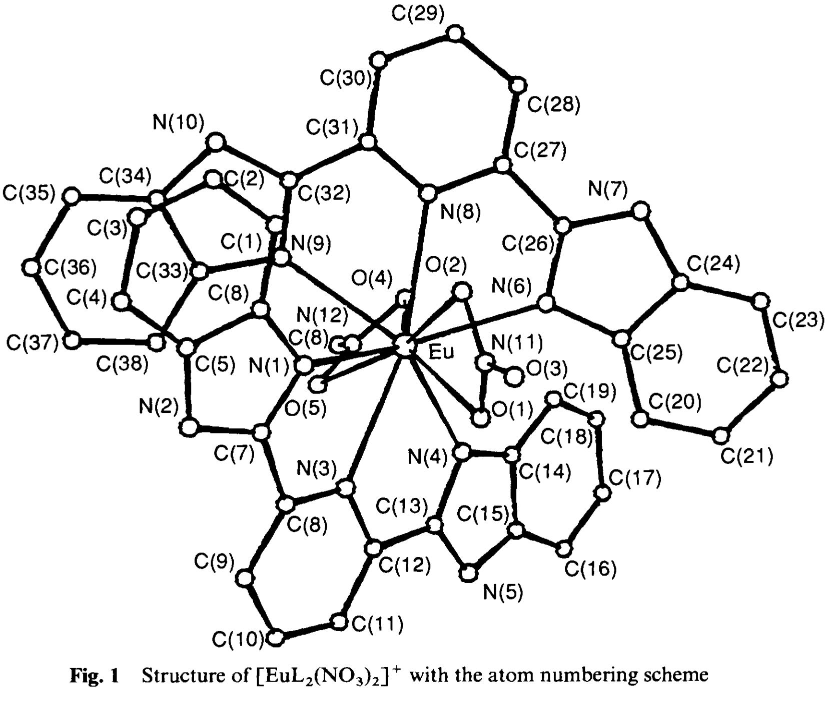


Fig. 1 Structure of $[EuL_2(NO_3)_2]^+$ with the atom numbering scheme

by the two planar trapezoidal faces meeting at an angle of approximately 102°.[19–21] The parameters for the polyhedron are listed in Table 4. The two trapezoidal faces defined by O(1), N(2), N(7), N(6) and N(1), O(4), N(7), N(2) are planar with maximum deviations of 0.015 and 0.039 Å from the least-squares planes respectively. The two trapezoidal faces make dihedral angles of 99° which is very close to the ideal value of 102°. It is noteworthy that ten-co-ordinated complexes having sphenocoronal geometry are rare, because the most stable geometry for such complexes is a bicapped square antiprism.[19–21]

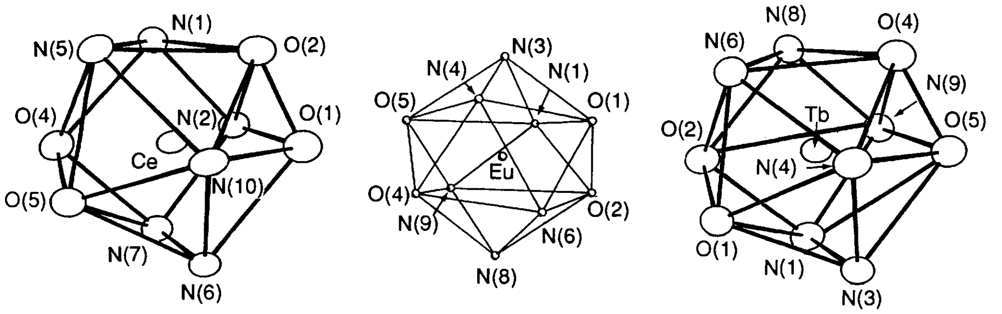
The co-ordination polyhedra for complexes **3** and **4** can be regarded as distorted bicapped square antiprisms [Fig. 2(*b*) and (*c*)]. The atoms N(4), O(5), N(1), O(1) and N(9), O(2), N(6), O(4) for **3**, N(6), O(4), N(9), O(2) and O(1), N(4), O(5), N(1) for **4** form the upper and lower square faces. The nitrogen atoms, N(3), N(8) cap the square faces for **3** and **4**. The angles N(3)–Eu–N(8) 165.9(2)° and N(8)–Tb–N(3) 166.8(1)° are significantly distorted from the ideal value of 180°.

Although complexes **1**, **3** and **4** are isostructural, the Ln–O and Ln–N bond lengths decrease from **1** to **4** due to the lanthanide contraction. Besides, the parameters of the unit cell for **1** significantly differ from those of the unit cells for **3** and **4** (see Table 1). This partly arises from the fact that the complexes differ in solvent contents, there being three MeOH molecules for **1** and two for **3** and **4**, and also partly from the lanthanide contraction.

In complexes **1**, **3** and **4** the unco-ordinated nitrate group and $[LnL_2(NO_3)_2]^+$ are linked by a hydrogen bond between the NH group of the benzimidazole rings and O atom of the nitrate group. Detailed data on the hydrogen bonds are summarized in Table 5. In **4** the hydroxyl O(10)–H group of one solvent molecule (MeOH) is hydrogen bonded to the O(3) atom of the co-ordinated nitrate. For **1** and **3**, since the hydrogen atoms of the hydroxyl groups of the solvent methanol molecules cannot be located, the hydrogen bonds about them were not precisely identified. However, short contacts (see Table 5) between the O atoms of these solvent molecules and the O atoms of the nitrate groups could be interpreted as hydrogen bonds. Despite these hydrogen bonds and short contacts the crystal packings for **1**, **3** and **4** are mainly determined by van der Waals forces.

Infrared Spectroscopy.—The most relevant feature of the IR spectra of the complexes **1**–**4** concerns the nitrogen–oxygen stretching frequencies of the nitrate groups because they can be diagnostic of the co-ordination modes of the nitrate group. The spectra exhibit three bands at ≈1496–1384 and ≈1288 cm^{-1} assigned to ν(N–O) modes of the nitrate groups, suggesting the simultaneous presence of bidentate and unco-ordinated nitrate.[22] The 1 : 1 electrolyte behaviour in methanol supports these results, *i.e.* two of the three nitrate groups in each complex molecule are co-ordinated to Ln^{III} as bidentate ligands and the other is unco-ordinated. This is also consistent with the crystal structure.

Proton NMR Spectra.—The ^{1}H NMR spectra of L and complexes **2**–**4** were recorded in CD_3OD and are shown in Fig.



(*a*) (*b*) (*c*)

Fig. 2 Co-ordination polyhedra of complexes **1** (*a*), **3** (*b*) and **4** (*c*)

Table 1 Crystallographic data for $[LnL_2(NO_3)_2]NO_3{\cdot}n$MeOH[a]

	1 (Ln = Ce, *n* = 3)	**3** (Ln = Eu, *n* = 2)	**4** (Ln = Tb, *n* = 2)
Formula	$C_{41}H_{38}CeN_{13}O_{12}$	$C_{40}H_{34}EuN_{13}O_{11}$	$C_{40}H_{34}N_{13}O_{11}Tb$
M	1044.96	1024.75	1031.72
a/Å	10.907(1)	10.864(8)	10.847(1)
b/Å	14.498(1)	14.57(1)	14.567(2)
c/Å	16.187(2)	15.95(1)	15.847(2)
α/°	63.02(1)	116.92(8)	117.25(1)
β/°	75.54(1)	90.46(8)	90.39(1)
γ/°	74.54(1)	106.32(8)	106.37(1)
U/Å^3	2173.7	2132	2108.6
Crystal size/mm	0.45 × 0.25 × 0.25	0.34 × 0.41 × 0.16	0.25 × 0.20 × 0.10
D_c/g cm^{-3}	1.596	1.60	1.625
D_m/g cm^{-3}	1.597	1.61	1.624
μ/cm^{-1}	89.5	15.44	88.9
F(000)	1058	1032	1036
h, *k*, *l* ranges	−12 to 12, −16 to 16, 0–18	0–12, −16 to 16, −18 to 18	0–17, −18 to 18, −12 to 12
θ range/°	1–60	1–24	1–65
No. of reflections collected	6730	6926	7503
No. of reflections for refinement[b]	6231	5040	6507
No. of variables	604	586	586
R	0.041	0.062	0.053
R'	0.058	0.079	0.059

[a] Details in common = triclinic, space group $P\bar{1}$; $Z = 2$. [b] $I > 3\sigma(I)$ for **1** and **4**, $> 4\sigma(I)$ for **3**.

Table 2 Atom coordinates

Atom	*x*	*y*	*z*
Complex **1**			
Ce	0.254 92(2)	0.220 40(1)	0.731 19(1)
O(1)	0.039 8(3)	0.234 4(2)	0.848 9(2)
O(2)	0.015 7(3)	0.249 4(2)	0.714 6(2)
O(3)	−0.150 6(3)	0.239 6(3)	0.825 0(3)
O(4)	0.477 3(3)	0.243 6(2)	0.615 3(2)
O(5)	0.470 5(3)	0.095 3(2)	0.736 5(2)
O(6)	0.654 4(4)	0.131 2(3)	0.655 7(3)
O(7)	0.299 0(8)	0.300 9(4)	0.257 4(3)
O(8)	0.225 6(8)	0.185 3(7)	0.274 6(5)
O(9)	0.269 8(5)	0.294 3(4)	0.135 2(3)
O(10)	0.139 2(5)	−0.782 0(3)	0.428 2(3)
O(11)	0.445 9(7)	0.672 6(5)	0.970 5(4)
O(12)	0.300 3(6)	0.511 3(4)	0.062 7(4)
N(1)	0.204 2(3)	0.366 7(2)	0.561 1(2)
N(2)	0.162 9(4)	0.413 8(3)	0.710 6(2)
N(3)	0.143 2(4)	0.585 7(3)	0.626 2(3)
N(4)	0.269 4(4)	0.182 1(3)	0.455 5(2)
N(5)	0.267 7(4)	0.155 7(3)	0.602 1(2)
N(6)	0.311 3(3)	0.119 6(3)	0.907 7(2)
N(7)	0.409 8(4)	0.292 7(3)	0.779 6(2)
N(8)	0.465 2(4)	0.323 5(3)	0.886 9(2)
N(9)	0.143 6(4)	−0.096 8(3)	0.976 6(2)
N(10)	0.173 4(3)	0.041 3(3)	0.840 4(2)
N(11)	−0.033 7(4)	0.241 0(3)	0.797 0(3)
N(12)	0.537 2(4)	0.157 0(3)	0.667 9(2)
N(13)	0.267 0(5)	0.258 6(4)	0.221 4(3)
C(1)	0.171 7(4)	0.468 9(3)	0.543 5(3)
C(2)	0.159 2(4)	0.490 5(3)	0.625 6(3)
C(3)	0.149 3(5)	0.461 6(3)	0.770 2(3)
C(4)	0.149 8(5)	0.418 9(4)	0.866 6(3)
C(5)	0.141 3(6)	0.488 1(4)	0.905 6(3)
C(6)	0.130 3(7)	0.595 8(4)	0.851 9(4)
C(7)	0.127 0(6)	0.640 5(4)	0.757 2(4)
C(8)	0.138 0(5)	0.571 3(4)	0.716 9(3)
C(9)	0.147 8(5)	0.546 9(4)	0.455 7(3)
C(10)	0.155 3(5)	0.516 4(4)	0.384 7(3)
C(11)	0.184 3(5)	0.410 7(4)	0.402 9(3)
C(12)	0.209 6(4)	0.339 2(3)	0.491 6(3)
C(13)	0.247 6(4)	0.224 3(3)	0.517 6(3)
C(14)	0.305 8(5)	0.075 2(3)	0.504 6(3)
C(15)	0.340 7(5)	−0.007 5(4)	0.476 5(3)
C(16)	0.374 0(6)	−0.106 6(4)	0.544 2(4)
C(17)	0.375 6(6)	−0.122 5(4)	0.635 6(3)
C(18)	0.342 5(5)	−0.041 0(4)	0.663 6(3)
C(19)	0.307 9(5)	0.059 7(3)	0.595 9(3)
C(20)	0.375 1(4)	0.159 6(3)	0.940 7(3)
C(21)	0.418 9(4)	0.256 8(3)	0.869 4(3)
C(22)	0.452 1(4)	0.388 2(3)	0.735 6(3)
C(23)	0.459 6(5)	0.462 1(4)	0.642 0(3)
C(24)	0.492 1(5)	0.556 0(4)	0.619 7(4)
C(25)	0.520 5(5)	0.577 2(4)	0.689 9(4)
C(26)	0.519 3(5)	0.505 1(4)	0.781 0(4)
C(27)	0.484 2(4)	0.410 2(3)	0.802 0(3)
C(28)	0.397 0(5)	0.115 6(4)	1.031 8(3)
C(29)	0.351 5(5)	0.022 9(4)	1.093 4(3)
C(30)	0.288 7(5)	−0.021 2(4)	1.060 9(3)
C(31)	0.269 6(4)	0.028 4(3)	0.967 5(3)
C(32)	0.197 7(4)	−0.009 6(3)	0.928 2(3)
C(33)	0.077 3(4)	−0.103 4(3)	0.917 0(3)
C(34)	0.007 0(5)	−0.176 2(3)	0.930 4(3)
C(35)	−0.050 9(5)	−0.257 6(3)	0.856 8(3)
C(36)	−0.036 9(5)	−0.067 8(4)	0.771 5(3)
C(37)	0.035 1(5)	0.003 2(4)	0.758 5(3)
C(38)	0.094 9(4)	−0.015 1(3)	0.832 4(3)
C(39)	0.057 7(7)	0.866 5(5)	0.495 4(5)
C(40)	0.402 4(8)	0.727 3(7)	0.891 1(5)
C(41)	0.185 9(9)	0.543 3(8)	0.114 4(6)
Complex **3**			
Eu	0.753 99(5)	0.045 75(4)	0.266 21(4)
O(1)	0.966 3(7)	0.163 5(6)	0.262 6(5)
O(2)	0.970 0(7)	0.137 1(6)	0.384 8(5)
O(3)	1.150 4(8)	0.217 0(7)	0.350 2(6)
O(4)	0.516 9(8)	0.026 3(7)	0.280 9(5)
O(5)	0.545 2(7)	−0.089 1(6)	0.143 4(5)
O(6)	0.352 2(8)	−0.081 6(8)	0.167 2(6)
O(7)	1.228(1)	0.424(1)	0.139(1)
O(8)	1.308(1)	0.521(2)	0.286(1)
O(9)	1.156(2)	0.534(2)	0.239(1)
O(10)	1.363(1)	0.261 9(8)	0.482 7(7)
O(11)	0.965(2)	0.349(1)	0.053(1)
N(1)	0.908 1(8)	−0.070 9(7)	0.218 4(6)
N(2)	0.967(1)	−0.204 9(8)	0.108 4(7)
N(3)	0.807 8(8)	−0.025 1(7)	0.091 5(6)
N(4)	0.669 5(8)	0.119 5(7)	0.166 6(6)
N(5)	0.642 3(9)	0.128 3(7)	0.031 9(6)
N(6)	0.772 5(8)	0.235 8(7)	0.389 0(6)
N(7)	0.767 (1)	0.360 6(7)	0.536 8(6)
N(8)	0.704 2(8)	0.070 3(7)	0.433 5(6)
N(9)	0.664 2(8)	−0.125 9(6)	0.282 9(6)
N(10)	0.641(1)	−0.213 9(8)	0.368 2(7)
N(11)	1.031(1)	0.172 9(7)	0.332 5(7)
N(12)	0.471(1)	−0.050 3(8)	0.195 8(7)
N(13)	1.228(2)	0.487(1)	0.221(1)
C(1)	0.959(1)	−0.103(1)	0.356 4(8)
C(2)	0.993(1)	−0.173(1)	0.379(1)
C(3)	1.023(1)	−0.261(1)	0.308(1)
C(4)	1.022(1)	−0.280(1)	0.216(1)
C(5)	0.987(1)	−0.207(1)	0.193 7(9)
C(6)	0.952(1)	−0.120 5(9)	0.263 0(8)
C(7)	0.920(1)	−0.121 9(9)	0.128 4(8)
C(8)	0.873(1)	−0.094 9(9)	0.057 1(7)
C(9)	0.891(1)	−0.144(1)	−0.037 6(8)
C(10)	0.845(1)	−0.108(1)	−0.097 2(8)
C(11)	0.783(1)	−0.034(1)	−0.061 6(7)
C(12)	0.766(1)	0.008 6(8)	0.033 0(7)
C(13)	0.695(1)	0.084 9(8)	0.076 5(7)
C(14)	0.591(1)	0.162 7(8)	0.176 3(8)
C(15)	0.576(1)	0.189 1(8)	0.093 0(7)
C(16)	0.506(1)	0.254(1)	0.084 8(9)
C(17)	0.450(1)	0.306(1)	0.160(1)
C(18)	0.460(1)	0.294(1)	0.241 6(9)
C(19)	0.532(1)	0.235(1)	0.252 8(8)
C(20)	0.851(1)	0.371(1)	0.325 8(9)
C(21)	0.884(1)	0.479(1)	0.353(1)
C(22)	0.877(1)	0.558(1)	0.446(1)
C(23)	0.839(1)	0.528(1)	0.513(1)
C(24)	0.808(1)	0.418 1(9)	0.486 8(8)
C(25)	0.812(1)	0.340 6(8)	0.396 5(8)
C(26)	0.748(1)	0.255 3(8)	0.476 5(7)
C(27)	0.710(1)	0.169 6(8)	0.504 3(7)
C(28)	0.684(1)	0.187(1)	0.594 8(8)
C(29)	0.655(1)	0.101(1)	0.612 2(8)
C(30)	0.648(1)	−0.001(1)	0.541 2(8)
C(31)	0.671(1)	−0.013 7(8)	0.452 5(7)
C(32)	0.660(1)	−0.117 3(9)	0.368 2(8)
C(33)	0.650(1)	−0.233 5(9)	0.222 8(8)
C(34)	0.636(1)	−0.290(1)	0.275 6(9)
C(35)	0.626(1)	−0.399(1)	0.234(1)
C(36)	0.629(1)	−0.448(1)	0.138(1)
C(37)	0.641(1)	−0.396(1)	0.083(1)
C(38)	0.650(1)	−0.288(1)	0.125 1(9)
C(39)	1.439(1)	0.373(1)	0.512(1)
C(40)	0.882(2)	0.390(2)	0.079(2)

Table 2 (*continued*)

Atom	x	y	z
Complex **4**			
Tb	0.753 26(3)	0.544 90(2)	0.265 60(2)
O(1)	0.964 6(4)	0.662 8(3)	0.262 8(3)
O(2)	0.968 4(4)	0.636 7(3)	0.385 7(3)
O(3)	1.148 5(5)	0.717 3(4)	0.352 1(4)
O(4)	0.519 5(4)	0.524 0(3)	0.279 8(3)
O(5)	0.547 6(4)	0.409 1(3)	0.141 2(3)
O(6)	0.352 3(4)	0.416 0(4)	0.166 0(3)
O(7)	0.230 1(8)	−0.079 6(6)	0.137 5(6)
O(8)	0.314 5(7)	0.028 5(7)	0.287 9(5)
O(9)	0.144 9(8)	0.030 5(7)	0.231 1(7)
O(10)	0.363 0(6)	0.762 3(4)	0.483 3(4)
O(11)	0.034 5(8)	0.150 0(7)	0.945 6(7)
N(1)	0.905 9(5)	0.430 7(3)	0.218 4(3)
N(2)	0.967 6(5)	0.296 4(4)	0.107 1(4)
N(3)	0.806 3(4)	0.476 3(3)	0.092 2(3)
N(4)	0.667 7(5)	0.617 0(3)	0.167 2(3)
N(5)	0.641 9(5)	0.630 0(3)	0.033 9(3)
N(6)	0.772 5(5)	0.735 6(3)	0.387 8(3)
N(7)	0.766 3(5)	0.861 7(4)	0.535 6(3)
N(8)	0.705 2(4)	0.571 3(3)	0.433 2(3)
N(9)	0.663 9(5)	0.375 3(3)	0.281 6(3)
N(10)	0.641 2(5)	0.286 6(3)	0.367 8(3)
N(11)	1.029 2(5)	0.673 0(3)	0.334 4(3)
N(12)	0.470 6(5)	0.447 3(4)	0.194 4(3)
N(13)	0.228 9(7)	−0.010 0(5)	0.219 8(5)
C(1)	0.956 2(6)	0.397 9(4)	0.356 8(4)
C(2)	0.991 5(7)	0.324 1(5)	0.375 8(5)
C(3)	1.022 3(7)	0.236 6(5)	0.303 8(5)
C(4)	1.023 6(7)	0.220 4(5)	0.212 1(5)
C(5)	0.987 0(6)	0.293 7(4)	0.191 9(4)
C(6)	0.951 3(6)	0.379 5(4)	0.262 3(4)
C(7)	0.917 9(6)	0.378 2(4)	0.126 8(4)
C(8)	0.873 3(6)	0.404 4(4)	0.056 5(4)
C(9)	0.892 6(6)	0.358 4(5)	−0.038 2(4)
C(10)	0.845 3(7)	0.390 8(5)	−0.098 4(4)
C(11)	0.781 9(6)	0.467 5(5)	−0.061 8(4)
C(12)	0.764 0(5)	0.508 0(4)	0.032 7(4)
C(13)	0.694 0(5)	0.586 7(4)	0.079 3(3)
C(14)	0.590 0(6)	0.682 9(4)	0.180 3(4)
C(15)	0.576 2(6)	0.692 3(4)	0.097 0(4)
C(16)	0.507 5(7)	0.757 1(4)	0.089 0(4)
C(17)	0.449 4(7)	0.809 1(5)	0.165 8(5)
C(18)	0.458 5(7)	0.796 6(5)	0.248 0(5)
C(19)	0.528 0(6)	0.734 0(5)	0.257 3(4)
C(20)	0.854 6(7)	0.868 9(4)	0.323 7(4)
C(21)	0.886 4(8)	0.979 2(5)	0.350 7(5)
C(22)	0.878 2(8)	1.055 2(5)	0.441 8(5)
C(23)	0.839 4(7)	1.027 3(5)	0.511 9(5)
C(24)	0.806 6(6)	0.917 1(4)	0.484 7(4)
C(25)	0.812 0(6)	0.838 7(4)	0.393 2(4)
C(26)	0.748 0(5)	0.755 4(4)	0.476 0(4)
C(27)	0.709 8(5)	0.670 5(4)	0.503 9(4)
C(28)	0.684 6(6)	0.688 7(4)	0.594 5(4)
C(29)	0.657 0(6)	0.602 9(5)	0.614 7(4)
C(30)	0.649 8(6)	0.499 0(4)	0.541 9(4)
C(31)	0.671 8(5)	0.486 1(4)	0.452 4(4)
C(32)	0.658 7(6)	0.382 7(4)	0.367 6(4)
C(33)	0.648 4(6)	0.265 6(4)	0.220 4(4)
C(34)	0.636 3(6)	0.210 1(4)	0.274 1(4)
C(35)	0.626 2(8)	0.100 0(5)	0.232 0(5)
C(36)	0.628 9(9)	0.048 8(5)	0.135 2(6)
C(37)	0.639 3(7)	0.101 8(5)	0.079 6(5)
C(38)	0.648 7(7)	0.211 1(5)	0.121 8(4)
C(39)	0.439 4(9)	0.873 5(6)	0.514 1(6)
C(40)	0.133(1)	0.113(1)	0.943(1)

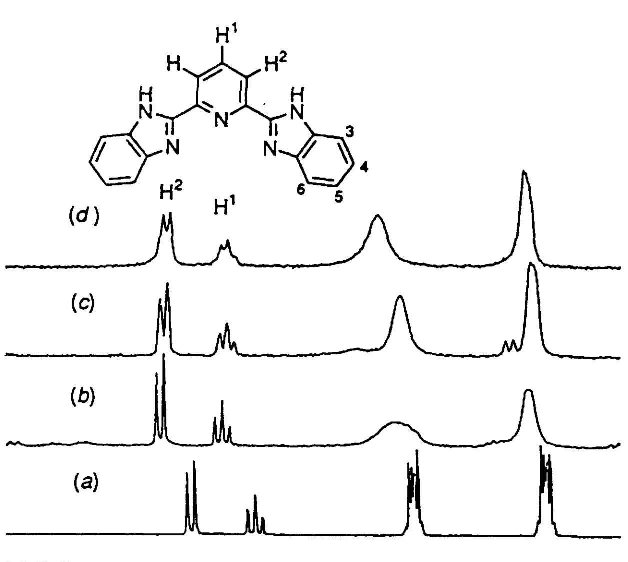


Fig. 3 Proton NMR spectra of (*a*) L, (*b*) complex **2**, (*c*) **3**, and (*d*) **4** in CD_3OD

3. The spectrum of free L shows, as described,[23] a pseudo-first-order spectrum for the pyridine protons with a doublet at δ 8.28 for H^2 and a triplet at δ 8.18 for H^1, and two equivalent benzimidazoles giving two multiplets at δ 7.60–7.71 and 7.30–7.38 for protons H^{3-6}. The signals of the pyridine and benzimidazole protons of the complexes are all shifted downfield compared with that of free L, suggesting the co-ordination of the ligand in methanol solution. A difference observed is that the signals for the benzimidazole protons broaden, which may be attributed to an exchange of a benzimidazole side arm with the solvent MeOH on the NMR time-scale, where MeOH is thought to compete with the side arm for complexation to Ln^{III}, as suggested previously.[23] The signal of the pyridine proton H^2 in the spectra of the complexes still appears at the lowest field, in contrast to the H^1 being at lowest field for copper(I) complexes upon N-co-ordination of pyridine rings.[23,24] This may be due to the weak co-ordination ability of Ln^{III} towards N atoms, especially in the present complexes with large distances [2.583(4)–2.633(8) Å] between the metal and pyridine nitrogen atom which results in a small deshielding effect of the metal ions towards the pyridine protons of the ligand. Consequently, relatively small changes in the signals of the pyridine protons take place. The ^1H NMR spectra of the complexes in the strongly co-ordinating solvent $(CD_3)_2SO$ showed little change with only a slightly broadening for the benzimidazole protons compared with those of L, indicating that exchange of the ligand with the solvent occurs, forming the multisolvated Ln^{3+}.

Luminescence Spectra.—The luminescence spectra of complexes **2**–**4** were obtained for the powdered solids at room temperature (Fig. 4 and Table 6). The complexes show strong luminescence, especially for complex **3**. However, in methanol solution the complexes give low quantum yields (Table 6) in the order of Eu > Tb > Sm, probably due to the presence of the high-energy hydroxyl groups of the methanol molecules which deactivate the luminescent excited state. The complexes are less soluble in other organic solvents such as MeCN and Me_2CO which limits further study.

Since the Eu^{3+} ion is highly luminescent and environmentally sensitive, we analysed the luminescence spectrum of the complex **3** to get more information on the detailed structure. The complex exhibits strong red luminescence which arises from

Table 3 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses

Complex **1**

Ce–O(1)	2.654(3)	Ce–O(5)	2.552(2)	Ce–N(5)	2.613(3)	Ce–N(7)	2.629(3)
Ce–O(2)	2.592(2)	Ce–N(1)	2.687(3)	Ce–N(6)	2.699(3)	Ce–N(10)	2.635(2)
Ce–O(4)	2.666(2)	Ce–N(2)	2.608(3)				

N(1)–Ce–N(2)	61.41(8)	N(5)–Ce–N(7)	136.08(9)	O(2)–Ce–O(5)	144.30(9)	O(4)–Ce–N(5)	69.00(8)
N(1)–Ce–N(5)	62.38(8)	N(5)–Ce–N(2)	123.12(8)	O(4)–Ce–O(5)	48.84(8)	O(4)–Ce–N(7)	67.17(9)
N(1)–Ce–N(6)	164.34(8)	N(10)–Ce–N(6)	62.17(8)	O(1)–Ce–N(1)	105.81(8)	O(4)–Ce–N(6)	107.19(8)
N(1)–Ce–N(10)	131.53(8)	N(10)–Ce–N(7)	122.93(8)	O(1)–Ce–N(5)	121.44(9)	O(5)–Ce–N(1)	116.59(8)
N(1)–Ce–N(7)	105.52(8)	N(10)–Ce–N(2)	132.88(9)	O(1)–Ce–N(6)	71.53(8)	O(5)–Ce–N(2)	139.60(9)
N(5)–Ce–N(10)	81.85(8)	N(6)–Ce–N(7)	61.16(8)	O(1)–Ce–N(10)	64.91(8)	O(5)–Ce–N(5)	75.64(9)
N(5)–Ce–N(6)	132.60(9)	N(10)–Ce–O(4)	126.12(8)	O(1)–Ce–N(7)	102.41(8)	O(5)–Ce–N(6)	69.51(8)
N(6)–Ce–N(2)	104.21(8)	O(2)–Ce–N(6)	116.11(8)	O(2)–Ce–N(1)	68.23(7)	O(5)–Ce–N(7)	73.82(8)
N(7)–Ce–N(2)	68.94(8)	O(2)–Ce–N(7)	141.28(8)	O(2)–Ce–N(2)	75.38(8)	O(5)–Ce–N(10)	81.12(8)
O(1)–Ce–O(2)	48.61(8)	O(2)–Ce–N(10)	72.79(8)	O(2)–Ce–N(5)	76.88(8)	O(4)–Ce–O(2)	136.19(7)
O(1)–Ce–O(4)	167.48(8)	O(4)–Ce–N(1)	71.91(7)	O(1)–Ce–N(2)	67.99(8)		
O(1)–Ce–O(5)	136.99(8)	O(4)–Ce–N(2)	100.89(2)				

Complex **3**

Eu–O(1)	2.477(8)	Eu–O(5)	2.604(8)	Eu–N(4)	2.567(8)	Eu–N(8)	2.609(8)
Eu–O(2)	2.598(8)	Eu–N(1)	2.592(8)	Eu–N(6)	2.51(1)	Eu–N(9)	2.551(8)
Eu–O(4)	2.536(8)	Eu–N(3)	2.633(8)				

O(1)–Eu–N(6)	73.9(3)	O(1)–Eu–N(8)	116.4(3)	0(4)–Eu–N(1)	140.1(3)	N(1)–Eu–O(2)	67.1(3)
O(1)–Eu–O(4)	146.1(3)	O(1)–Eu–N(3)	69.2(3)	O(4)–Eu–O(2)	135.4(2)	N(1)–Eu–O(5)	101.1(3)
O(1)–Eu–N(9)	138.6(3)	N(6)–Eu–O(4)	79.4(3)	O(4)–Eu–O(5)	49.8(3)	N(1)–Eu–N(8)	105.8(3)
O(1)–Eu–N(4)	83.3(3)	N(6)–Eu–N(9)	126.3(3)	O(4)–Eu–O(8)	67.8(2)	N(1)–Eu–N(3)	62.4(3)
O(1)–Eu–N(1)	73.3(3)	N(6)–Eu–N(4)	77.6(3)	O(4)–Eu–N(3)	115.5(2)	O(2)–Eu–N(5)	166.0(2)
O(1)–Eu–O(2)	50.1(2)	N(6)–Eu–O(2)	68.7(3)	N(9)–Eu–N(4)	133.4(3)	O(2)–Eu–N(3)	108.8(3)
O(1)–Eu–O(5)	135.7(2)	N(6)–Eu–N(1)	135.3(3)	N(9)–Eu–N(1)	68.2(3)	O(2)–Eu–N(8)	70.5(2)
N(6)–Eu–O(5)	123.6(3)	N(4)–Eu–N(1)	126.2(3)	N(9)–Eu–O(2)	99.7(3)	O(5)–Eu–N(8)	107.5(3)
N(6)–Eu–N(8)	64.2(3)	N(4)–Eu–O(2)	127.0(3)	N(9)–Eu–O(5)	68.0(3)	N(8)–Eu–N(3)	165.9(2)
N(6)–Eu–N(3)	129.3(3)	N(4)–Eu–O(5)	65.7(3)	N(9)–Eu–N(8)	62.6(3)	O(5)–Eu–N(3)	69.6(3)
O(4)–Eu–N(9)	74.7(3)	N(4)–Eu–N(8)	128.0(3)	N(9)–Eu–N(3)	104.3(3)		
O(4)–Eu–N(4)	71.7(2)	N(4)–Eu–N(3)	64.3(3)				

Complex **4**

Tb–O(5)	2.580(3)	Tb–O(1)	2.461(3)	Tb–N(8)	2.583(4)	Tb–N(1)	2.549(3)
Tb–O(4)	2.492(3)	Tb–N(6)	2.500(4)	Tb–N(4)	2.535(3)	Tb–N(3)	2.590(3)
Tb–O(2)	2.591(4)	Tb–N(9)	2.518(3)				

N(6)–Tb–N(9)	127.1(2)	N(9)–Tb–N(1)	68.5(2)	O(2)–Tb–N(9)	99.7(1)	O(5)–Tb–N(8)	108.33(9)
N(6)–Tb–N(8)	64.6(1)	N(9)–Tb–N(3)	104.9(2)	O(2)–Tb–N(8)	69.91(9)	O(5)–Tb–N(4)	65.5(1)
N(6)–Tb–N(4)	76.9(2)	N(6)–Tb–N(1)	135.1(1)	O(2)–Tb–N(4)	127.5(1)	O(5)–Tb–N(1)	100.7(2)
N(8)–Tb–N(4)	127.5(1)	N(6)–Tb–N(3)	128.0(1)	O(2)–Tb–N(1)	66.9(2)	O(5)–Tb–N(3)	69.2(1)
N(8)–Tb–N(1)	105.8(2)	N(9)–Tb–N(8)	63.0(2)	O(2)–Tb–N(3)	109.1(1)	O(4)–Tb–O(2)	135.27(9)
N(8)–Tb–N(3)	166.8(1)	N(9)–Tb–N(4)	132.9(2)	O(1)–Tb–N(6)	73.3(1)	O(4)–Tb–O(1)	146.43(9)
N(4)–Tb–N(1)	126.7(2)	N(1)–Tb–N(3)	63.0(1)	O(1)–Tb–N(9)	138.8(1)	O(4)–Tb–N(6)	80.1(2)
N(4)–Tb–N(3)	64.1(1)	O(5)–Tb–O(4)	50.27(9)	O(1)–Tb–N(8)	115.8(1)	O(4)–Tb–N(9)	74.1(2)
O(4)–Tb–N(1)	139.8(2)	O(5)–Tb–O(2)	165.56(9)	O(1)–Tb–N(4)	82.8(1)	O(4)–Tb–N(8)	68.00(9)
O(4)–Tb–N(3)	115.4(1)	O(5)–Tb–O(1)	135.45(9)	O(1)–Tb–N(1)	73.2(2)	O(4)–Tb–N(4)	71.5(9)
O(2)–Tb–O(1)	50.31(9)	O(5)–Tb–N(6)	124.1(2)	O(1)–Tb–N(3)	69.1(1)		
O(2)–Tb–N(6)	68.8(1)	O(5)–Tb–N(9)	67.9(1)				

Table 4 Structural parameters of the sphenocorona for complex **1**

Plane A	$-0.1036x - 0.7242y - 0.6818z + 15.1043 = 0$			
Atom	O(1)	N(2)	N(7)	N(6)
Deviation/Å	−0.013	0.014	−0.015	0.014
Vertex angle/°	N(2)–O(1)–N(6) 87.2	O(1)–N(2)–N(7) 88.4	N(2)–N(7)–N(6) 95.0	N(7)–N(6)–O(1) 89.4
Edge length/Å	O(1)–N(2) 2.942	N(2)–N(7) 2.964	N(7)–N(6) 2.711	N(6)–O(1) 3.129
Plane B	$0.5134x + 0.6595y - 0.5491z - 4.4624 = 0$			
Atom	N(1)	O(4)	N(7)	N(2)
Deviation/Å	−0.037	0.034	−0.036	0.039
Vertex angle/°	O(4)–N(1)–N(2) 87.8	N(1)–O(4)–N(7) 88.3	O(4)–N(7)–N(2) 87.2	N(7)–N(2)–N(1) 96.5
Edge length/Å	N(1)–O(4) 3.142	O(4)–N(7) 2.928	N(7)–N(2) 2.964	N(2)–N(1) 2.704

Dihedral angle between A and B: 99.0°.

Table 5 Hydrogen-bond distances (Å) and angles (°)

1 $[CeL_2(NO_3)_2]NO_3\cdot 3MeOH$			
N(4)–H	0.873	O(10)···O(6)*	2.819
N(4)···O(7)	2.850	O(12)···O(9)*	2.897
H···O(7)	1.997		
N(4)–H···O(7)	159.2		
3 $[EuL_2(NO_3)_2]NO_3\cdot 2MeOH$			
N(7)–H(3)	0.952	O(3)···O(10)*	2.84
N(7)···O(8)	2.840	O(7)···O(11)*	2.85
H(3)···O(8)	1.933		
N(7)–H(3)···O(8)	157.03		
4 $[TbL_2(NO_3)_2]NO_3\cdot 2MeOH$			
N(7)–H	0.878	O(10)–H	1.026
N(7)···O(8)	2.810	O(10)···O(3)	2.83
H···O(8)	1.994	H···O(3)	1.918
N(7)–H···O(8)	153.3	O(10)–H···O(3)	146.1

* Short contact which could be interpreted as a hydrogen bond.

Table 6 Observed transitions in the luminescence spectra and quantum yields[a] of complexes **2**–**4**

Complex	λ/nm	Assignment
2[b]	563	$^4G_{\frac{5}{2}} \longrightarrow {}^6H_{\frac{5}{2}}$
	596	$^4G_{\frac{5}{2}} \longrightarrow {}^6H_{\frac{7}{2}}$
	642	
	653	$^4G_{\frac{5}{2}} \longrightarrow {}^6H_{\frac{9}{2}}$
3[c]	581	$^5D_0 \longrightarrow {}^7F_0$
	593	$^5D_0 \longrightarrow {}^7F_1$
	594	
	595	
	615	$^5D_0 \longrightarrow {}^7F_2$
	618	
	619	
	621	
	652	$^5D_0 \longrightarrow {}^7F_3$
	654	
	683	$^5D_0 \longrightarrow {}^7F_4$
	688	
4[d]	491	$^5D_4 \longrightarrow {}^7F_6$
	544	$^5D_4 \longrightarrow {}^7F_5$
	563	
	596	$^5D_4 \longrightarrow {}^7F_4$
	618	$^5D_4 \longrightarrow {}^7F_3$
	651	$^5D_4 \longrightarrow {}^7F_2$

[a] λ_{ex} = 390 nm in MeOH. [b] λ_{ex} = 270 nm; quantum yield 0.015%. [c] λ_{ex} = 388.5 nm; quantum yield 1.26%. [d] λ_{ex} = 404 nm; quantum yield 0.35%.

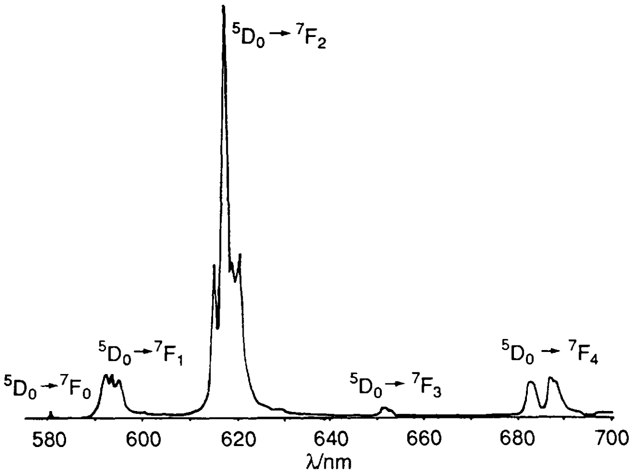


Fig. 4 Luminescence spectra of $[EuL_2(NO_3)_2]NO_3$ **3** in the solid state (λ_{ex} = 388.5 nm)

a $^5D_0 \longrightarrow {}^7F_{0-4}$ transition. Since the $^5D_0 \longrightarrow {}^7F_0$ transition cannot be split by any crystal field, the existence of a single peak at 581 nm (Fig. 4) indicates the presence of only one site for the Eu^{3+} ion, which is consistent with the crystal structure discussed. The electric dipole transitions $^5D_0 \longrightarrow {}^7F_2$ and $^5D_0 \longrightarrow {}^7F_4$ are more intense than is the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$, the integrated and corrected relative intensities of the $^5D_0 \longrightarrow {}^7F_{0,1,2,4}$ transitions being 0.1, 9.1, 100 and 12.3 respectively, reflecting the low site symmetry (C_1) of the Eu^{3+} ion.[25,26] The $^5D_0 \longrightarrow {}^7F_1$ transition contains three components which further supports this conclusion. The $^5D_0 \longrightarrow {}^7F_2$ region shows four instead of the expected five bands for a complex of low symmetry (C_1) which may be attributed to the unseen band being less intense and buried under other transitions or that two bands are too close together to be resolved by our instrument. It has been shown by X-ray diffraction that the co-ordination sphere about the Eu^{3+} could be viewed as a bicapped square antiprism, the symmetry of which is D_{4d} under ideal conditions. However, since all the ligating atoms of **3** are not identical and when the chelate rings and the sterically induced geometrical distortion are included, the symmetry about the metal ion would be reduced to C_1. The luminescence spectrum is consistent with the crystallographic results. The emissions of complexes **4** and **2** in the solid state, as expected, arise mainly from the transitions $^5D_4 \longrightarrow {}^7F_{6-2}$ and $^4G_{\frac{5}{2}} \longrightarrow {}^6H_{\frac{5}{2}-\frac{9}{2}}$ respectively.

Acknowledgements

This research was supported by grants from the National Natural Science Foundation of China and Fuzhou State Key Laboratory of Structural Chemistry. We also thank Dr. Jianqiu Shi (Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou) for the data collection and structure solution of the europium complex.

References

1 W. D. Horrocks, jun., and M. Albin, *Prog. Inorg. Chem.*, 1984, **31**, 1.
2 W. D. Horrocks, jun., and D. R. Sudnick, *Science*, 1978, **1**, 1194.
3 F. S. Richardson, *Chem. Rev.*, 1982, **82**, 541.
4 W. D. Horrocks, jun., and D. R. Sudnick, *Acc. Chem. Res.*, 1981, **14**, 384.
5 J.-C. G. Bunzli, *Inorg. Chim. Acta*, 1987, **139**, 219.
6 B. Alpha, R. Ballardini, V. Balzani, J.-M. Lehn, S. Perathoner and N. Sabbatini, *Photochem. Photobiol.*, 1990, **52**, 2996.
7 V. Balzani and R. Ballardini, *Photochem. Photobiol.*, 1990, **52**, 409.
8 (*a*) S. Wang, Q. Luo, X. Zhou and Z. Zeng, *Polyhedron*, 1993, **12**, 1939 and refs. therein; (*b*) Y. Zhou, S. Wang and J. Wang, XVI Congress and General Assembly, International Union of Crystallography, Beijing, 21–29 August, 1993, Collected abstract PS-070412.
9 J. A. W. Addison and P. J. Burke, *J. Heterocycl. Chem.*, 1981, **18**, 803.
10 J. N. Demas and G. A. Grosky, *J. Phys. Chem.*, 1971, **75**, 991.
11 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
12 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
13 SDP Structure Determination Package, Enraf-Nonius, Delft, 1985.
14 TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985.
15 A. M. Arif, J. D. Julius Backer-Dirks, C. J. Gray, F. A. Hart and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1987, 1665.
16 G. H. Frost, F. A. Hart, C. Heath and M. B. Hursthouse, *Chem. Commun.*, 1969, 1421.
17 C. Piguet, A. F. Williams, G. Bernardinelli, E. Moret and J.-C. G. Bunzli, *Helv. Chim. Acta*, 1992, **75**, 1697.

18 S. Wang, Y. Zhu, F. Zhang, Q. Wang and L. Wang, *Polyhedron*, 1992, **11**, 1909.

19 M. C. Favas, D. L. Kepert, J. M. Patrick and A. M. White, *J. Chem. Soc., Dalton Trans.*, 1983, 571.

20 M. C. Favas and D. L. Kepert, *Prog. Inorg. Chem.*, 1981, **28**, 309.

21 M. G. B. Drew, *Coord. Chem. Rev.*, 1977, **24**, 179.

22 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn., Wiley, New York, 1978.

23 C. Piguet, G. Bernardinelli and A. F. Williams, *Inorg. Chem.*, 1989, **28**, 2920; S. Ruttimann, C. Piguet, G. Bernardinelli, B. Bocquet and A. F. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 4230.

24 R. A. Abramovitch and J. B. Davis, *J. Chem. Soc. B*, 1966, 1137.

25 J.-C. G. Bunzli, B. Klein, D. Wessner and N. W. Alcock, *Inorg. Chim. Acta*, 1982, **59**, 269.

26 J.-C. G. Bunzli, B. Klein, G. Chapuis and K. J. Schenk, *Inorg. Chem.*, 1982, **21**, 808.

Received 8*th April* 1994; *Paper* 4/02113D