

Structure-Based Description of a Step-by-Step Synthesis of Homo- and Heterodinuclear (4f, 4f') Lanthanide Complexes

Jean-Pierre Costes,* Françoise Dahan, and Franck Nicodème

Laboratoire de Chimie de Coordination du CNRS, UPR 8241, liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique de Toulouse, 205 route de Narbonne, 31077 Toulouse Cedex 4, France

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The stepwise course of the synthesis of homo- (4f, 4f) and heterodilanthanide (4f, 4f') complexes has been investigated through structural determination of the intermediate and final products occurring in the process. In the first step, the tripodal ligand H₃L is reacted with Ln(NO₃)₃·5H₂O to give a complex (H₃L)Ln(NO₃)₃ in which the ligand does exist in a zwitterionic form. This unexpected feature has been definitely supported by a structural determination performed on a closely related complex (HL')₃Ln(NO₃)₃ (**1**). These species are fairly stable and may be isolated. In basic medium, (H₃L)Ln(NO₃)₃ is deprotonated to yield a neutral LLn complex crystallized as LLnNaClO₄ (**2**), the lanthanide ion being linked to the inner N₄O₃ coordination site of the ligand. Finally, addition of Ln'(NO₃)₃·5H₂O (Ln' being similar or different from Ln) to the LLn complex yields the desired homo- or heterodinuclear LLnLn'(NO₃)₃ complex **3**, where the Ln' ion is coordinated to the outer O₃O₃ coordination site of the tripodal ligand. Complex **1** (Ln = La) crystallizes in the triclinic space group $P\bar{1}$ (No. 2): $a = 11.1883(7)$ Å, $b = 11.8993(9)$ Å, $c = 16.4197(10)$ Å, $\alpha = 81.900(6)^\circ$, $\beta = 79.406(5)^\circ$, $\gamma = 79.470(6)^\circ$, $V = 2099.5(2)$ Å³, $Z = 2$. Complex **2** (Ln = Eu) crystallizes in the monoclinic space group $P2_1/n$ (No. 14): $a = 13.6333(13)$ Å, $b = 15.3799(12)$ Å, $c = 17.1473(13)$ Å, $\beta = 111.283(10)^\circ$, $V = 3350.2(5)$ Å³, $Z = 4$. Complex **3** (Ln = Ln' = Dy) crystallizes in the trigonal space group $R\bar{3}$ (No. 148) with $a = b = 23.847(3)$ Å, $c = 42.982(2)$ Å, $V = 21168(4)$ Å³, $Z = 18$. Complex **3** possesses a Dy(O_{phenoxo})₃Dy core, and a nitrate anion has been replaced by a η^2 -chelated *o*-vanillin anion. We did not succeed in obtaining crystals of any of the heterodinuclear LLnLn'(NO₃)₃ entities, but their existence was unambiguously confirmed by positive fast atom bombardment mass spectrometry experiments.

Introduction

Several studies aimed at evaluating the nature and magnitude of the magnetic interaction between a paramagnetic lanthanide ion (Ln) and a second spin carrier (M) have been performed.^{1–8} However, they are doubly restricted since, very generally, the 4f ion is Gd^{III} and the second center is

either an organic radical or a Cu^{II} ion. Very few bimetallic (M, Gd) complexes in which M is different from Cu^{II} have been reported, they include VO^{II},⁹ Ni^{II},¹⁰ Co^{II},¹¹ Cr^{III},¹² Fe^{II},¹³ Fe^{III},¹⁴ and Zn^{II}.¹⁵ Until recently, there are only a few reports on structural determinations of bimetallic complexes assembling two different Ln ions. Indeed, to synthesize genuine heterodinuclear Ln–Ln' complexes, ligands with two different coordination sites are needed. Use of symmetrical

* Author to whom correspondence should be addressed. Phone: 33 (0)5 61 33 31 52. Fax: 33 (0)5 61 55 30 03. E-mail: costes@lcc-toulouse.fr.

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cryptates¹⁶ or macrocycles¹⁷ yielded homodinuclear complexes, although mononuclear complexes¹⁸ liable to lead to heterodinuclear entities in a second step have been isolated. Schiff base and amino phenol ligands with one coordination site have also furnished homodinuclear complexes by phenoxo¹⁹ or keto bridges.²⁰ The structural determination of a discrete (Gd^{III}, Ce^{III}) triple-decker-sandwich complex has previously been published.²¹ Triple-stranded helicates also yielded homodinuclear Ln–Ln complexes,²² but more recently, a discrete (La^{III}, Eu^{III}) complex resulting from the self-assembly of triple-stranded helicates has appeared.²³ In this last example, the two Ln centers are far from each other and not directly linked by a material bridge. A cationic species containing two Ln ions directly linked by three phenoxo bridges belonging to a tripodal Schiff-base ligand is known.²⁴ Synthesis of 3d–4f complexes with compartmental Schiff-base ligands was facilitated by the specific

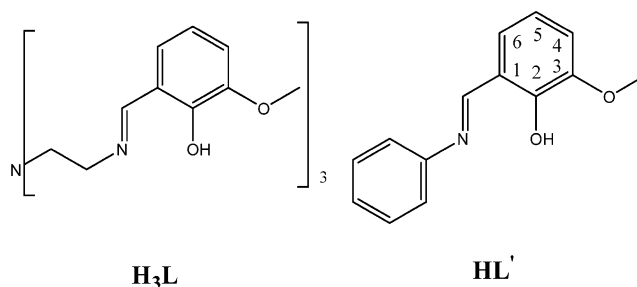


Figure 1. Ligands used in the present work with the NMR numbering scheme.

affinity of 3d centers for the smaller and inner coordination site. In the present case, introduction of two 4f ions in a tripodal compartmental Schiff-base ligand makes the affinity parameters much less efficient. This offers the opportunity of using a stepwise experimental procedure in order to isolate genuine heterodinuclear complexes and to avoid synthesis of a mixture of homo- and heterodinuclear complexes. The structural determination of a (Yb, La) complex²⁴ derived from the H₃L ligand (Figure 1) and the magnetic properties of a (Fe^{III}, Gd) complex²⁵ and of five (Gd, Ln) complexes²⁶ have been previously published. The present contribution describes the different steps of the new synthetic process with the structural determination of a typical complex isolated at each step.

Experimental Section

Materials and Methods. All starting materials were purchased from Aldrich and used without further purification. H₃L and HL' ligands were obtained as previously described.²⁷

Caution. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and handled with care.

(HL')₃La(NO₃)₃. A mixture of *o*-vanillin (1.52 g, 1.0 × 10^{−2} mol) and anilin (0.93 g, 1.0 × 10^{−2} mol) in methanol (60 mL) was stirred for 10 min. Then La(NO₃)₃·5H₂O (1.40 g, 0.33 × 10^{−2} mol) was added as a solid, quickly yielding a red precipitate, which was stirred for 1 h at room temperature, filtered off, and washed with a minimum amount of cold methanol and then with diethyl ether. Yield: 2.9 g (87%). Anal. Calcd for C₄₂H₃₉LaN₆O₁₅: C, 50.1; H, 3.9; N, 8.4. Found: C, 49.7; H, 3.7; N, 8.2. IR (KBr, cm^{−1}): 3436 br, 1634 s, 1593 s, 1508 s, 1441 s, 1384 m, 1367 m, 1302 s, 1230 s, 1170 s, 1016 m, 748 m, 732 m. ¹H NMR ((CD₃NO₂): δ 4.04 (s, 3 H, CH₃), 6.94 (t, *J* = 8 Hz, 1 H, CH-5), 7.26 (dd, *J* = 8 and 1.2 Hz, 1 H, CH-4), 7.32 (dd, *J* = 8 and 1.2 Hz, 1 H, CH-6), 7.50 (t, *J* = 7.5 Hz, 1 H, phenyl), 7.63 (t, *J* = 7.5 Hz, 2 H, phenyl), 7.72 (d, *J* = 7.5 Hz, 2 H, phenyl), 9.17 (d, 1 H, HC=N), 14.18 (br, 1 H, C=NH⁺).

H₃LLa(NO₃)₃(H₂O)₂. Addition of La(NO₃)₃·5H₂O (0.42 g, 1.0 × 10^{−3} mol) to H₃L (0.55 g, 1.0 × 10^{−3} mol) in methanol (20 mL) gave a yellow precipitate that was filtered off 30 min later and washed with methanol and diethyl ether. Yield: 0.7 g (73%). Anal. Calcd for C₃₀H₄₀LaN₇O₁₇: C, 39.6; H, 4.4; N, 10.8. Found: C, 39.5; H, 4.3; N, 10.7. IR (KBr, cm^{−1}): 3434 br, 1652 s, 1496 s, 1453 s, 1384 s, 1345 m, 1219 s, 1170 m, 1076 m, 853 m, 751 m, 731 m.

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^1H NMR ((CD_3NO_2)): δ 2.61 (m, 2 H, CH_2), 3.45 (t, br, 2 H, CH_2), 3.64 (s, 3 H, CH_3), 3.95 (s, 4 H, H_2O), 6.31 (t, $J = 8$ Hz, 1 H, CH-5), 6.70 (d, $J = 8$ Hz, 1 H, CH-4), 6.80 (d, $J = 8$ Hz, 1 H, CH-6), 8.13 (d, 1 H, $\text{HC}=\text{N}$), 12.74 (br, 1 H, $\text{C}=\text{NH}^+$).

$\text{H}_3\text{LDy}(\text{NO}_3)_3(\text{H}_2\text{O})_2$. Addition of $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.44 g, 1.0×10^{-3} mol) to H_3L (0.55 g, 1.0×10^{-3} mol) in methanol (20 mL) gave a yellow precipitate that was filtered off 30 min later and washed with methanol and diethyl ether. Yield: 0.85 g (84%). Anal. Calcd for $\text{C}_{30}\text{H}_{40}\text{DyN}_7\text{O}_{17}$: C, 38.6; H, 4.3; N, 10.5. Found: C, 38.5; H, 4.3; N, 10.5. IR (KBr, cm^{-1}): 3412 br, 1653 s, 1495 s, 1456 s, 1384 s, 1295 m, 1221 s, 1170 m, 1077 m, 853 m, 746 m, 737 m.

$\text{LEu}(\text{H}_2\text{O})$. Addition of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.86 g, 2.0×10^{-3} mol) to H_3L (1.1 g, 2.0×10^{-3} mol) in methanol (20 mL) gave a yellow precipitate that was filtered off 30 min later. This precipitate corresponds to the $\text{H}_3\text{LEu}(\text{NO}_3)_3$ entity. The precipitate was suspended in methanol; addition of triethylamine (0.8 g, 8.0×10^{-3} mol) yielded a new pale-yellow precipitate that was filtered off and washed with methanol and then with diethyl ether. Yield: 0.5 g (35%). Anal. Calcd for $\text{C}_{30}\text{H}_{35}\text{EuN}_4\text{O}_7$: C, 50.4; H, 4.9; N, 7.8. Found: C, 50.0; H, 4.7; N, 7.7. IR (KBr, cm^{-1}): 3434 br, 1627 s, 1468 s, 1443 s, 1405 m, 1332 m, 1325 m, 1241 s, 1219 s, 1083 m, 858 m, 749 m, 740 m.

The other mononuclear complexes were prepared with the experimental process described for $\text{LEu}(\text{H}_2\text{O})$ with use of the desired lanthanide ions.

$\text{LDy}(\text{H}_2\text{O})$. Yield: 70%. Anal. Calcd for $\text{C}_{30}\text{H}_{35}\text{DyN}_4\text{O}_7$: C, 49.6; H, 4.9; N, 7.7. Found: C, 49.4; H, 4.7; N, 7.5. IR (KBr, cm^{-1}): 3426 br, 1627 s, 1469 s, 1445 s, 1406 m, 1333 m, 1242 s, 1220 s, 1083 m, 859 m, 749 m, 740 m.

$\text{LTb}(\text{H}_2\text{O})$. Yield: 38%. Anal. Calcd for $\text{C}_{30}\text{H}_{35}\text{N}_4\text{O}_7\text{Tb}$: C, 49.9; H, 4.9; N, 7.8. Found: C, 49.5; H, 4.7; N, 7.5. IR (KBr, cm^{-1}): 3435 br, 1627 s, 1469 s, 1444 s, 1406 m, 1326 m, 1242 s, 1219 s, 1083 m, 858 m, 749 m, 740 m.

$\text{LY}(\text{H}_2\text{O})$. Yield: 80%. Anal. Calcd for $\text{C}_{30}\text{H}_{35}\text{N}_4\text{O}_7\text{Y}$: C, 55.2; H, 5.4; N, 8.6. Found: C, 54.8; H, 5.2; N, 8.5. IR (KBr, cm^{-1}): 3420 br, 1627 s, 1470 s, 1447 s, 1407 m, 1334 m, 1242 s, 1220 s, 1083 m, 859 m, 749 m, 741 m. ^{13}C MAS SSNMR: δ 168.0 ($\text{HC}=\text{N}$), 159.0 ($\text{C}-\text{O}$), 153.0 ($\text{C}-\text{OMe}$), 127.7 (CH), 123.0 ($\text{C}-1$), 113.9 (CH), 113.7 (CH), 62.9 ($\text{CH}_2\text{N}=\text{}$), 60.2 (CH_2N), 56.3 (CH_3).

$[\text{LEu}(\text{H}_2\text{O})\text{NaClO}_4]$. Addition of NaClO_4 (0.04 g, 3.2×10^{-4} mol) to a stirred suspension of $\text{LEu}(\text{H}_2\text{O})$ (0.10 g, 1.4×10^{-4} mol) in acetone first induced dissolution of the neutral complex and then appearance of a new precipitate which was filtered off 2 h later. Slow evaporation of a dimethyl sulfoxide solution of this complex gave crystals suitable for X-ray study. Yield: 0.06 g (52%). Anal. Calcd for $\text{C}_{30}\text{H}_{35}\text{ClEuN}_4\text{NaO}_{11}$: C, 43.0; H, 4.2; N, 6.7. Found: C, 42.7; H, 4.0; N, 6.5. IR (KBr, cm^{-1}): 3576 m, 3420 br, 1620 s, 1468 s, 1456 s, 1411 m, 1319 m, 1240 m, 1227 s, 1211 m, 1114 s, 1082 s, 855 m, 742 m, 625 m. ^1H NMR ($(\text{CD}_3)_2\text{SO}$): δ -15.17 (s, 1 H, $\text{HC}=\text{N}$), -7.98 (s, 2 H, $\text{CH}_2\text{N}=\text{}$), -1.10 (s, 2 H, CH_2N), 2.52 (s, 3 H, CH_3), 4.08 (d, $J = 8$ Hz, 1 H, CH-6), 7.12 (t, $J = 8$ Hz, 1 H, CH-5), 7.61 (d, $J = 8$ Hz, 1 H, CH-4).

$[\text{LY}(\text{H}_2\text{O})\text{NaClO}_4]$. The experimental procedure used for $[\text{LEu}(\text{H}_2\text{O})\text{NaClO}_4]$ gave the corresponding yttrium derivative. Yield: 60%. Anal. Calcd for $\text{C}_{30}\text{H}_{35}\text{ClYNa}_4\text{O}_{11}$: C, 46.5; H, 4.6; N, 7.2. Found: C, 46.2; H, 4.5; N, 6.9. IR (KBr, cm^{-1}): 3571 m, 3436 br, 1621 s, 1469 s, 1457 s, 1412 m, 1322 m, 1241 m, 1229 s, 1212 m, 1115 s, 1082 s, 858 m, 743 m, 627 m. ^1H NMR ($(\text{CD}_3)_2\text{SO}$): δ 3.10 (s, 2 H, CH_2N), 3.49 (s, 2H, H_2O), 3.83 (s, 3 H, CH_3), 3.87 (br, 2 H, $\text{CH}_2\text{N}=\text{}$), 6.47 (t, $J = 7.8$ Hz, 1 H, CH-5), 6.89 (d, $J = 7.8$ Hz, 1 H, CH-4), 6.95 (d, $J = 7.8$ Hz, 1 H, CH-6),

8.34 (s, 1 H, $\text{HC}=\text{N}$). ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$): δ 168.3 ($\text{HC}=\text{N}$), 157.1 ($\text{C}-\text{O}$), 150.4 ($\text{C}-\text{OMe}$), 126.2 (CH), 120.2 ($\text{C}-1$), 113.0 (CH), 111.9 (CH), 60.9 ($\text{CH}_2\text{N}=\text{}$), 59.2 (CH_2N), 55.9 (CH_3).

$\text{LTbEu}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$. Addition of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.071 g, 1.7×10^{-4} mol) to a stirred suspension of $\text{LTb}(\text{H}_2\text{O})$ (0.103 g, 1.5×10^{-4} mol) in methanol (10 mL) gave a light-yellow precipitate that was filtered off 2 h later and washed with methanol and diethyl ether. Yield: 0.123 g (78%). Anal. Calcd for $\text{C}_{30}\text{H}_{37}\text{EuN}_7\text{O}_{17}\text{Tb}$: C, 33.4; H, 3.5; N, 9.1. Found: C, 33.4; H, 3.2; N, 8.8. IR (KBr, cm^{-1}): 3412 br, 1625 s, 1467 s, 1384 s, 1301 s, 1229 s, 1075 m, 853 m, 737 m.

$[\text{LDy}_2(\text{H}_2\text{O})_2(\text{o-van})](\text{NO}_3)_2(\text{H}_2\text{O})_2$. Addition of *o*-vanillin (0.09 g, 6.0×10^{-4} mol), triethylamine (0.06 g, 6.0×10^{-4} mol), and $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ to a suspension of $\text{LDy}(\text{H}_2\text{O})$ (0.15 g, 2.0×10^{-4} mol) in methanol gave a solution that was stirred for 20 min and filtered off. Evaporation of the filtrate gave a few crystals suitable for a X-ray study. Yield: 0.03 g (12%). Anal. Calcd for $\text{C}_{38}\text{H}_{48}\text{Dy}_2\text{N}_6\text{O}_{19}$: C, 37.5; H, 4.0; N, 6.9. Found: C, 37.3; H, 3.8; N, 6.7. IR (KBr, cm^{-1}): 3401 br, 1627 s, 1470 s, 1448 s, 1407 m, 1384 s, 1334 m, 1241 s, 1220 s, 1082 m, 859 m, 741 m.

Crystallographic Data Collection and Structure Determination for $[(\text{HL}')_3\text{La}(\text{NO}_3)_3]$ (1), $[\text{LEu}(\text{H}_2\text{O})\text{NaClO}_4]$ (2), and $[\text{LDy}_2(\text{H}_2\text{O})_2(\text{ovan})](\text{NO}_3)_2(\text{H}_2\text{O})_2$ (3). Crystals suitable for X-ray analyses were obtained by slow evaporation of the corresponding solutions (methanol for **1**, DMSO for **2**, methanol/ethanol for **3**). The selected crystal of **1** (red parallelepiped, $0.40 \times 0.35 \times 0.25$ mm³) was mounted on an Oxford-Diffraction Xcalibur diffractometer using a graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and equipped with an Oxford Instruments Cryojet cooler device. Data were collected²⁸ at 160 K with four runs ($\phi = 0, 90, 180, 270^\circ$) and ω scans up to $\theta = 30.0^\circ$ (164 frames with a maximum time of 40 s). The selected crystal of **2** (yellow plate, $0.25 \times 0.20 \times 0.10$ mm³) was mounted on a Stoe imaging plate diffractometer system (IPDS) using a graphite monochromator ($\lambda = 0.71073$ Å) and equipped with an Oxford Cryosystems cooler device. Data were collected²⁹ at 180 K with a φ oscillation movement ($\varphi = 0.0-250.6^\circ$, $\Delta\varphi = 1.4^\circ$) and the crystal-to-detector distance being equal to 70 mm (max 2θ value 52.3°). The selected crystal of **3** (yellow parallelepiped, $0.30 \times 0.25 \times 0.15$ mm³) was mounted on an Enraf-Nonius CAD4 diffractometer using a graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Data were collected at 293 K up to 27° in the $\omega-2\theta$ scan mode and reduced with the MolEN package.³⁰ Reflections (18 730) were collected for **1**, of which 11228 were independent ($R_{\text{int}} = 0.0363$). Gaussian absorption corrections³¹ were applied ($T_{\text{min-max}} = 0.4826-0.6862$). Reflections (32 575) were collected for **2**, of which 6538 were independent ($R_{\text{int}} = 0.0397$). Numerical absorption corrections³² were applied ($T_{\text{min-max}} = 0.494-0.7528$). Reflections (7287) were collected for **3**, of which 7212 were independent ($R_{\text{int}} = 0.0195$). Absorption corrections³³ from ψ scans were applied ($T_{\text{min-max}} = 0.7003-0.9991$).

The structures were solved using SHELXS-97³⁴ and refined on F^2 by full-matrix least-squares using SHELXL-97³⁵ with anisotropic

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Table 1. Crystallographic Data for [(HL')₃La(NO₃)₃] (**1**), L(H₂O)EuNa(ClO₄) (**2**), and [LDy(H₂O)₂Dy(ovan)](NO₃)₂(H₂O)₂ (**3**)

	1	2	3
chem. formula	C ₄₂ H ₃₉ LaN ₆ O ₁₅	C ₃₀ H ₃₅ ClEuN ₄ NaO ₁₁	C ₃₈ H ₄₈ Dy ₂ N ₆ O ₁₉
fw	1006.70	838.02	1217.82
space group	P $\bar{1}$ (No. 2)	P ₂ /m (No. 14)	R $\bar{3}$ (No. 148)
a, Å	11.1883(7)	13.6333(13)	23.847(3)
b, Å	11.8993(9)	15.3799(12)	23.847(3)
c, Å	16.4197(10)	17.1473(16)	42.982(3)
α , deg	81.900(6)		
β , deg	79.406(5)	111.283(10)	
γ , deg	79.470(6)		
V, Å ³	2099.5(2)	3350.2(5)	21168(4)
Z	2	4	18
ρ_{calcd} , g cm ⁻³	1.592	1.661	1.720
λ , Å	0.71073	0.71073	0.71073
T, K	160(2)	180(2)	293(2)
μ (Mo K α) cm ⁻¹	11.08	20.29	32.31
R ^a (obs, all)	0.0289, 0.0330	0.0358, 0.0419	0.0248, 0.0421
R _w ^b (obs, all)	0.0517, 0.0529	0.0858, 0.0876	0.0320, 0.0492

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum [w(|F_o|^2 - |F_c|^2)^2] / \sum w|F_o|^2]^{1/2}.$$

displacement parameters for all non-hydrogen atoms. H atoms were introduced in calculations using the riding model except those bonded to the water oxygen atoms in **2** and **3** that were allowed to vary. Isotropic U_H were 1.1 times higher than those of the atom to which they are bonded. The perchlorate anion in **2** was found disordered and, after refinement of occupancy factors, was refined in two positions in the 50/50 ratio. The atomic scattering factors and anomalous dispersion terms were taken from the standard compilation.³⁶ The maximum and minimum peaks on the final difference Fourier map were 1.050 and -0.583 e Å^{-3} for **1**, 1.114 and -1.107 e Å^{-3} for **2**, and 0.461 and -0.436 e Å^{-3} for **3**. Drawings of the molecules were performed with the program ZORTEP.³⁷ Crystal data collection and refinement parameters are given in Table 1, and selected bond distances and angles are gathered in Table 2.

Physical Measurements. Elemental analyses were carried out at the Laboratoire de Chimie de Coordination Microanalytical Laboratory in Toulouse, France, for C, H, and N. IR spectra were recorded on a GX system 2000 Perkin-Elmer spectrophotometer; samples were run as KBr pellets. One-dimensional ¹H NMR spectra were acquired at 250.13 MHz on a Bruker WM250 spectrometer using (CD₃)₂SO or CD₃NO₂ as solvents. One-dimensional ¹³C spectra using ¹H broadband decoupling {¹H}¹³C and gated ¹H decoupling with selective proton irradiation during acquisition were performed with the Bruker WM250 apparatus working at 62.89 MHz. Chemical shifts are given in ppm vs TMS (¹H and ¹³C) with the numbering scheme specified in Figure 1. The solid-state spectra were obtained on a Varian InfinityPlus spectrometer with a 9.4 T magnet using a Chemagnetics 4-mm triple-resonance cross polarization/magic angle spinning probe in double-resonance mode. The two-pulse, phase-modulated (TPPM) decoupling field was 125 kHz with 12° phase toggle every 4.1 μ s. Magic-angle spinning was at 15 kHz at 25 °C. Cross polarization was applied for 10 ms with a linearly increasing ramp on the ¹³C spin lock and with the rf field spanning a 25% range centered on 96 kHz. The repetition time was 5 s, the acquisition time was 50 ms, and 10 164 transients were

Table 2. Selected Bond Lengths (Å) and Distances (Å) for Complexes **1**, **2**, and **3**

(HL') ₃ La(NO ₃) ₃			
La—O(1)	2.499(1)	La—O(7)	2.670(1)
La—O(2)	3.076(1)	La—O(8)	2.682(1)
La—O(3)	2.479(1)	La—O(10)	2.722(1)
La—O(4)	3.020(1)	La—O(11)	2.613(1)
La—O(5)	2.460(1)	La—O(13)	2.658(1)
La—O(6)	2.879(1)	La—O(14)	2.663(1)
LEuNa(ClO ₄)			
Eu—O(1)	2.272(3)	Na—O(1)	2.443(3)
Eu—O(3)	2.286(2)	Na—O(2)	2.453(3)
Eu—O(5)	2.359(2)	Na—O(3)	2.343(3)
Eu—O(7)	2.452(3)	Na—O(4)	2.500(3)
Eu—N(1)	2.593(3)	Na—O(5)	2.690(3)
Eu—N(2)	2.536(3)	Na—O(6)	2.546(4)
Eu—N(3)	2.506(3)	Na—O(8)	2.525(7)
Eu—N(4)	2.674(3)	Na—O(9)	2.652(7)
Eu...Na	3.504(2)		
[LDyDy(ovan)](NO ₃) ₂			
Dy(1)—O(1)	2.391(2)	Dy(2)—O(1)	2.318(2)
Dy(1)—O(2)	2.541(3)	Dy(2)—O(3)	2.358(2)
Dy(1)—O(3)	2.363(2)	Dy(2)—O(5)	2.336(2)
Dy(1)—O(4)	2.533(3)	Dy(2)—O(11)	2.323(3)
Dy(1)—O(5)	2.335(3)	Dy(2)—N(1)	2.439(3)
Dy(1)—O(6)	2.523(3)	Dy(2)—N(2)	2.467(3)
Dy(1)—O(7)	2.208(3)	Dy(2)—N(3)	2.495(3)
Dy(1)—O(8)	2.378(3)	Dy(2)—N(4)	2.660(3)
Dy(1)—O(9)	2.459(3)	Dy(1)...Dy(2)	3.5214(2)

averaged. No apodization was applied, and the data were zero filled from 2500 points to 32K prior to Fourier transformation. Mass spectroscopy spectra fast atom bombardment (FAB⁺) were recorded in DMF as a solvent and 3-nitrobenzyl alcohol matrix with a Nermag R10-10 spectrometer.

Results and Discussion

Syntheses. Starting with the tripodal ligand H₃L, the synthetic pathway comprises three steps that yield samples with respective formulas corresponding to the mononuclear H₃LLn^{III}(NO₃)₃ precursor, the related neutral and mononuclear LLn^{III} complex, and eventually to the desired homo- or heterodinuclear LLnLn'(NO₃)₃ complex. The first step corresponds to coordination of Ln to the ligand with a proton migration (or transfer) from the phenol function to the imine function, giving the ligand a zwitterionic phenoxo-iminium form. Deprotonation occurs in the second step, involving a

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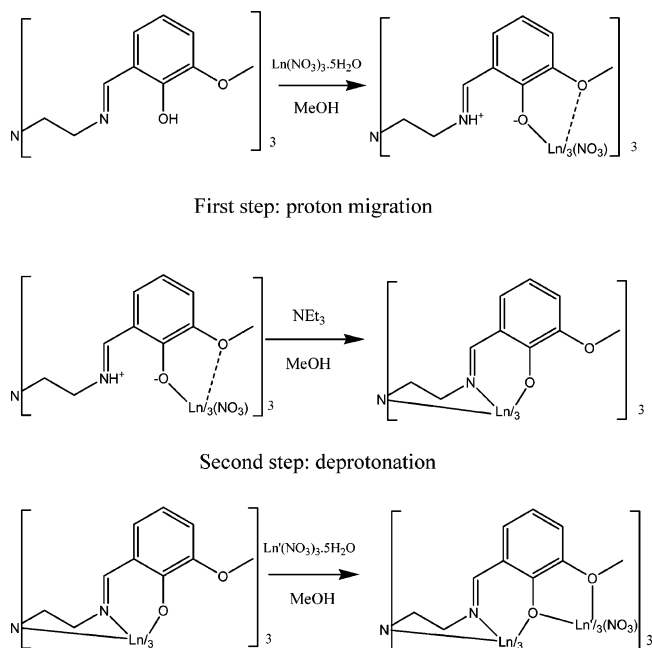


Figure 2. Summary of the stepwise experimental process.

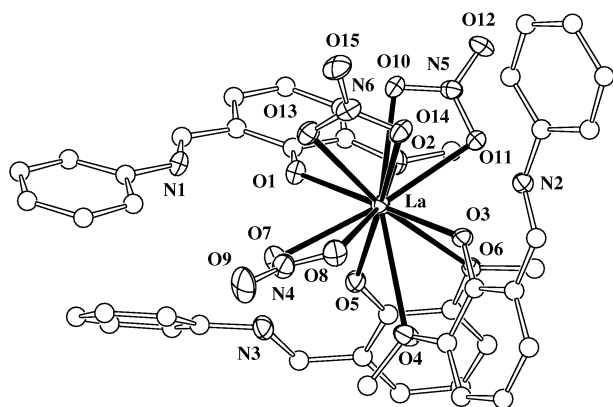


Figure 3. ZORTEP view of complex **1** with ellipsoids drawn at the 50% probability level, carbon atoms represented at an arbitrary scale for clarity.

change of coordination site while the third step corresponds to the addition of a second Ln ion. The advantage of the process described in this paper resides in avoiding the use of an inorganic base that facilitates isolation of the neutral LLn complex in a pure state, without any trace of an inorganic salt coordinated in the outer site, as previously described.³⁸ The experimental procedure is reported in Figure 2.

Description of the Structures. Complex **1** is derived from the ligand resulting from the reaction of *o*-vanillin and aniline and crystallizes in the triclinic $P\bar{1}$ space group. The unit cell contains two neutral $(HL')_3La(NO_3)_3$ species without any additional solvent molecules. The asymmetric unit appears in Figure 3. Relevant structural parameters are gathered in Table 2. La^{III} is 12-coordinate with six oxygen atoms from the phenoxo groups and the methoxy sidearms of the three L' ligands and six oxygen atoms from three bidentate nitrate anions (η^2 chelated). The shorter La–O bonds involve the

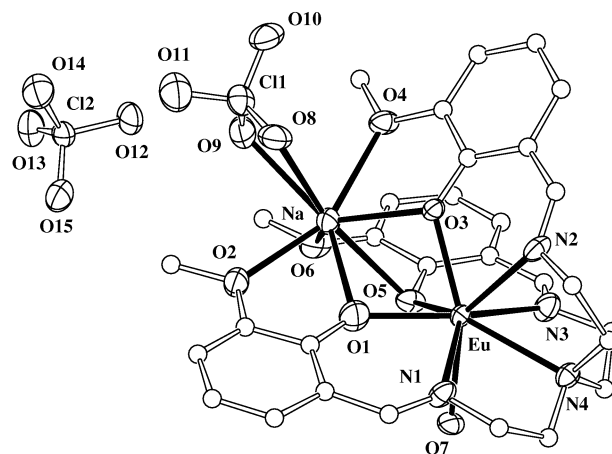


Figure 4. ZORTEP view of complex **2** with ellipsoids drawn at the 50% probability level, carbon atoms represented at an arbitrary scale for clarity.

deprotonated phenol oxygen atoms (from 2.4597(13) to 2.4991(12) Å). The La–O (methoxy) links are longer (from 2.8790(12) to 3.0762(13) Å) while the La–O bonds involving the η^2 chelating nitrate ions vary from 2.6129(12) to 2.6824(14) Å. These bond lengths correspond to those previously observed, except for the La–O (methoxy) ones, which are longer.²⁴ Hydrogen atoms located on the three nitrogen atoms are involved in intramolecular hydrogen bonds with the deprotonated phenol oxygen atoms, thus indicating that a proton migration is involved in the lanthanum complexation.

The structure of $[LEu(H_2O)NaClO_4] \mathbf{2}$ is shown in Figure 4. The structure results from insertion of a europium ion into the inner N_4O_3 coordination site of the tripodal ligand. The europium ion is eight-coordinate to the four nitrogen atoms and to the three μ -phenolate oxygen atoms of the ligand. The last bond involves a water molecule. As previously observed,³⁹ the Eu–N (tertiary amine) bond length involving the bridgehead nitrogen atom is longer than the Eu–N (imine) links. The sodium ion is also eight-coordinate into the outer O_3O_3 coordination site of the tripodal ligand. It is bound to the three μ -phenoxo and the three methoxy oxygen atoms, the two last bonds involving a η^2 chelating perchlorate anion. Surprisingly the Na–O bond lengths do not depend on the nature of the oxygen atom. As an example, the shortest (2.343(3) Å) and the largest (2.690(3) Å) Na–O bond lengths are issued from the phenoxo oxygen atoms. The shortest intermolecular Eu–Eu distance is equal to 5.8170(3) Å and larger than the intramolecular $Eu \cdots Na$ distance (3.5043(17) Å), clearly indicating that complex **2** may be considered as a genuine example of strictly dinuclear (Eu^{III}, Na^I) species.

The asymmetric unit of **3** consists of the $[LDy_2(H_2O)_2(ovan)]^{2+}$ cation, which is shown in Figure 5, with two well-separated nitrate anions and two water molecules of crystallization. The dysprosium ion in the inner N_4O_3 coordination site is linked to the seven donor atoms of the tripodal ligand and to the oxygen atom of a water molecule. The other dysprosium ion is nine-coordinate to

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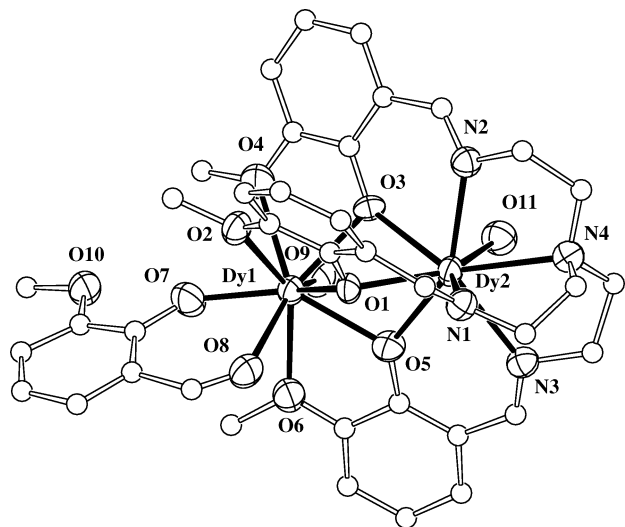


Figure 5. Zortep view of the core of complex **3** with ellipsoids drawn at the 50% probability level, carbon atoms represented at an arbitrary scale for clarity.

oxygen atoms, six coming from the outer O_6 ligand coordination site, two belonging to the aldehyde and deprotonated phenol functions of the supplementary *o*-vanillin ligand, and the last one coming from a water molecule. So, the core of each molecular unit is built up from two dysprosium ions, triply bridged by three phenoxo oxygen atoms of L, O(1), O(3), and O(5).

The three structures have common structural points. The three L' ligands in **1** and the three branches of the L^{3-} ligand in **2** and **3** introduce helicity. So, the three figures do present the Δ enantiomers of the different complexes. As these complexes crystallize in achiral space groups, we are in the presence of racemate samples with Δ and Λ enantiomers in equal amount. Moreover, complexation of the endo tertiary amine and of the three imine nitrogen atoms forces the tris-(2-aminoethyl) part of the tripodal ligand to form three five-membered pseudochelate rings that adopt a $(\lambda\lambda\delta)_5$ conformation. These $\Delta(\lambda\lambda\delta)_5$ or $\Lambda(\delta\delta\lambda)_5$ enantiomers have been found in the lanthanide coordination sphere of macrobicyclic $ZnLn$ cryptates.³⁹ Relevant structural parameters for the three structures are gathered in Table 2.

Discussion

The complexation of heptadentate ligands derived from ring-substituted salicylaldehydes and tris(2-aminoethyl)amine (tren) with lanthanide ions was known to be dominated by the sensitivity of ligands to hydrolysis which prevented isolation of the expected neutral lanthanide complexes in the case of the nonsubstituted H_3 -saltren ligand.⁴⁰ Lanthanide salts were also replaced by an anhydrous starting material such as $Ln[N(SiMe_3)_2]_3$.⁴¹ An elegant way to overcome hydrolysis was found in using reduced ligands without imine functions.^{19c,d} It was also reported that deprotonation of

ligands with cesium hydroxide or sodium methoxide prior to addition of lanthanide salts avoids hydrolysis.^{42,43}

Starting with *o*-vanillin instead of salicylaldehyde gives a tripodal ligand with two different coordination sites that, owing to their natures (N_4O_3 vs O_6), are expected to display different reactivities. This feature is expected to favor insertion of two different lanthanide ions, according to a controlled stepwise process. To avoid the presence of any ion other than the lanthanide ion, we have found a new experimental process. Indeed, mixing at room temperature the Schiff-base ligand with a $Ln(NO_3)_3 \cdot 5H_2O$ salt does not cause hydrolysis of the ligand, as previously described,⁴⁰ but simply induces proton migration from the phenol to the imine function. The presence of an iminium in the first isolated precipitate has been easily characterized by the structural determination of complex **1** (see above) and also by 1H NMR. A nice coupling between the hydrogen atoms of the $HC=N^+H$ group gives two doublets centered at 9.17 and 14.18 ppm for the HC and HN^+ signals, respectively. Similar NMR data are obtained at 8.13 and 12.74 ppm with the $H_3LLa(NO_3)_3(H_2O)_2$ complex, which confirms the complexation of the H_3L ligand under its zwitterionic phenoxo-iminium form. Observation of a proton migration in closely related species has been previously reported.^{44,45}

Addition of triethylamine to a methanol suspension of the $H_3LLn(NO_3)_3(H_2O)_2$ complexes induces a color change and precipitation of a new light-yellow complex formulated as $LLn(H_2O)$ on the basis of elemental analysis. Insolubility prevents any NMR characterization in solution. Nevertheless, these neutral entities can be dissolved in an acetone or DMSO solution containing sodium ions and then crystallized under their cationic forms, as exemplified by the structural determination of complex **2**. NMR spectroscopy confirms that **2** is stable in DMSO solution. The observed chemical shifts are consistent with the presence of europium in the inner N_4O_3 coordination site. The equivalence of the IR $C=N$ stretching bands of **2** and $LEu(H_2O)$ indicates that in the two complexes the europium ion is retained in the N_4O_3 inner site. But the most conclusive proof is given by the equivalence of the ^{13}C chemical shifts observed for $LY(H_2O)$ in ^{13}C MAS spectra and for $LYNaClO_4$ in DMSO solution. The full spectrum of $LY(H_2O)$ obtained in SSNMR shows nine peaks (Figure 6). Ten signals are expected in a C_3 symmetry, but we can see that two methine signals are very close at 113.8 ppm, so that the 10 expected signals are really present. Their assignments, made with help of dipolar dephasing experiments at 5 kHz,⁴⁶ are in agreement with those obtained for $LYNaClO_4$ in DMSO solution. Expansions of the solid-state spectrum show clear evidence of splitting. The symmetry cannot be exactly C_3 , and it is difficult to measure

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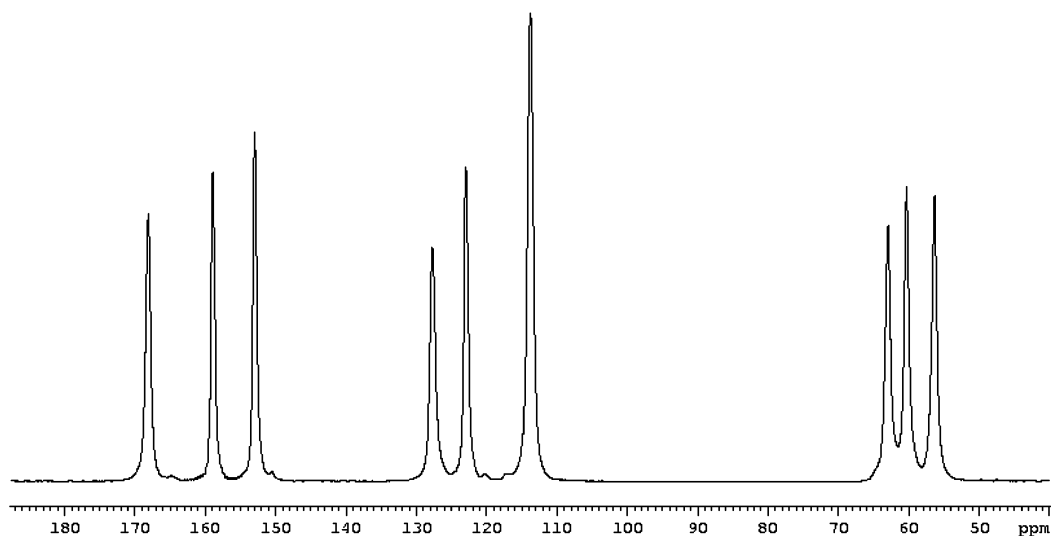


Figure 6. Solid-state NMR spectrum of LY(H₂O).

from NMR how far the geometry departs from ideal. A further interest of this experiment is to evidence an easy way to lanthanide–alkali metal entities. We must note that other Ln–alkali metal complexes have been isolated with an asymmetric macrocycle possessing a N₃O₂ Schiff base coordination site and a O₃O₂ crown-ether-like site⁴⁷ or with a triple-stranded helicate.⁴⁸

The last step introduces the second lanthanide ion in the outer O₃O₃ coordination site. The electroneutrality of the resulting complex implies participation of three monocharged anions. Until now, we only succeeded in crystallizing the heterodinuclear [LYbLa(NO₃)₂]₂[La(NO₃)₅] complex,²⁴ starting with LYb(H₂O) and a large excess of La(NO₃)₃·5H₂O with acetone as solvent. Synthesis in methanol with only a slight excess of the added ion (1/1.1 ratio) yields a powder that analyzes as LYbLa(NO₃)₃·2H₂O. This powder differs also from the [LYbLa(NO₃)₂]₂[La(NO₃)₅] sample by its IR spectrum. Now, a very sharp and strong band typical for an ionic and uncoordinated NO₃ group⁴⁹ appears at 1384 cm⁻¹, thus demonstrating that the powder compound is correctly formulated as [LYbLa(NO₃)₂(H₂O)₂](NO₃). Unfortunately, we have been unable to crystallize this entity or other heterodinuclear complexes with only nitrate anions. Several attempts for crystallizing and substituting the nitrate anions with other anions or with 2,4-pentanedione and salicylaldehyde, at least partially, have been unsuccessful. Until now, we only succeeded in isolating crystals by introduction of deprotonated *o*-vanillin in a methanol solution containing the neutral LDy(H₂O) complex and Dy(NO₃)₃·5H₂O. In this last case, the structural determination clearly indicates that we deal now with a dicationic [LDyDy(ovan)]²⁺ and two ionic nitrate counterions.

Hopefully, the [LLnLn'(NO₃)₂](NO₃) complexes can be nicely characterized with help of positive FAB mass

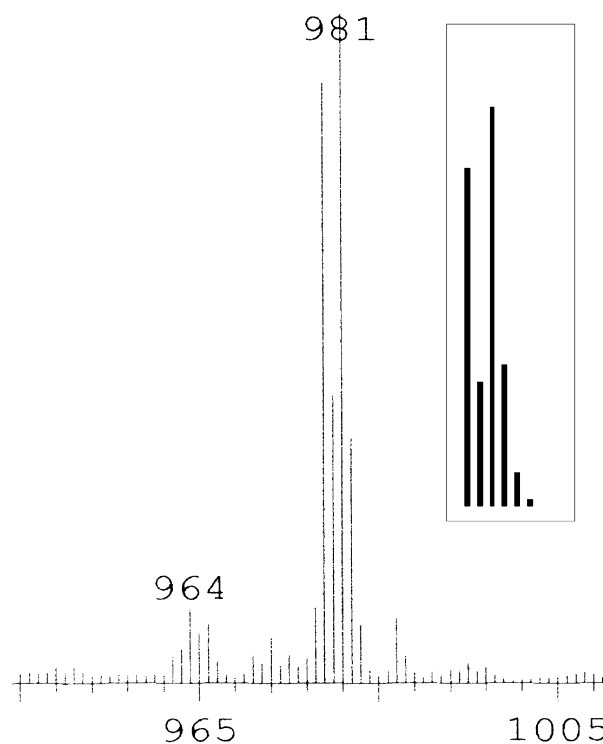


Figure 7. Experimental and simulated isotope patterns for the main peak appearing in the mass spectrum of the LTbEu(NO₃)₃·2H₂O complex.

spectrometry. Some examples have been given before.²⁶ As a supplementary example, we give the spectrum corresponding to the LTbEu(NO₃)₃·2H₂O complex. The signal pattern (Figure 7) is characteristic of the [LTbEu(NO₃)₂]⁺ cation, without any trace of signal coming from scrambling of the two Ln ions. It compares very well with the theoretical pattern given in the inset of Figure 7. This result confirms pairing of two Ln ions located in close vicinity in the periodic table without scrambling if the lanthanide ion with the higher Lewis acidity (or the smaller ionic radius) is coordinated in the inner N₄O₃ coordination, as in this case. So, from the 196 possible (Ln, Ln') species (if we do not take into account the radioactive Pm³⁺ ion), 91 may be expected as possible

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with this experimental process, along with the 14 homodinuclear entities.

As concluding remarks, we will emphasize the main points of this work allowing an easy access to a large number of heterodinuclear (4f, 4f') complexes and giving structural proofs for characterization of the necessary intermediates and final products. From these structural data, it is quite clear that the first step consists of a proton transfer while the second step corresponds to a deprotonation. The key point in our stepwise strategy is the preparation of the mononuclear LLn species in which the Ln ion is complexed in the inner N₄O₃ coordination site of the tripodal ligand. The improvement of the new process consists of avoiding use of mineral bases that could contaminate the mononuclear neutral complex by introduction of the alkaline ions in the free O₃O₃ coordination site. We must emphasize that the synthesis of complexes such as **2** are not necessary in our process but that it has only been used here to structurally characterize the insoluble neutral complex LLn(H₂O) isolated in the

second step. Then the synthesis of genuine heterodinuclear species starting from the mononuclear entities requires introduction of a lanthanide(III) ion with a larger ionic radius, or a lower Lewis acidity, as previously demonstrated with help of positive FAB mass spectra and of magnetic susceptibility studies.²⁶

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Supporting Information Available: X-ray crystallographic files including the structural data for [(HL')₃La(NO₃)₃] (**1**), [LEu(H₂O)NaClO₄] (**2**), and [LDy₂(H₂O)₂(ovan)](NO₃)₂(H₂O)₂ (**3**) in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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