# Macrocyclic Complexes with Lanthanoid Salts Part 38.†
# Synthesis and Luminescence Study of Homo- and Hetero-binuclear Complexes of Lanthanides with a New Cyclic Compartmental Schiff Base‡

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Homo- and hetero-binuclear lanthanide(III) complexes with the macrocyclic ligand $H_2L^1$ derived from the condensation of 4-chloro-2,6-diformylphenol and the polyamine $NH_2(CH_2)_2O(CH_2)_2O-(CH_2)_2NH_2$ have been synthesized: $[Ln_2L^1(NO_3)_4]\cdot nH_2O$ (Ln = La, Pr, Sm, Eu, Gd, Tb, or Dy; $n$ = 1 or 2) and $[Ln_xLn'_{2-x}L^1(NO_3)_4]\cdot nH_2O$ (Ln,Ln' = La,Sm; La,Gd; La,Dy; La,Eu; Dy,Gd; Dy,Eu; Gd,Eu; Gd,Tb; Eu,Tb; or La,Tb; $n$ = 1 or 2). Their possible structure and the interaction between metal ions are discussed on the basis of spectroscopic, mass spectrometric, and magnetic data together with scanning electron microprobe analyses. Electron microscopy with X-ray fluorescence analysis as well as magnetic susceptibility measurements suggest that the complexes containing two different lanthanide ions may be truly heterobinuclear, with the two metal centres lying at a long distance from each other and not connected by any bridging heteroatoms. Laser-excited luminescence spectra and lifetimes also point to the presence of heterobinuclear species. The yield of the $Tb^{III}$ to $Eu^{III}$ energy transfer was quantified and the intermetallic distance evaluated.

Many mononuclear lanthanide complexes with simple or cyclic Schiff bases of the types (I)—(III) have been obtained (Scheme 1) and characterized by several techniques, including X-ray diffraction.[1–5] In particular the encapsulation of all the lanthanide ions (except radioactive promethium) by different macrocyclic cavities has been studied also by a combination of spectroscopic techniques. These Schiff-base complexes are easily prepared by metal template condensation of suitable diamine and dicarbonyl precursors. On the contrary, less attention has been devoted to binuclear lanthanide complexes in spite of much interest in their physico-chemical properties. It was observed that the presence in close proximity of two equal or different metal ions can considerably vary the properties of the systems which are not simply the sum of the properties of the individual components.[6,7]

Recently the synthesis of homobinuclear lanthanide complexes with the large binucleating macrocyclic ligand (IV), obtained by condensation of 2,6-diformyl-4-methylphenol and triethylenetetramine (3,6-diazaoctane-1,8-diamine) has been reported.[8,9] With the preparation of complexes of this type, appropriate study of the interactions between lanthanide ions is becoming feasible.

We have extended the binucleating systems by using the keto-precursor 4-chloro-2,6-diformylphenol and the polyamine 1,8-diamino-3,5-dioxaoctane for the formation of the macrocycle $H_2L^1$. Reaction between lanthanide nitrates and the ligand $H_2L^1$ leads to the formation of binuclear lanthanide complexes. The two-step formation reaction allows the synthesis of both homo- and hetero-binuclear compounds $[Ln_2L^1(NO_3)_4]\cdot nH_2O$ (Ln = La, Pr, Sm, Eu, Gd, Tb, or Dy; $n$ = 1 or 2) and $[Ln_xLn'_{2-x}L^1(NO_3)_4]\cdot nH_2O$ (LnLn' = LaSm, LaGd, LaDy, DyEu, DyGd, GdEu, GdTb, EuTb, or LaTb; $n$ = 1 or 2). The present paper reports the preparation and characterization of these lanthanide complexes, together with their physico-chemical properties. A luminescence investigation has also been performed to confirm the presence of heterobinuclear species and to quantify the $Tb^{III}$ to $Eu^{III}$ energy transfer in order to evaluate the intermetallic distance.

## Experimental

4-Chloro-2,6-diformylphenol was prepared by literature methods;[10–12] 1,8-diamino-3,5-dioxaoctane and the lanthanide salts were commercial products (Aldrich).

*Synthesis of the Ligand $H_2L^1$.*—A methanolic solution (10 cm³) of 1,8-diamino-3,5-dioxaoctane (2 mmol) was added to a solution of 4-chloro-2,6-diformylphenol (2 mmol) in methanol (30 cm³). The resulting yellow solution was stirred for 1 h; an oil separated which was dissolved in chloroform and dried overnight over sodium sulphate. The solvent was removed and the yellow oil was dissolved in the minimum volume of methanol and treated with diethyl ether or n-pentane. The solid obtained was filtered off, washed with methanol–chloroform (1 : 1), and dried *in vacuo*.

*Synthesis of the Homobinuclear Complexes* $[Ln_2L^1(NO_3)_4]\cdot nH_2O$ (Ln = La, Pr, Sm, Eu, Gd, Tb, or Dy; n = 1 or 2).—*Method (a).* A solution of 1,8-diamino-3,5-dioxaoctane (2 mmol) in methanol (10 cm³) was added dropwise to a pale yellow methanolic solution (25 cm³) of 4-chloro-2,6-diformylphenol (2 mmol). An orange oil appeared after a few minutes and was dissolved in chloroform (15 cm³), LiOH (2 mmol) and the appropriate $Ln(NO_3)_3\cdot xH_2O$ salt (2 mmol) were added. The resulting yellow suspension was refluxed for 30 min, partially evaporated, and filtered. The pale yellow precipitate obtained in high yield (80%) was washed with diethyl ether and dried *in vacuo*.
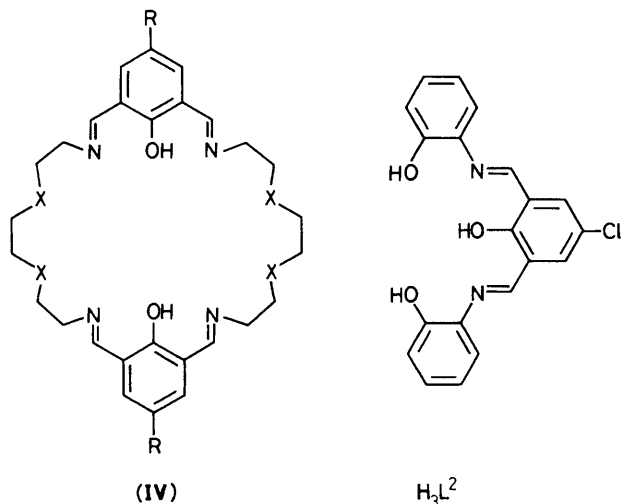
*Method (b).* A methanolic solution (30 cm³) of the appropriate $Ln(NO_3)_3\cdot xH_2O$ salt (2 mmol) and 4-chloro-2,6-diformylphenol (2 mmol) was refluxed for a few minutes; 1,8-diamino-3,5-dioxaoctane (2 mmol) in methanol (10 cm³) was

(I)

(II)

(III)
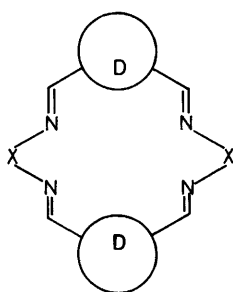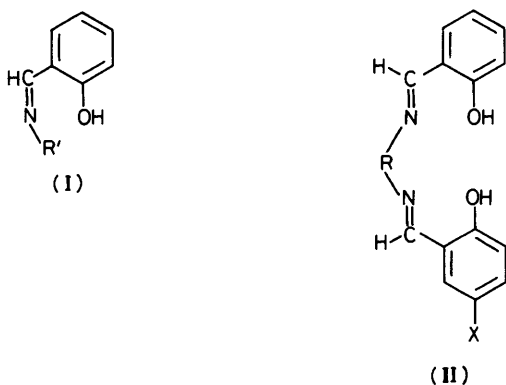
D = pyridine, furan, thiophene, or pyrrole;

X = 1, n -diamine

(IV)

$H_3L^2$

**Scheme 1.** $H_2L^1 = $ (IV; R = Cl, X = O)

added dropwise. A yellow precipitate formed within a few minutes and the suspension was refluxed for 4 h. The pale yellow precipitate obtained in low yield (15—20%) was filtered off, washed with diethyl ether, and dried in vacuo. The yield decreased in going from La to Dy.

*Synthesis of the Heterobinuclear Complexes* $[Ln_xLn'_{2-x}L^1-(NO_3)_4]\cdot nH_2O$ (Ln,Ln' = La,Sm; La,Gd; La,Dy; La,Eu; Dy,Gd; Dy,Eu; Gd,Eu; Gd,Tb; Eu,Tb; *or* La,Tb; n = 1 *or* 2).—A solution of 1,8-diamino-3,5-dioxaoctane (2 mmol) in methanol (10 cm³) was added dropwise to a pale yellow solution of 4-chloro-2,6-diformylphenol (2 mmol) in methanol (25 cm³). An orange oil formed within a few minutes and was dissolved by addition of chloroform (15 cm³). Then LiOH (2 mmol) and $Ln(NO_3)_3\cdot xH_2O$ (1 mmol) were successively added. After the

colour of the solution changed (*ca.* 10 min), $Ln'(NO_3)_3\cdot xH_2O$ (1 mmol) was added. The resulting suspension was refluxed for 30 min and the white-pale yellow precipitate obtained in high yield (80%) was filtered off, washed with methanol, and dried in vacuo. After drying, the colour of the precipitate turned yellow.

$[(LnLn')L^1(NO_3)_4]\cdot nH_2O$ (Ln = Tb *or* Gd, dopant = 1% Eu; Ln = Gd, dopant = 1% Tb). The syntheses were carried out in the same way as for the heterobinuclear complexes, the second addition being a methanolic solution of $Ln(NO_3)_3\cdot xH_2O$ (98%) and the dopant $Ln'(NO_3)_3\cdot xH_2O$ (2%).

All the complexes are slightly soluble in chloroform, dichloromethane, and methanol, and very soluble in warm dimethyl sulphoxide.

*Physico-chemical Measurements.*—Analytical data for $H_2L^1$ and for the prepared complexes are given in Table 1. The metal content of the reported complexes was determined by atomic absorption or emission spectroscopy, using a Varian AA-257 atomic absorption spectrophotometer. The Ln:Ln' ratio in the heterobinuclear lanthanide(III) complexes was established by a new procedure using a secondary mass spectrometry (s.i.m.s.) apparatus.[13] In the case of spot analyses, metal ratios were conveniently determined by the integral counting of back-scattered X-ray fluorescence radiation from a Philips SEM 505 model scanning electron microscope equipped with an EDAX model data station.[14] Samples for scanning electron microscopy (s.e.m.) analysis were prepared by suspending the micro-crystalline powders in diethyl ether. A few drops of the resulting suspension were deposited on a graphite plate and, after evaporation of the solvent, the samples were metallized successively with graphite and gold (this latter only when photographs were taken) in an Edwards S150B sputter coater.[14]

The i.r. spectra (SUP 56773) were measured as KBr pellets by use of a Perkin-Elmer 580B model spectrometer. Magnetic susceptibilities were determined by the Faraday method at room temperature, by use of an Oxford Instrument; the apparatus was calibrated with $HgCo(NCS)_4$.[15] Diamagnetic corrections were carried out using Pascal's constants.[16] The magnetic moments are reported in Table 2.

Mass spectrometric measurements (Table 3) were performed on a VG ZAB-ZF instrument operating in electron-impact (e.i.) (70 eV, 200 µA, ion-source temperature 200 °C) and fast atom bombardment (f.a.b.) modes (8-keV Xe atoms bombarding thioglycerol solutions of the samples).

The experimental procedures for luminescence experiments have been previously published.[17,18] The $[(LnLn')L^1(NO_3)_4]\cdot nH_2O$ samples used for these studies were the $Eu_2$, $Gd_2$, and $Tb_2$ homobinuclear complexes and the EuLa (50:50), TbLa (50:50), EuGd (1:99, 50:50), TbGd (1:99, 50:50), and EuTb (1:99, 50:50) heterobinuclear complexes.

**Results and Discussion**

Reaction of 4-chloro-2,6-diformylphenol with a stoicheiometric amount of 1,8-diamino-3,5-dioxaoctane yields ligand $H_2L^1$, which is obtained as a yellow powder. Its i.r. spectrum displays a band at 1 652 cm⁻¹ attributable to v(C=N); furthermore, the absence of a v(C=O) band at 1 670 cm⁻¹ evidences the condensation reaction. It is noteworthy that the i.r. spectrum of the open ligand obtained by condensation of 4-chloro-2,6-diformylphenol and 1,8-diamino-3,5-dioxaoctane in a 2:1 molar ratio displays a v(C=O) band at 1 670 cm⁻¹ and a v(C=N) vibration at 1 642 cm⁻¹. The f.a.b. mass spectrum shows the parent peak for $H_2L^1$ at the expected m/z value 592. The pattern of the parent peak confirms the presence of two chlorine atoms in the ligand. The spectrum is also consistent with the proposed cyclic structure of the ligand.

The homobinuclear and heterobinuclear complexes have

**Table 1.** Elemental analyses (%)

| Compound | | Found | | | | | | Calc. | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Ln | $n$ | C | H | N | Cl | Ln | Ln' | C | H | N | Cl | Ln | Ln' |
| $H_2L^1$ | | 56.40 | 5.85 | 9.30 | 12.25 | | | 56.65 | 5.80 | 9.45 | 12.00 | | |
| $[Ln_2L^1(NO_3)_4] \cdot nH_2O$ | | | | | | | | | | | | | |
| La | 1 | 30.15 | 3.15 | 9.45 | 6.35 | 25.20 | | 29.60 | 3.00 | 9.85 | 6.25 | 24.45 | |
| Pr | 2 | 28.70 | 3.00 | 9.50 | 6.10 | 24.85 | | 29.05 | 3.15 | 9.70 | 6.15 | 24.35 | |
| Sm | 1 | 29.05 | 2.85 | 9.40 | 6.30 | 26.20 | | 29.05 | 2.95 | 9.65 | 6.10 | 25.95 | |
| Eu | 1 | 29.15 | 2.85 | 9.55 | 6.05 | 26.75 | | 28.95 | 2.95 | 9.65 | 6.10 | 26.15 | |
| Gd | 2 | 28.15 | 2.95 | 9.75 | 5.90 | 26.20 | | 28.25 | 3.05 | 9.40 | 5.95 | 26.45 | |
| Tb | 2 | 28.40 | 3.15 | 8.95 | 6.05 | 26.35 | | 28.20 | 3.05 | 9.40 | 5.95 | 26.65 | |
| Dy | 1 | 28.65 | 2.85 | 8.95 | 6.20 | 27.00 | | 28.45 | 2.90 | 9.45 | 6.00 | 27.50 | |
| $[LnLn'L^1(NO_3)_4] \cdot nH_2O$ | | | | | | | | | | | | | |
| LaSm | 2 | 28.70 | 2.90 | 9.40 | 6.15 | 11.50 | 12.35 | 28.85 | 3.10 | 9.60 | 6.00 | 11.95 | 12.90 |
| LaGd | 2 | 28.95 | 2.90 | 9.25 | 6.00 | 11.70 | 13.20 | 28.70 | 3.10 | 9.55 | 6.05 | 11.85 | 13.40 |
| LaDy | 1 | 28.90 | 2.90 | 9.50 | 6.00 | 11.55 | 13.80 | 29.00 | 2.95 | 9.65 | 6.10 | 12.00 | 14.00 |
| LaEu | 2 | 29.00 | 3.35 | 9.45 | 5.95 | 12.05 | 12.80 | 28.85 | 3.10 | 9.60 | 6.10 | 11.90 | 13.05 |
| DyGd | 2 | 27.95 | 2.85 | 9.30 | 6.25 | 13.00 | 13.50 | 28.15 | 3.05 | 9.35 | 5.95 | 13.60 | 13.15 |
| DyEu | 1 | 28.60 | 2.85 | 9.35 | 5.90 | 12.90 | 12.70 | 28.70 | 2.90 | 9.55 | 6.05 | 13.05 | 12.95 |
| GdEu | 2 | 28.65 | 2.90 | 9.20 | 5.85 | 13.00* | 12.75* | 28.40 | 3.05 | 9.45 | 6.00 | 13.25 | 12.85 |
| GdTb | 1 | 28.55 | 2.80 | 9.40 | 6.20 | 13.20 | 13.85 | 28.65 | 2.90 | 9.55 | 6.05 | 13.40 | 13.55 |
| EuTb | 2 | 28.55 | 2.90 | 9.30 | 5.90 | 12.60* | 13.70* | 28.35 | 3.05 | 9.45 | 6.00 | 12.80 | 13.40 |
| LaTb | 2 | 28.85 | 2.85 | 9.45 | 6.30 | 11.45 | 13.80 | 28.65 | 3.10 | 9.55 | 6.05 | 11.85 | 13.55 |

* From atomic absorption data.

**Table 2.** Experimental and calculated * magnetic moments (295 K, B.M.) of the binuclear complexes $[LnLn'L^1(NO_3)_4] \cdot nH_2O$

| LnLn' | $n$ | $\mu_{exptl.}$ | $\mu_{exptl.}^{corr}$ | $\mu_{calc.}$ |
| --- | --- | --- | --- | --- |
| $La_2$ | 1 | Diam | Diam | Diam |
| $Pr_2$ | 2 | 4.59 | 4.65 | 4.9 |
| $Sm_2$ | 1 | 1.96 | 2.10 | 2.19 |
| $Eu_2$ | 1 | 4.58 | 4.65 | 4.9 |
| $Gd_2$ | 2 | 11.28 | 11.30 | 11.17 |
| $Tb_2$ | 2 | 13.19 | 13.20 | 13.43 |
| $Dy_2$ | 1 | 14.70 | 14.72 | 14.78 |
| LaSm | 2 | 1.01 | 1.34 | 1.55 |
| LaGd | 2 | 7.68 | 7.72 | 7.85 |
| LaDy | 1 | 9.61 | 9.65 | 10.45 |
| LaEu | 2 | 3.34 | 3.45 | 3.5 |
| DyGd | 2 | 12.67 | 12.70 | 13.2 |
| DyEu | 1 | 9.63 | 9.67 | 11.02 |
| GdEu | 2 | 7.65 | 7.70 | 8.64 |
| GdTb | 1 | 12.41 | 12.44 | 12.32 |
| EuTb | 2 | 9.92 | 9.96 | 10.12 |
| LaTb | 2 | 9.19 | 9.22 | 9.5 |

* Assuming no magnetic interaction.

**Table 3.** F.a.b. mass spectral data for $[Ln_2L^1(NO_3)_4] \cdot nH_2O$, where Ln = La or Tb

| Fragment | $m/z$ (La) | $m/z$ (Tb) |
| --- | --- | --- |
| $M^+ - NO_3$ | 1 054 | 1 094 |
| $M^+ - Ln(NO_3)_2 + 2H^+$ | 855 | 875 |
| $M^+ - Ln(NO_3)_3 + H^+$ | 792 | 812 |
| $M^+ - La(NO_3)_4$ | 729 | 749 |

been obtained by *in situ* procedure (see Experimental section), and can be formulated as $[Ln_2L^1(NO_3)_4] \cdot nH_2O$ (Ln = La, Pr, Sm, Eu, Gd, Tb, or Dy; $n$ = 1 or 2) and $[Ln_xLn'_{2-x}L^1-(NO_3)_4] \cdot nH_2O$ (Ln,Ln' = La,Sm; La,Gd; La,Dy; La,Eu; Dy,Gd; Dy,Eu; Gd,Eu; Gd,Tb; Eu,Tb or La,Tb; $n$ = 1 or 2; $x$ = 1.0 or 1.99). Again, the complete cyclization of the ligand

is strongly supported by the presence of a very strong i.r. absorption band centred at 1 650—1 652 cm$^{-1}$ and assigned to the $v(C=N)$ stretching mode. No peaks attributable to unreacted formyl or amine groups are detectable; strong peaks in the range 1 541—1 567 cm$^{-1}$ are characteristic of the phenolic $>C-O$ groups acquiring partial double-bond character through conjugation. Nitrate vibrational modes occur at *ca*. 715 ($v_5$), 740 ($v_3$), 815—817 ($v_6$), 1 036—1 045 ($v_2$), 1 293—1 295 ($v_4$), and 1 460—1 485 cm$^{-1}$ ($v_1$, masked by $CH_2$ vibrations) and are typical of bidentate nitrates. The observed separation of the $v_1$ and $v_4$ modes (*ca*. 165—190 cm$^{-1}$) is in agreement with this conclusion and is in line with data reported for other macrocyclic complexes.[19] The absence of vibration from ionic nitrate is ascertained by the Raman spectrum of the europium complex.

F.a.b. mass spectra of the lanthanum and terbium samples are reported in Table 3. The pseudomolecular ions are not observed, but the spectra strongly evidence the presence of binuclear species: peaks attributable to $M^+ - NO_3$, $M^+ - Ln(NO_3)_2 + 2H^+$, $M^+ - Ln(NO_3)_3 + H^+$, and $M^+ - Ln(NO_3)_4$, are detected. Moreover, the spectrum of the terbium complex exhibits the relative abundance patterns expected in the presence of both Cl and Tb.

Electron-probe microanalysis proved a useful technique further to characterize the complexes. Images of microcrystals were obtained with a scanning electron microscope and demonstrated the homogeneity of the samples, while integration of back-scattered $X$-rays yielded the Ln:Cl and Ln:Ln' ratios. Homobinuclear complexes appear as microcrystals, 5—10 μm thick, in which the Ln:Cl ratio is 1:1, within experimental errors. An image of the gadolinium complex is shown in Figure 1(*a*) and its $X$-ray fluorescence spectrum is displayed in Figure 1(*b*). The homogeneity of the sample is obvious and results in an equal occupancy of the two compartments of the ligand. Attempts to prepare mononuclear lanthanide complexes with such a ligand failed; Ln:Cl ratios different from 1:1 were found. Moreover, the samples were not homogeneous and appeared to be a mixture of mononuclear and binuclear complexes.
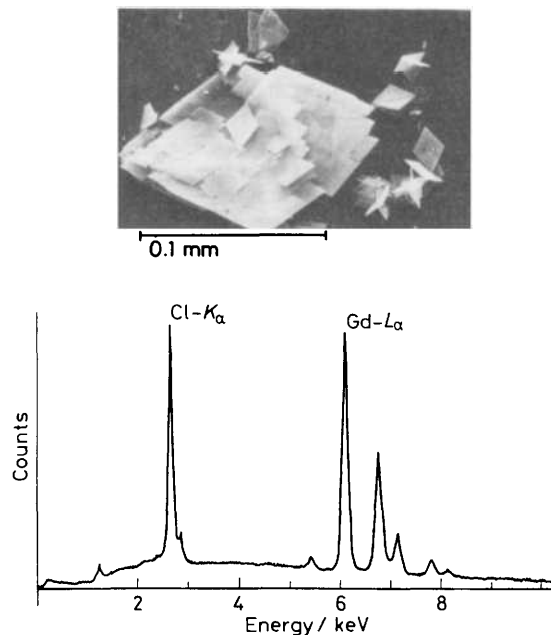
**Figure 1.** S.e.m. photograph (top) and $X$-ray fluorescence spectrum (bottom) of microcrystals of $[Gd_2L^1(NO_3)_4]\cdot2H_2O$
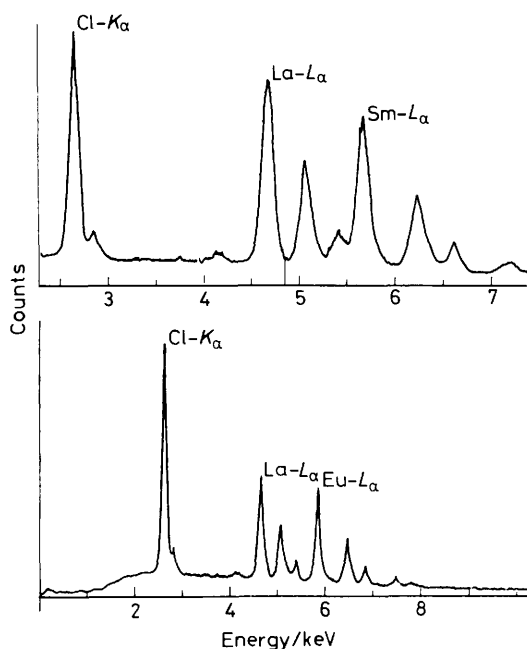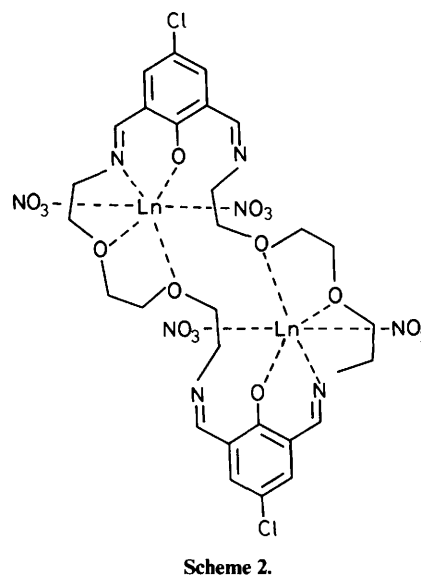


**Scheme 2.**



**Figure 2.** $X$-Ray fluorescence spectra of microcrystals of $[LaLn'L^1(NO_3)_4]\cdot2H_2O$, where $Ln' = Sm$ (top) or Eu (bottom).



**Figure 3.** S.e.m. photograph (top) and $X$-ray fluorescence spectrum (bottom) of microcrystals of $[La_{0.4}Sm_{1.6}L^1(NO_3)_4]\cdot2H_2O$

The heterobinuclear complexes are homogeneous microcrystals with an expected $Ln:Ln':Cl$ ratio of $1:1:2$. As an example, spectra of the LaSm and the LaEu microcrystalline powders are shown in Figure 2.

These data support the formation of heterobinuclear species (Scheme 2) but do not prove it unambiguously. The microcrystalline powders could also be thought of as formed by two different homobinuclear complexes packed in the crystal structure in such a way as to give the illusion that the microcrystals are comprised of heterobinuclear species. Indeed, the two compartments of the ligand are not selective enough totally to prevent metal exchange between the two co-
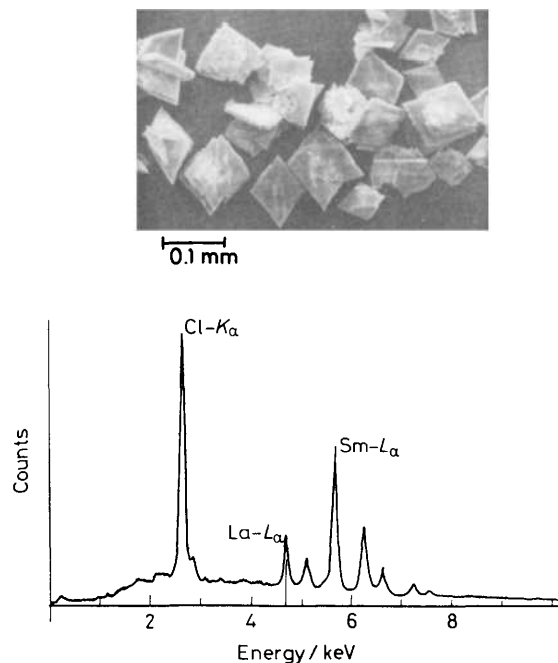
ordination sites; positional heterobinuclear complexes and scrambling can then occur. For instance, crystals of the LaSm complex grown from the mother-liquor have the right $Ln:Cl$ ratio, but the content of samarium is about four times that of lanthanum. Spot analyses over the whole specimen (Figure 3) show that the distribution of the two metal ions in the various crystals is homogeneous, suggesting a stoicheiometry of the type $[La_{0.4}Sm_{1.6}L^1(NO_3)_4]$. A similar behaviour was found for the crystals containing La and Dy, the dysprosium content being about a tenth of the lanthanum content. This points to a selectivity of the ligand compartments with respect to the ionic radius of the metal.

The magnetic moments of the heterobinuclear complexes (Table 2) show the absence of metal–metal interaction and point to the presence of two magnetically dilute lanthanide(III) ions.

An explanation of these experimental results is that the ligand does not behave as a compartmental molecule, but as a
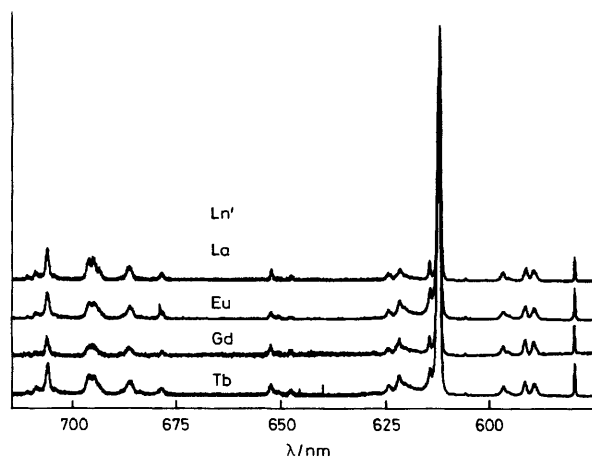
**Figure 4.** Luminescence spectra of $[EuLn'L^1(NO_3)_4]\cdot nH_2O$ at 77 K. Excitation on $^5L_6 \longleftarrow {}^7F_0$ transition (395 nm)
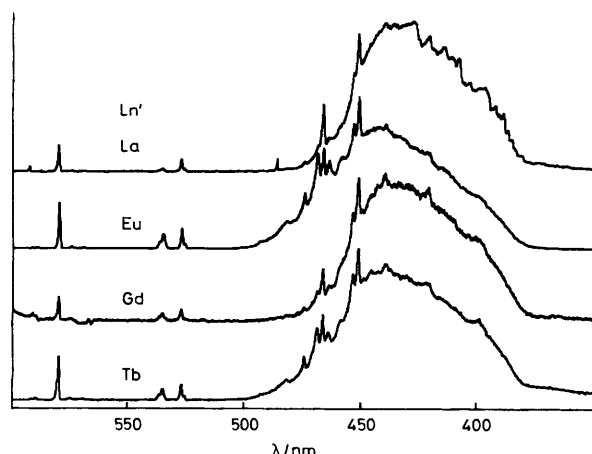


**Figure 5.** Excitation spectra of $[EuLn'L^1(NO_3)_4]\cdot nH_2O$ at 77 K. Analysis on $^5D_0 \longrightarrow {}^7F_2$ transition (611.8 nm)
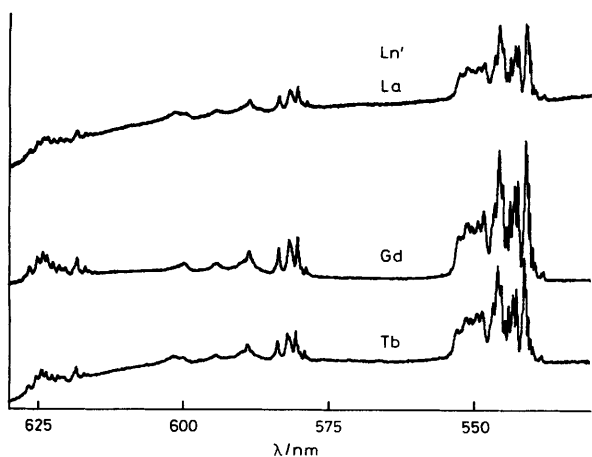


**Figure 6.** Luminescence spectra of $[TbLn'L^1(NO_3)_4]\cdot nH_2O$ at 77 K. Excitation on the $^5D_4 \longleftarrow {}^7F_6$ transition (488 nm)

macrocyclic binucleating ligand in which the two metal ions are co-ordinated at a long distance from each other, with no bridging heteroatom between them.

It is noteworthy that a magnetic interaction was observed for the complexes $LnL^2\cdot nH_2O$ ($n$ = 0 or 1), obtained by reaction of $H_3L^2$ (cf. Scheme 1) with the appropriate lanthanide(III) nitrate in the presence of a stoicheiometric amount of base $(LiOH)$.[20] The smaller magnetic moments of the prepared complexes may

be caused by the formation of a dimer or by oligomerization. Due to geometrical constraints, there is a difficulty for $H_3L^2$ to behave as a quinquedentate ligand towards one lanthanide ion. Moreover, there is a co-ordination unsaturation about the metal ion, even if one considers the solvation molecules and, consequently, an oligomerization of the complex is likely. The binucleating ability of $H_3L^2$ has been recently demonstrated for the complex $Mg[Th_2L^2{}_3]_2\cdot 6H_2O$, obtained by reaction of the preformed ligand or of the keto and amino precursors with thorium(IV) nitrate in the presence of $LiOH$ and magnesium acetate. Each complex anion is a binuclear unit in which two Th atoms are bridged by three oxygen atoms from the three different ligands.[18] Complexes of the type $Mg_3[Ln_2L^2{}_3]_2\cdot nH_2O$ or $Li_3[Ln_2L^2{}_3]\cdot nH_2O$ were also synthesized, in which the anion stoicheiometry is the same as in the thorium complex.

*Luminescence Study.*—We have addressed the luminescent properties of the europium(III) ion to probe the chemical environment of the two co-ordination sites in the binuclear complexes, and to evaluate the interionic distance. In order to assess the $Tb^{III} \longrightarrow Eu^{III}$ energy transfer, reference compounds needed to be measured. We have therefore studied two series of compounds, one containing $Eu^{III}$, either in the homobinuclear complex or in doped lanthanum and gadolinium compounds, and the other containing $Tb^{III}$.

*Europium luminescence (samples* $Eu_2$, $EuLa$, *and* $EuGd$). The non-selective excitation of the $^5L_6 \longleftarrow {}^7F_0$ transition at 395 nm results in very similar luminescence spectra for all three complexes (Figure 4). The compounds display a very intense europium(III) luminescence and the transitions originating from the $^5D_0$ level possess a maximum number of $(2J + 1)$ components (cf. SUP 56773 for the $Eu_2$ complex). This may be explained by the lanthanum(III) sites having a low local symmetry, which leads to a relatively intense $^5D_0 \longrightarrow {}^7F_0$ transition and to a very strong hypersensitive $^5D_0 \longrightarrow {}^7F_2$ transition. The excitation spectra obtained by setting the analysing wavelength on the intense $^5D_0 \longrightarrow {}^7F_2$ emission line at 612 nm are shown in Figure 5. They display transitions to levels higher than $^5D_0$, namely $^5D_1$ and $^5D_2$. In addition, they contain a broad band with a maximum around 435 nm resulting from a ligand absorption followed by a ligand to $Eu^{III}$ energy transfer.

In order to determine the number of chemically different metal-ion environments, we have examined the excitation spectra in the region of the $^5D_0 \longleftarrow {}^7F_0$ transition (SUP 56773). The latter transition is comprised of a single band at 17 253 cm$^{-1}$ with a shoulder on its high-energy side (17 256 cm$^{-1}$). There is no difference between the various samples, at least within experimental error ($\pm 1$ cm$^{-1}$). Varying the analysing wavelength, however, results in changes in the intensity of the shoulder. This points to the existence of at least two different chemical environments for the lanthanide ions. Selective excitations in the region of the $^5D_0 \longleftarrow {}^7F_0$ transition yield emission spectra having the same general shape, with small differences in the $^5D_0 \longrightarrow {}^7F_1$ spectral range (SUP 56773). The four Eu-containing complexes seem therefore to be isostructural. The relative intensities of the $^5D_0 \longrightarrow {}^7F_J$ transitions reported in Table 4 confirm this conclusion as well as the energies of the identified $^7F_J$ sublevels, which are listed in SUP 56773. All these data also point to very similar metal-ion environments; the two closely spaced components of the $^5D_0 \longleftarrow {}^7F_0$ transition and the small differences observed in the emission data may be accounted for by the presence of molecules with somewhat different chemical environments around the metal-ion sites.

*Terbium luminescence (samples* $Tb_2$, $TbLa$, *and* $TbGd$). The emission spectra of the Tb-containing samples, obtained by excitation of the $^5D_4 \longleftarrow {}^7F_6$ transition at 488 nm, are reported in Figure 6. The three spectra do not show significant differences

**Table 4.** Corrected and integrated intensities ($\pm 10\%$) of the $^5D_0 \longrightarrow {}^7F_J$ transitions in the luminescence spectra at 77 K of $[EuLn'L^1(NO_3)_4]\cdot nH_2O$ complexes. The $^5D_0 \longrightarrow {}^7F_1$ transition is taken as reference

| Ln' | $^5D_0 \longrightarrow {}^7F_0$ | $^5D_0 \longrightarrow {}^7F_1$ | $^5D_0 \longrightarrow {}^7F_2$ | $^5D_0 \longrightarrow {}^7F_3$ | $^5D_0 \longrightarrow {}^7F_4$ |
|---|---|---|---|---|---|
| La | 0.26 | 1.0 | 6.7 | 0.32 | 3.5 |
| Eu | 0.27 | 1.0 | 6.3 | 0.30 | 3.4 |
| Gd | 0.31 | 1.0 | 6.2 | 0.33 | 3.6 |
| Tb | 0.27 | 1.0 | 6.5 | 0.34 | 3.7 |
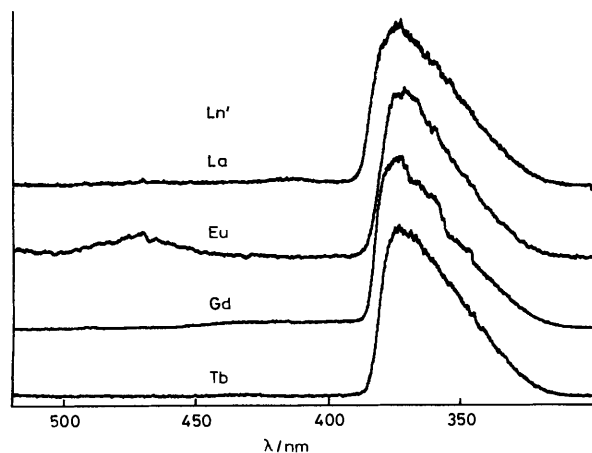


**Figure 7.** Excitation spectra of $[TbLn'L^1(NO_3)_4]\cdot nH_2O$ at 77 K. Analysis on the $^5D_4 \longrightarrow {}^7F_5$ transition (545.8 nm)



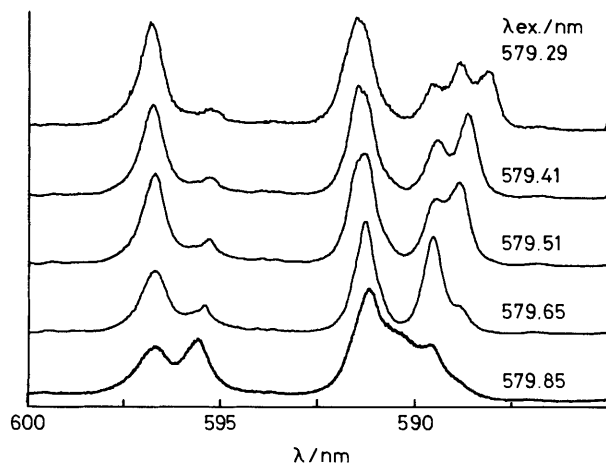**Figure 8.** $^5D_0 \longrightarrow {}^7F_1$ Emission spectra of $[EuTbL^1(NO_3)_4]\cdot 2H_2O$ at 77 K. Selective excitations on the $^5D_0 \longleftarrow {}^7F_0$ transition

and point to the $^5D_4 \longrightarrow {}^7F_5$ band as the most convenient transition for studying the luminescent properties of $Tb^{III}$ in these complexes. In the excitation spectra (Figure 7) measured with the analysing wavelength set on the maximum of the $^5D_4 \longrightarrow {}^7F_5$ transition (545.8 nm) a broad band centred at 370 nm reveals the presence of an energy-transfer process between the ligand and the $Tb^{III}$. All the Eu-containing compounds also undergo a similar process (see above), but the excitation band ascribed to it occurs at lower energy. In the case of the Tb-containing compounds, the excitation spectra do not contain bands attributable to direct excitation of the $Tb^{III}$. The luminescence spectra from the $^5D_4(Tb)$ level (SUP 56773) is obtained under excitation at 370 nm, which corresponds to the maximum of the ligand excitation band. At 77 K the relative intensities of the $^5D_4 \longrightarrow {}^7F_J$ transitions of the TbGd complex are 1.0, 4.1, 0.70, 0.40, 0.14, 0.023, and 0.020 for $J = 6$ (reference), 5, 4, 3, 2, 1, and 0, respectively.

**Table 5.** Lifetimes ($\tau$, ms) of the $^5D_0(Eu)$ and $^5D_4(Tb)$ levels of the binuclear complexes $[LnLn'L^1(NO_3)_4]\cdot nH_2O$ at 77 K. The europium-(III) excitation was achieved through the $^5D_0 \longleftarrow {}^7F_0$ transition at 579.6 nm and that of $Tb^{III}$ through the $^5D_4 \longleftarrow {}^7F_6$ at 487.4 nm

| LnLn' | % Ln | $\tau[^5D_0(Eu)]$ |
|---|---|---|
| EuLa | 50 | 0.94 $\pm$ 0.02 |
| Eu$_2$ | 100 | 0.99 $\pm$ 0.02 |
| EuGd | 50 | 0.98 $\pm$ 0.02 |
| | 1 | 1.00 $\pm$ 0.02 |
| EuTb | 50 | 0.98 $\pm$ 0.02 |
| | 1 | 0.98 $\pm$ 0.02 |
| | | $\tau[^5D_4(Tb)]$ |
| TbLa | 50 | 1.69 $\pm$ 0.03 |
| TbEu | 50 | 1.46 $\pm$ 0.06 |
| TbGd | 50 | 1.73 $\pm$ 0.02 |
| | 1 | 1.74 $\pm$ 0.04 |
| Tb$_2$ | 100 | 1.72 $\pm$ 0.02 |

*Luminescence from mixed terbium–europium samples* (50:50 *and* 1:99). The TbEu samples display the same europium(III) ion luminescence spectra as those measured previously with the homo- and hetero-binuclear Eu-containing compounds (SUP 56773). In particular, high-resolution spectra of the $^5D_0 \longrightarrow {}^7F_1$ transition, obtained by scanning the excitation wavelength through the $^5D_0 \longleftarrow {}^7F_0$ band (Figure 8), reveal the presence of several metal-ion environments having slightly different crystal-field splittings. Since the same phenomenon is observed with the Eu$_2$ homobinuclear complex, we may rule out the influence of the second lanthanoid(III) ion as the major cause of these asymmetries. Rather, we think that the complex molecules probably crystallize with somewhat different conformations in the unit cells, generating slightly different chemical environments for the metal ions, as was observed for other macrocyclic compounds.[17,18]

The study of the terbium(III) photophysical properties in these compounds is not straightfoward: direct excitation of $Tb^{III}$ at 488 nm ($^5D_4 \longleftarrow {}^7F_6$ transition) and indirect excitation *via* the ligand band at 370 nm both lead to luminescence spectra containing emission bands of both $Eu^{III}$ and $Tb^{III}$, suggesting an important energy transfer to $Eu^{III}$ (SUP 56773). The question arises whether this transfer occurs through the ligand or through the $Tb^{III}$. To elucidate this, we have recorded the emission spectra of the homobinuclear europium complex under excitation at 308, 370, 468, and 488 nm. All the luminescence spectra contain emission bands from the $^5D_0(Eu)$ level exclusively. No transition from an europium level higher than $^5D_0$ is observed. We conclude that energy migration from the ligand to the $^5D_0(Eu)$ level is the dominant phenomenon. Nevertheless, a $Tb^{III}$ to $Eu^{III}$ energy transfer is not precluded, but cannot be seen from these experiments. In order to find out whether such a process exists or not, we have measured the luminescence lifetimes of the complexes.

*Luminescence lifetimes at* 77 K. All the luminescence decay curves observed for both the $^5D_0(Eu)$ and $^5D_4(Tb)$ levels are monoexponential, in agreement with the presence of two metal sites with very similar chemical environments. The mean

**Table 6.** Band positions (nm) in the reflectance spectra of the homobinuclear complexes $[Ln_2L^1(NO_3)_4]\cdot nH_2O$ and of the free ligand $H_2L^1$

| | Band | | | |
|---|---|---|---|---|
| Sample | I | II | III | IV |
| $H_2L^1$ | 255 | 300 | 370 | 455 |
| $Gd_2L^1$ | 250 | 290 | 365 | 425 |
| $Eu_2L^1$ * | 245 | 290 | 360 | 425 |
| $Tb_2L^1$ | 250 | 290 | 365 | 425 |

* A weak additional band at 530 nm may be assigned to $^5D_1 \longleftarrow {}^7F_0$ transition of Eu.
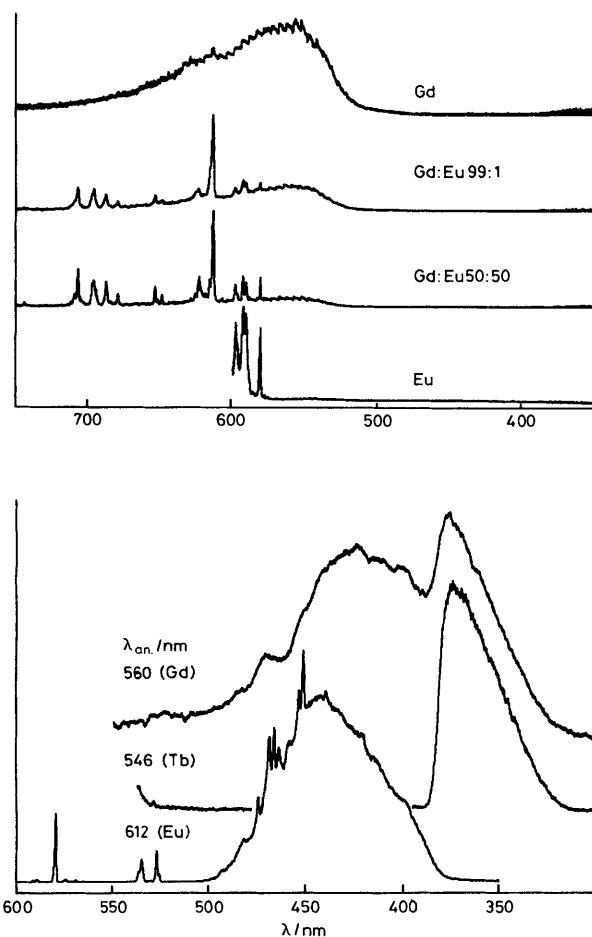


**Figure 9.** Luminescence (top, excitation at 308 nm) and excitation (bottom) spectra at 77 K of $[Ln_2L^1(NO_3)_4]\cdot 2H_2O$

lifetime observed for the $^5D_0$(Eu) level is 980 ± 20 μs (Table 5). No significant differences appear between the $^5D_0$(Eu) lifetimes recorded for the various compounds, pointing again to isostructural species. Moreover, there is no concentration quenching since the lifetimes for the 1 and 50% europium-doped compounds are identical. The $^5D_0$(Eu) lifetime is considerably higher than the value reported for binuclear complexes with similar Schiff bases (200—300 μs).[21] A possible explanation for this difference is the change in the position of the ligand absorption bands, which may influence the quenching processes. Another reason would be the presence of water molecules bonded to the Eu[III]. Indeed, Kahwa *et al.*[22] have isolated complexes containing hydration molecules and water is

known to be a very efficient quencher of the europium(III) luminescence. Thermal analysis of the prepared samples shows that water molecules are released in one step in the temperature range 70—90 °C; in some cases they may even be removed at room temperature after 24 h under a nitrogen flux, indicating their presence as crystallization molecules not directly bonded to the central metal ion.

The Tb($^5D_4$) lifetimes for the Eu-free compounds are also constant with a mean value of 1.72 ± 0.02 ms, and the same comments may be formulated as for the $^5D_0$(Eu) data. The lifetime in the mixed TbEu complex is, however, significantly smaller, which proves the presence of an energy-transfer process between the Tb[III] and the Eu[III]. Its yield η and the Ln–Ln' distance $R_{12}$ may be calculated from the known formula[23] (i)

$$\eta = 1 - (\tau/\tau_0) = 1/[1 + (R_{12}/R_0)^6]\qquad(i)$$

where τ is the lifetime in the presence of the acceptor, here Eu[III], and $\tau_0$ the lifetime in the absence of the acceptor. The quantity $R_0$ is defined as the distance giving rise to a 50% transfer of energy. For TbEu systems its value lies usually between 6 and 8 Å.[23,24] For the investigated binuclear Schiff-base complex, η amounts to 15 ± 5% and the estimated $R_{12}$ distance is therefore 8.0 ± 0.5, 9.3 ± 0.7, and 10.7 ± 0.7 Å for $R_0$ = 6, 7, and 8 Å, respectively. Both the absence of concentration quenching and this calculated distance are good evidence for the presence of true heterobinuclear complexes. A Ln–Ln' distance of 7—8 Å may indeed be measured from space-filling molecular models based on the formula proposed in Scheme 2.

*Photophysical study of the ligand.* A more thorough interpretation of the energy-migration processes occurring in the binuclear complexes necessitates additional data on the nature of the energy levels of the ligand and on how they are influenced by the complexation. We have recorded the reflectance spectra of $H_2L^1$ and of the binuclear complexes. Data for the ligand and for the $Eu_2$, $Gd_2$, and $Tb_2$ homobinuclear complexes are reported in SUP 56773 and in Table 6. In the spectra of the complexed ligand the two bands at longer wavelengths correspond to the maxima observed in the excitation spectra of the homobinuclear complexes at *ca.* 370 nm for Tb[III] and 430—440 nm for Eu[III]. Moreover, the reflectance bands undergo a blue shift upon complexation, which demonstrates that the energy of the ligand absorption bands (especially band IV) is affected by the co-ordination at the phenolate ion.[21]

Additional information was gained by recording the excitation and emission spectra of both the protonated ligand $H_2L^1$ and the homobinuclear $Gd_2$ complex. Upon co-ordination the ligand bands in the excitation spectrum undergo a blue shift with respect to those of the free ligand (SUP 56773), in agreement with the reflectance data (see above). The emission spectrum of the ligand, which displays three broad bands with maxima at 380, 420, and 530 nm, is also much affected by complexation: the spectrum of the co-ordinated ligand exhibits only two bands, at 580 and 620 nm (SUP 56773). Excitation of the homobinuclear $Gd_2$ complex at wavelengths corresponding to the absorption maxima of the ligand (308, 350, 370, 400, and 435 nm) provides luminescence spectra displaying one broad band with a maximum in the range 560—580 nm and two shoulders at 600—620 and 500 nm. The relative intensity of the latter increases when the excitation wavelength increases from 350 to 430 nm. When Eu[III] is introduced into the gadolinium complex, the europium luminescence ($\lambda_{ex.}$ = 308 nm) appears and increases with increasing europium content, while the ligand emission is quenched [Figure 9(a)]. This evidences the resonant energy transfer occurring between the 560—580 nm emitting level of the ligand and the $^5D_0$ level of Eu[III].

The excitation spectrum of the complexed ligand in the

**Table 7.** Lifetimes (ms) of the $^5D_0$(Eu), $^5D_4$(Tb), and ligand levels at 77 K. The excitation was achieved through the ligand level at 308 nm

| Sample | $\tau_{obs.}$ | Analysing wavelength(s)/nm |
|---|---|---|
| $Eu_2L^1$ | $0.99 \pm 0.02$ ms | 611.8, 706.0 |
| $Tb_2L^1$ | $1.73 \pm 0.02$ ms | 541.4, 581.8 |
| $Gd_2L^{1*}$ | $2.0 \pm 0.2$ ms | 520, 550, 580, 600, 620, 650 |
| $La_2L^{1*}$ | $5.4 \pm 0.6$ μs | 580 |
| $H_2L^{1*}$ | $123 \pm 10$ μs | 420, 510 |

* Calculated using the end part of the curves (see text); the main parts of the curves yield lifetimes smaller than 0.4 μs.
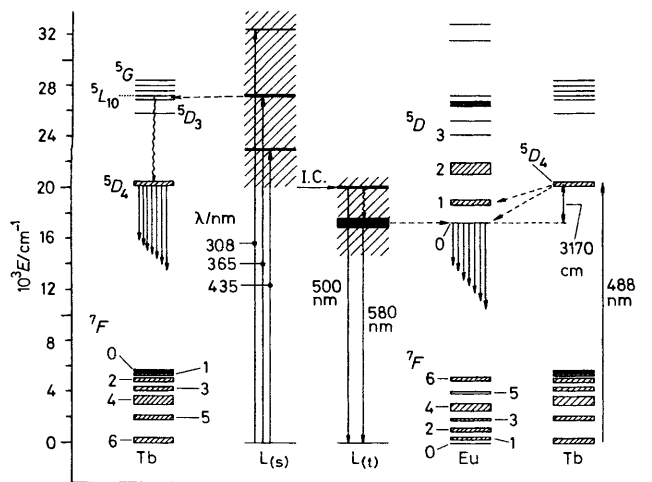


**Figure 10.** Schematic energy-level diagram of $[Ln_2L^1(NO_3)_4] \cdot nH_2O$ complexes showing energy migration paths; $L_{(s)}$ and $L_{(t)}$ stand for ligand singlet and triplet states, respectively

homobinuclear $Gd_2$ sample was recorded with the analysing wavelength set at 560 nm [Figure 9(b)]. It contains three large bands at 370, 420—430, and 470 nm corresponding to those observed in the reflectance spectra. Moreover, two different-energy transfer processes from the ligand to the lanthanide ions can now be identified: the first one is a direct resonant transfer from the ligand level involved in the 360—370 nm absorption band to the $^5L_{10}$, $^5G_6$, or $^5D_3$ levels of Tb$^{III}$. The second is more complex, involving the absorbing and the emitting levels of the ligand before excitation of the $^5D_0$(Eu) level.

Finally, the emission decay curves have been measured under ligand excitation at 308 nm (Table 7). The lanthanoid lifetimes of the $Eu_2$- and $Tb_2$-homobinuclear complexes are identical to those listed in Table 5 and obtained through selective excitation of the lanthanoid levels. In the case of the $La_2$ and $Gd_2$-homobinuclear complexes and of the free ligand, the ligand emisson decay curves are not monoexponential, pointing to a complex mechanism of internal energy migration. Taking the end parts of the curves into account only allowed us to calculate the lifetimes which are typical of a phosphorescence process and which are the same for any analysis wavelength used. This proves that an intersystem crossing is taking place between the singlet and the triplet states of the ligand. Moreover the substantially longer lifetime of the gadolinium complex, with respect to that of the free ligand, points to a many-step migration of energy involving the gadolinium levels. A similar phenomenon was observed for a complex of Gd with another Schiff base:[21] the phosphorescence lifetime reported is 200 μs, while the fluorescence lifetimes of the two singlet levels of the ligand (<3 and 4 ns) are ca. two times shorter than the values obtained for yttrium or lanthanum complexes (5—6 and 8 ns, respectively).

## Conclusions

The present study allows us to draw the following conclusions. First, the $^5D_0 \longleftarrow\ ^7F_0$ excitation spectra and the $^5D_0 \longrightarrow\ ^7F_J$ emission spectra, recorded under several selective excitation wavelengths, of the $Eu_2$ homobinuclear complex show the presence of metal-ion sites with low local symmetry and very similar chemical environments. The shoulder observed on the $^5D_0 \longleftarrow\ ^7F_0$ transition and its large width at half height (10—11 cm$^{-1}$), as well as the small changes in the position and intensity of some $^5D_0 \longrightarrow\ ^7F_J$ emission bands upon variation of the excitation wavelength, reflect the existence of slightly different metal-ion environments, possibily due to the fluxionality of the ligand. The substitution of Eu$^{III}$ by either La$^{III}$, Gd$^{III}$, or Tb$^{III}$ results in minute differences in the emission spectra. The same is true when monitoring the luminescence of Tb-containing complexes, which is consistent with an isostructural series of complexes. X-Ray powder diffraction studies on homo- and hetero-binuclear homogeneous complexes containing different metal ratios indeed show that the compounds are always isostructural, independently of the Ln:Ln′ ratio.[21] Moreover, a comparison of the emission spectra recorded for the Eu-containing complexes with those published for compounds of comparable structure[22] or for the monomeric complex with an analogous Schiff base[18] reveals that all these spectra are very similar, pointing to almost identical environments for the metal ion. Finally, the lifetimes of both Eu$^{III}$ and Tb$^{III}$ in heterobinuclear complexes with different hydration numbers being identical, we conclude that the water molecules are not bound in the inner co-ordination sphere.

Secondly, we have experimental facts indicating that the mixed LnLn′ complexes are true heterobinuclear moieties and not mixtures of two homobinuclear compounds. Indeed, the reported lifetime data unambiguously demonstrate the presence of a Tb $\longrightarrow$ Eu energy transfer and the distance calculated from the yield of this transfer ($9 \pm 1.5$ Å) is consistent with the interionic distance measured on molecular models (7—8 Å). Since there is no significant difference between the lifetimes recorded for samples of La and Gd containing 1 and 50% Eu or Tb, these lifetimes are not affected by any radiative energy transfer and the distance calculated above may be regarded as reliable. This conclusion is in line with the magnetic susceptibility data which reflect the absence of magnetic interaction between the two lanthanoid ions. It is further supported by e.s.r. measurements carried out at 4.2 K on powdered samples of the LnGd complexes (Ln = La, Dy, Eu, or Gd): the spectra are all similar, except for some variations in the linewidth. The similarity of the spectrum of the Gd$_2$ complex with those of the heterobinuclear complexes points to a very small interaction between the lanthanoid ions.

Thirdly, our experimental data point to an efficient ligand $\longrightarrow$ lanthanoid(III) energy-transfer process. It is noteworthy that the ligand states involved are not the same for Eu and Tb. In the latter case, the ligand level at ca. 27 000 cm$^{-1}$ transfers energy in a more or less resonant way to one of the $^5D_3$, $^5G_6$, or $^5L_{10}$ levels of Tb. In the case of the europium compounds, the more efficient transfer occurs between the ligand state at ca. 17 000—18 000 cm$^{-1}$ and the $^5D_0$ state of Eu. A schematic representation of these energy-transfer processes is given in Figure 10.

## References

1 P. A. Vigato and D. E. Fenton, *Inorg. Chim. Acta*, 1987, **139**, 39.
2 D. E. Fenton and P. A. Vigato, *Chem. Soc. Rev.*, 1988, **17**, 69.
3 S. Mangani, A. Takeuchi, S. Yamada, and P. Orioli, *Inorg. Chim. Acta*, 1988, **155**, 149.
4 A. M. Arif, J. D. J. Backer-Dirks, C. J. Gray, F. A. Hart, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1987, 1665.
5 W. Radecka-Paryzek, *Inorg. Chim. Acta*, 1985, **109**, L21.
6 O. Kahn, *Struct. Bonding, (Berlin)*, 1987, **68**, 89.
7 R. D. Willet, D. Gatteschi, and O. Kahn, in 'Magneto-structural Correlations in Exchange Coupled Systems,' D. Riedel, Dordrecht, 1985.
8 I. A. Kahwa, F. R. Fronczek, and J. Selbin, *Inorg. Chim. Acta*, 1987, **126**, 227 and refs. therein.
9 I. A. Kahwa, J. Selbin, C-Y. Hsieh, and R. A. Laine, *Inorg. Chim. Acta*, 1986, **118**, 179.
10 A. Zinke, F. Hanus, and E. Ziegler, *J. Prakt. Chem.*, 1939, **152**, 126.
11 S. Taniguchi, *Bull. Chem. Soc. Jpn.*, 1983, **57**, 2683.
12 H. Firouzabadi and Z. Mostafavipoor, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 914.
13 S. Daolio, E. Bullita, B. Facchin, P. Guerriero, C. Pagura, and P. A. Vigato, Proceedings of the Symposium on the Basic and Applied Aspects of Rare Earths, Venice 26—27th May, 1988, p. 165.
14 U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato, and R. Graziani, *Inorg. Chim. Acta*, 1986, **119**, 215.
15 C. J. O'Connor, E. Sinn, E. J. Cukauskas, and B. S. Deaver, jun., *Inorg. Chim. Acta*, 1979, **32**, 29.
16 C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **29**, 208.
17 J-C. G. Bünzli and G-O. Pradervand, *J. Chem. Phys.*, 1986, **85**, 2489; J-C. G. Bünzli, D. Plancherel, and G-O. Pradervand, *J. Phys. Chem.*, 1989, **93**, 980.
18 J-C. G. Bünzli, E. Moret, U. Casellato, P. Guerriero, and P. A. Vigato, *Inorg. Chim. Acta*, 1988, **150**, 133.
19 J-C. G. Bünzli, in 'Handbook on the Physics and Chemistry of Rare Earths,' eds. K. A. Gschneidner, jun., and L. Eyring, Elsevier, Amsterdam, 1987, vol. 9, ch. 60.
20 U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato, and R. Graziani, *Inorg. Chim. Acta*, 1987, **134**, 165.
21 P. Guerriero, S. Sitran, P. A. Vigato, and R. Zannetti, unpublished work.
22 I. A. Kahwa, J. Selbin, C. J. O'Connor, J. W. Foise, and G. L. McPherson, *Inorg. Chim. Acta*, 1988, **148**, 265.
23 C. L. A. Wang, in 'New Frontiers in Rare Earth Science and Applications,' eds. Xu Guangxian and Xiao Jimei, Science Press, Beijing, 1985, vol. 1, p. 146.
24 R. C. Holz, A. P. Snyder, and W. DeW Horrocks, jun., *Lanth. Actin. Res.*, 1988, **2**, 363.