

Synthesis, X-ray Structure, and Solution NMR Studies of Ln(III) Complexes with a Macrocyclic Asymmetric Compartmental Schiff Base. Preference of the Ln(III) Ions for a Crown-Like Coordination Site

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Received June 22, 1998

The compartmental ligand H₂L_A, containing an N₃O₂ Schiff base and an O₂O₃ crown like coordination site, has been prepared by reaction of 3,3'-(3-oxapentane-1,5-diylidioxo)bis(2-hydroxybenzaldehyde) with 1,5-diamino-3-azamethylpentane. The formation of a [1+1] macrocycle was inferred by IR, NMR, and mass spectrometry. When reacted with the rare-earth hydrate chlorides, LnCl₃·nH₂O (Ln = La, Ce, Pr, Nd, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y), H₂L_A or its precursors (template reaction) form the mononuclear complexes [Ln(H₂L_A)(H₂O)₄]Cl₃·nH₂O where the lanthanide ion coordinates the O₂O₃ crown like site. The solid-state X-ray structures of [Ln(H₂L_A)(H₂O)₄]Cl₃·nH₂O (Ln = Ce, Dy, Lu) have been determined. [Lu(H₂L_A)(H₂O)₄]Cl₃·3H₂O is monoclinic space group P2₁/n (Z = 4) with a = 15.269(5) Å, b = 11.484(5) Å, c = 19.389(6) Å, β = 102.85(5)°; [Ce(H₂L_A)(H₂O)₄]Cl₃·H₂O and [Dy(H₂L_A)(H₂O)₄]Cl₃·H₂O are isomorphous, space group P2₁ (Z = 2), with a = 10.959(5) Å, b = 16.978(5) Å, c = 9.017(4) Å, β = 97.73(5)°, and a = 10.874(5) Å, b = 16.797(5) Å, c = 9.046(4) Å, β = 97.86(5)° for the cerium and dysprosium complexes, respectively. In the three compounds the metal ion is coordinated in a similar manner by the five oxygens (two phenolic and three etheric) of the cyclic ligand and the nine coordination around the central atom is reached by the oxygen atoms of four coordinated water molecules. Three chlorine ions are present in the asymmetric unit. A detailed ¹H NMR study was carried out in CD₃OD for both the diamagnetic and paramagnetic [Ln(H₂L_A)(H₂O)₄]Cl₃ complexes in order to compare their structure in solution with that found in the solid state. The quantitative analysis of the paramagnetic proton shifts indicates that the complexes from La to Tm are isostructural, maintain in solution the same type of coordination polyhedron found at the solid state, with the metal ion invariably coordinated in the O₂O₃ compartment, and present a high degree of stereochemical nonrigidity. In the case of the Lu complex, the decreased fluxionality due to the reduced ionic radius allows the observation of two isomeric species in the ¹H NMR spectrum at low temperature.

Introduction

In the past decade a great attention has been devoted to the design and synthesis of Schiff bases with enhanced ability to selectively encapsulate given metal ions.^{1–6} In particular,

macrocyclic and acyclic Schiff bases have successfully been proposed as excellent systems in the formation of mono-, homo-, and hetero-polynuclear lanthanide complexes.^{3–6} Detailed investigations of their stereochemical, electronic, magnetic, and

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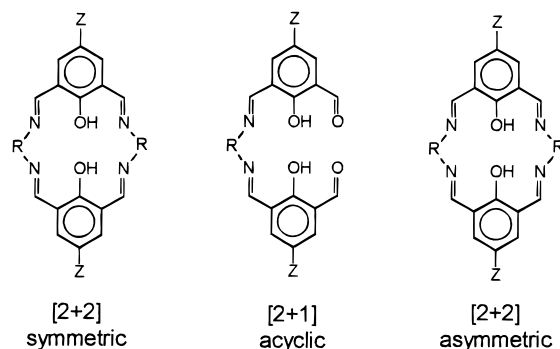
catalytic properties have allowed the proposal of new, highly efficient molecular devices or probes for a number of specific applications.^{7,8} Furthermore, they have been used as unconventional precursors in the formation of modified surfaces or otherwise not accessible mixed oxides.⁹

Moreover, several studies have been addressed to the synthesis of suitable crown ethers or related derivatives, containing cavities of different size and type, and to their interaction with lanthanide ions, with the specific aim of securing these metal ions into the coordination cavity and to study the transport phenomena across liquid membranes.^{10–12} Functionalized systems (such as lariat compounds, polymers bearing crown-ethers, and mono- or poly-brachial macrocycles) were also used in nonconventional separation process or in the preparation of new molecular materials.^{10–12} In these studies the synthesis and characterization of compartmental macrocyclic Schiff bases has received considerable attention owing to their ability to recognize charged or neutral molecules.^{2–6} The compartmental ligands contain two adjacent, similar or dissimilar compartments which can coordinate two identical or different metal ions. The close proximity of these ions favors their mutual interaction with the consequent formation of unusual molecular devices. The ion selectivity of these systems can be pursued by a proper design of the coordination sites, including the number and types of donor atoms and their structural arrangement, as well as the overall dynamics of the complex.

In the synthesis of these systems the symmetric tetraimine Robson-type cyclic ligands resulted particularly useful. They were obtained by [2+2] self-condensation of appropriate keto or formyl and amine precursors or by template reaction in the presence of a suitable metal ion.^{1–6} These tetraimines give rise solely to homo-dinuclear complexes. Compartmental macrocyclic ligands, containing dissimilar coordination sites, offer the additional possibility for a particular metal ion to choose the most appropriate coordination scheme, leaving the free site available for the coordination of another metal ion or for an additional recognition process.

Asymmetric [2+2] cyclic ligands and related complexes have been synthesized by a stepwise condensation process: the first

step is the preparation of the [2+1] acyclic ligand and/or its mononuclear complex which subsequently undergoes a further condensation reaction with a different polyamine in the presence of a suitable metal ion. By this synthetic pathway several dissimilar tetraimine macrocycles and/or related hetero-dinuclear complexes have been obtained, using 2,6-diformyl-4-substituted phenols and suitable polyamines as precursors.^{3–6}



However, in these systems the difference between the two adjacent coordination sites was not enough to address the formation of hetero-dinuclear complexes but rather homo-dinuclear or mixtures of these compounds were found. Furthermore transmetalation and migration processes may also occur.¹³ Different synthetic strategies have been proposed for the preparation of di- or poly-nucleating systems capable of selectively recognizing two (or more) different metal ions. These synthetic approaches consist in the formation of a stable mononuclear complex by using one coordination site, followed by a selective recognition process toward a specific second metal ion to be included at the second coordination site.^{1–6}

The fusion of a Schiff base and crown ether moieties can give rise to dinucleating ligands with two remarkably different coordination sites. In principle, such systems can coordinate rare earth and alkali ions. The coordination of a metal ion into the crown-ether cavity can markedly influence the physicochemical properties of the metal ion bound to the Schiff base site and the mutual interaction between the two ions can provide interesting properties useful for the development of new probes and sensors.

In the present paper we report on the synthesis and characterization of novel compartmental systems capable of securing lanthanide(III) ions forming mononuclear complex which will be tested for further recognition processes. In particular we have synthesized the asymmetric compartmental macrocycle H₂L_A containing one N₃O₂ Schiff base and one O₂O₃ crown-like site either by self-condensation of equimolecular amounts of the diformyl precursor 3,3'-(3-oxapentane-1,5-diylldioxy)bis(2-hydroxybenzaldehyde)(H₂L') and 1,5-diamino-3-azamethylpentane or by the demetalation procedure (Chart 1). The template procedure was also used, mainly for the related yttrium(III) and lanthanide(III) complexes.

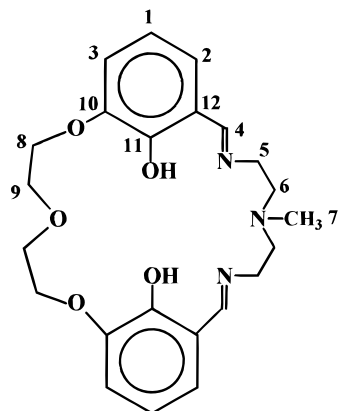
Experimental Section

Materials. The salts, the solvents, and the reagents were commercial products, used as received from Aldrich. Hexahydrate rare-earth chlorides LnCl₃·6H₂O were used, except the heptahydrate LaCl₃·7H₂O and CeCl₃·7H₂O. Dimethyl sulfoxide was purified by distillation.

Caution. Although during these experiments no accidents have occurred, *extreme care should be taken when perchlorates are handled,*

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Chart 1. Structure of the Ligand H_2L_A with the Labeling Used To Assign the Resonances in the NMR Spectra

because they may explode spontaneously and may be sensitive to shock. The perchlorates should only be prepared in small quantities.

H_2L' . The diformyl precursor 3,3'-(3-oxapentane-1,5-diylidioxy)bis(2-hydroxybenzaldehyde) (H_2L') was prepared by a modification of the literature procedure.¹⁴ To a suspension of NaH under N_2 (0.11 mmol) in 25 mL of dry DMSO was added a solution of 2,3-dihydroxybenzaldehyde (0.05 mmol) in dry DMSO over a period of 2 h, under vigorous stirring. The temperature was kept below 25 °C. After stirring for 1 h triethylene glycol ditosylate (0.025 mol) was added in 1 portion. The suspension was stirred at room temperature for 24 h. The yellow precipitate obtained by the addition of water (300 mL) was filtered, washed with water and methanol, and treated with chloroform (25 mL). After separation of the solid (which proved to be the disodic salt of the ligand), the organic layer was dried over $MgSO_4$ and the solvent removed to give the product as a slightly yellow solid (51% yield); mp 60 °C; 1H NMR ($CDCl_3$) δ 10.96 (s, 2H, OH), 9.94 (s, 2H, CHO), 7.24–6.89 (m, 6H, ArH), 4.28–4.23 (m, 4H, CH_2O), 4.02–3.93 (m, 4H, CH_2O); IR (KBr) 1654 cm^{-1} (C=O); mass spectrum m/z 344. Anal. Calcd: C, 62.2; H, 5.40. Found: C, 61.9; H, 5.20.

$Ba(H_2L')(ClO_4)_2$. It was also prepared by a modified literature method.¹⁴ To a solution of 3,3'-(3-oxapentane-1,5-diylidioxy)bis(2-hydroxybenzaldehyde) (0.857 mmol) in methanol (50 mL), an ethanolic solution (50 mL) of $Ba(ClO_4)_2 \cdot 2H_2O$ (0.857 mmol) was added. The solution was stirred overnight and the solvent removed by rotary evaporator, leaving a white residue. The crude product was washed with chloroform and tetrahydrofuran, collected by filtration and dried in vacuo (56% yield). 1H NMR ($CDOD_3$) δ 10.10 (s, 2H, CHO), 7.32–6.77 (m, 6H, ArH), 4.27–4.22 (m, 4H, CH_2O), 4.00–3.95 (m, 4H, CH_2O); IR (KBr) 1659 cm^{-1} (C=O); SEM, Ba:Cl ratio 1:2. Anal. Calcd: C, 31.68; H, 2.66. Found: C, 31.19; H, 2.85.

H_2L_A . H_2L_A has been prepared by two alternative methods.

(a) 1,5-Diamino-3-azamethylpentane (1 mmol) in acetonitrile (5 mL) was added dropwise to an acetonitrile solution (25 mL) of 3,3'-(3-oxapentane-1,5-diylidioxy)bis(2-hydroxybenzaldehyde) (1 mmol). The resulting yellow solution was refluxed for 2 h. The solvent was then removed under reduced pressure and the residue treated with chloroform and diethyl ether. The resulting yellow powder was collected by filtration and dried in vacuo (68% yield);

(b) $Ba(H_2L_A)(ClO_4)_2$ was suspended in chloroform, treated with an aqueous solution of guanidine sulfate and shaken for 3 h. The aqueous phase was eliminated; H_2L_A was recovered from the chloroform solution, after drying over $MgSO_4$ and removal of the solvent by rotary evaporator (10% yield), mp 96–97 °C. 1H NMR ($CDCl_3$) δ 8.19 (s, 2H, CHN), 6.96–6.54 (m, 6H, ArH), 4.20 (m, 4H, CH_2O), 3.95 (m, 4H, CH_2O), 3.63 (m, 4H, $CNCH_2$), 2.81–2.74 (m, 4H, CH_2NMe), 2.32 (d, 3H, CH_3); IR (KBr) 1634 cm^{-1} (C=N); mass spectrum m/z 428 $[MH]^+$. Anal. Calcd for $H_2L_A \cdot H_2O$: C, 62.29; H, 6.59; N, 9.47. Found: C, 62.71; H, 6.73; N, 9.28.

Table 1. Crystallographic Data for Ce, Dy, and Lu Complexes

	coordinated metal		
	Ce	Dy	Lu
chemical formula	$C_{23}H_{39}N_3O_{10}^-$ Cl_3Ce	$C_{23}H_{39}N_3O_{10}^-$ Cl_3Dy	$C_{23}H_{39}N_3O_{12}^-$ Cl_3Lu
fw	764.05	786.45	834.93
space group	$P2_1$ (No. 4) ^a	$P2_1$ (No. 4) ^a	$P2_1/n$ (No. 14)
<i>a</i>	10.983(5) Å	10.870(5) Å	15.269(5) Å
<i>b</i>	16.960(6) Å	16.785(6) Å	11.484(5) Å
<i>c</i>	9.058(4) Å	9.046(4) Å	19.389(7) Å
β	98.03(7)°	97.91(8)°	102.85(6)°
<i>V</i>	1670(1) Å ³	1635(1) Å ³	3315(2) Å ³
<i>Z</i>	2	2	4
<i>T</i>	295 °C	295 °C	295 °C
λ	0.7107 Å	0.7107 Å	0.7107 Å
ρ_{calcd}	1.52 g cm^{-3}	1.60 g cm^{-3}	1.67 g cm^{-3}
μ	0.1653 cm^{-1}	0.2582 cm^{-1}	0.3279 cm^{-1}
$R(F_o)^b$	0.086	0.049	0.080
$R_w(F_o^2)$	0.2185	0.1357	0.18

^a The correctness of the absolute structure was determined by refinement of the Flack parameter. ^b $R(F_o) = (\sum(|F_o| - |F_c|)/\sum|F_o|)$; $R_w(F_o^2) = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.1696P)^2 + 8.5897P]$ (for Ce); $w = 1/[\sigma^2(F_o^2) + (0.0832P)^2 + 4.3619P]$ (for Dy); $w = 1/[\sigma^2(F_o^2) + (0.0152P)^2 + 146.8345P]$ (for Lu), where $P = (F_o^2 + 2F_c^2)/3$.

$Ba(H_2L_A)(ClO_4)_2$. To 0.257 mmol of the acyclic complex $Ba(H_2L')-(ClO_4)_2$ in methanol (25 mL) was added 1,5-diamino-3-azamethylpentane (0.257 mmol) in methanol (5 mL) dropwise. The resulting yellow solution was stirred overnight at room temperature. The yellow precipitate was filtered off, washed in methanol, and dried in vacuo (32% yield). 1H NMR ($CDOD_3$) δ 8.28 (d, 2H, CHN), 6.94–6.37 (m, 6H, ArH), 4.24–4.13 (m, 4H, CH_2O), 4.00–3.90 (m, 4H, CH_2O), 3.82–3.70 (m, 4H, $CNCH_2$), 2.76–2.56 (m, 4H, $MeNCH_2$), 2.26 (s, 3H, CH_3); IR (KBr) 1647 cm^{-1} (C=N); SEM, Ba:Cl ratio 1:2. Anal. Calcd: C, 45.02; H, 5.09; N, 6.86. Found: C, 45.5; H, 5.06; N, 6.78.

$[Ln(H_2L_A)(H_2O)_4]Cl_3 \cdot nH_2O$ (Ln, *n* = La, 4; Ce, 1; Pr, 1; Nd, 1; Sm, 1; Eu, 3; Gd, 1; Tb, 1; Dy, 1; Ho, 1; Er, 1; Tm, 1; Yb, 4; Lu, 3; Y, 1). To a methanolic solution (25 mL) of the precursor 3,3'-(3,6-dioxaoctane-1,8-diylidioxy)bis(2-hydroxybenzaldehyde) (1 mmol) was added $LnCl_3 \cdot nH_2O$ (1 mmol) in methanol (5 mL), and the solution was stirred for 10 min. 1,5-Diamino-3-azamethylpentane (1 mmol) in methanol (5 mL) was added dropwise, and the resulting yellow or orange-yellow solution was refluxed for 4 h. The solvent was then removed by rotary evaporator, and the residue was dissolved in ethanol. To the resulting solution diethyl ether was added and the obtained yellow or orange precipitate was collected by filtration, dried in vacuo, and recrystallized from *n*-propyl or isopropyl alcohol (yields 80–90%). IR (KBr) ν (C=N) in the range 1653–1660 cm^{-1} ; SEM, Ln:Cl ratio 1:3. $[La(H_2L_A)(H_2O)_4]Cl_3 \cdot 4H_2O$ was prepared also by an alternative method: to a solution of H_2L_A (0.26 mmol) in chloroform (25 mL) was dropwise added a methanol solution (5 mL) of $LaCl_3 \cdot 7H_2O$ (0.26 mmol). The resulting yellow solution was refluxed for 3 h and was then reduced in volume. The yellow precipitate obtained by the addition of diethyl ether was filtered off, washed with methanol, and dried in vacuo (71% yield). Crystals were grown from *n*-propyl alcohol. 1H NMR ($CDOD_3$) δ 8.71 (d, 2H, CHN), 7.23 (dd, 2H, ArH), 7.15 (dd, 2H, ArH), 6.69 (t, 2H, ArH), 4.50 (d, 8H, CH_2O), 4.08 (t, 4H, $CNCH_2$), 2.85 (t, 4H, NCH_2), 2.42 (s, 3H, CH_3); IR (KBr) 1653 cm^{-1} (C=N); SEM, La:Cl ratio 1:3. Elemental analyses agree with the proposed formulation for all the complexes.

X-ray Crystallography. Diffraction data were collected at room temperature on a Philips PW1100 automatic four-circle diffractometer (FEBO System) using the graphite-monochromated Mo K α radiation and ω - 2θ scan method. Lattice parameters were obtained from least-squares refinement of the setting angles of 25 reflections with $12 \leq 2\theta \leq 24^\circ$. Table 1 lists a summary of the crystallographic data and structure refinement.

$C_{23}H_{39}N_3O_{10}Cl_3Ce$: yellow prisms, crystal dimensions 0.21 \times 0.14 \times 0.11, 3500 reflections measured ($-15 \leq h \leq 15$, $0 \leq k \leq 24$, $0 \leq l \leq 12$), 3268 unique reflections of which 3176 were observable.

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Table 2. Metal–Oxygen Bond Distances (Å) and Selected Bond Angles (deg) of Lanthanide Ion Coordination Polyhedrons

donor atom	central metal ion (M)		
	Ce	Dy	Lu
O(1)	2.40(2)	2.32(1)	2.22(1)
O(2)	2.36(2)	2.25(1)	2.27(1)
O(3)	2.73(2)	2.64(2)	2.48(1)
O(4)	2.60(1)	2.514(7)	2.54(1)
O(5)	2.72(2)	2.64(1)	2.52(1)
O(6)	2.55(1)	2.415(6)	2.33(1)
O(7)	2.65(2)	2.391(8)	2.38(1)
O(8)	2.55(3)	2.42(2)	2.35(1)
O(9)	2.50(2)	2.39(2)	2.35(1)
O(1)–M–O(2)	103.2(4)	101.1(2)	94.9(5)
O(1)–M–O(5)	61.7(8)	61.4(5)	65.4(4)
O(2)–M–O(3)	61.5(8)	65.0(5)	66.1(4)
O(3)–M–O(4)	56.2(8)	57.2(6)	63.8(4)
O(4)–M–O(5)	63.1(8)	62.7(5)	61.9(4)
O(1)–M–O(6)	71.7(6)	69.2(5)	72.6(4)
O(1)–M–O(7)	76.9(8)	75.1(7)	74.9(4)
O(1)–M–O(9)	84.2(7)	87.1(5)	80.1(4)
O(2)–M–O(6)	69.6(6)	71.8(5)	72.4(4)
O(2)–M–O(7)	77.3(9)	81.3(6)	73.4(4)
O(2)–M–O(8)	86.1(9)	82.6(5)	89.4(5)
O(3)–M–O(7)	75.7(9)	74.6(8)	71.3(4)
O(3)–M–O(8)	65.2(8)	66.0(6)	71.2(4)
O(4)–M–O(7)	72.9(5)	75.4(3)	90.4(4)
O(4)–M–O(8)	83.0(6)	82.8(5)	75.1(5)
O(4)–M–O(9)	86.2(8)	80.3(5)	76.4(4)
O(5)–M–O(7)	71(1)	69.8(7)	66.9(5)
O(5)–M–O(9)	66.1(9)	65.1(9)	69.9(4)
O(6)–M–O(8)	77.6(5)	77.9(6)	72.1(5)
O(6)–M–O(9)	81.3(7)	78.5(5)	73.1(4)
O(8)–M–O(9)	69.3(4)	70.9(3)	74.7(4)

C₂₃H₃₉N₃O₁₀Cl₃Dy: yellow prisms, crystal dimensions 0.17 × 0.12 × 0.10, 4665 reflections measured (−15 ≤ h ≤ 15, 0 ≤ k ≤ 24, 0 ≤ l ≤ 13), 4402 unique reflections of which 4247 were observable.

C₂₃H₄₃N₃O₁₂Cl₃Lu: yellow prisms, crystal dimensions 0.20 × 0.16 × 0.11, 5556 reflections measured (−19 ≤ h ≤ 18, 0 ≤ k ≤ 44, −3 ≤ l ≤ 22), 5357 unique reflections of which 4336 were observable. No sign of crystal deterioration was revealed by monitoring three standard reflections after every 200 measurements but the quality of the crystals of the cerium and dysprosium complexes was very poor, even after several attempts with different crystals. The structures were solved by standard Patterson methods and subsequently completed by a combination of least-squares techniques and Fourier syntheses with SHELX program.¹⁵ All the benzene rings were refined as rigid bodies, the hydrogen atoms were included in the idealized positions with fixed C–H distances (C–H = 1.08 Å) and isotropic temperature factors fixed to 1.2 times U(eq) of the preceding carbon atom.

The poor quality of the crystals grown from the solution of the Ce and Dy compounds precluded the obtainment of sufficiently good data and thus the resulting structures are only useful to understand the connectivity of the atoms. For these two complexes, in particular, serious disorder in the carbon atoms around the N(2) atom was found; repeated attempts to resolve the disorder failed, and high values of thermal parameters were maintained in order to absorb the disorder.

The asymmetric units of all the compounds contain three noncoordinated chlorine ions, one of which was found in two different positions that were refined to final values of about 40 and 60%. The correctness of the absolute structures reported was determined by refinement of the Flack parameter.¹⁶ Listings of selected bond distances and angles pertinent to the coordination sphere are summarized in Table 2. Additional crystallographic data, atomic coordinates, anisotropic thermal

parameters, and full listings of bond lengths and angles are provided as Supporting Information. Final geometrical calculations and drawings were carried out with the PARST program¹⁷ and the XP utility of the Siemens package,¹⁸ respectively, running on a Digital Alpha-AXP 300 computer.

Physicochemical Measurements. IR spectra were recorded as KBr pellets on a Mattson FTIR 3000 spectrometer. ¹H and ¹³C NMR spectra were recorded at 90, 200, and 400 MHz on a JEOL 90, on a Bruker AC200 equipped with an Aspect 3000 computer, and on a JEOL EX400 spectrometers, respectively. All the samples examined were dissolved in deuterated methanol used also as internal reference. The morphology, homogeneity and the metal:chlorine ratio 1:3 of the complexes were checked by using a Philips XL40 model scanning electron microscopy equipped with an EDAX DX PRIME X-ray energy dispersive spectrometer.¹⁹ The solvent content (H₂O or MeOH) was evaluated by thermal analysis curves using a Netzsch STA 429 thermoanalytical equipment. The tests were performed in a nitrogen atmosphere (flux rate 250 mL/min; heating rate 5 °C min^{−1}) and in air under the same conditions. Neutral alumina (Carlo Erba, Milano, Italy) was used as reference material. All mass spectrometric measurements were performed on a VG ZAB 2F instrument (VG Analytical Ltd.) operating in fast atom bombardment (FAB) conditions (8 keV Xe atom bombardment a nitrobenzyl alcohol solution of the sample).^{20,21} Magnetic susceptibilities were determined by the Faraday method at room temperature, the apparatus (Oxford Instruments) being calibrated with HgCo(NCS)₄.²² Diamagnetic corrections were performed.²³

Results and Discussion

Asymmetric Macrocycle H₂L_A and Related Complexes.

The asymmetric compartmental [1+1] Schiff base ligand H₂L_A, containing a N₃O₂ Schiff base and an O₂O₃ crown-like site has been synthesized by self-condensation in acetonitrile of equimolar amounts of 3,3'-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) and 1,5-diamino-3-azamethylpentane. It has also been prepared by demetalation reaction with guanidine sulfate of the barium complex [Ba(H₂L_A)](ClO₄)₂ obtained by the template condensation of equimolar amounts of the diformyl and amine precursors in the presence of Ba(ClO₄)₂.¹⁴ Alternatively, the acyclic barium complex [Ba(H₂L')](ClO₄)₂ derived from the reaction of Ba(ClO₄)₂ and the diformyl precursor H₂L' is converted into the cyclic analogue [Ba(H₂L_A)](ClO₄)₂ by condensation with 1,5-diamino-3-azamethylpentane in alcohol solution. The formation of the cyclic compound is evidenced by the lack of the ν(C=O) at 1693 cm^{−1}, as determined in the acyclic complex, and the presence of ν(C=N) at 1649 cm^{−1}. Eventually, the further reaction of [Ba(H₂L_A)](ClO₄)₂ with guanidine sulfate forms H₂L_A. The free macrocycle has been obtained by subsequent extraction of the crude reaction product with CHCl₃. The complete demetalation process has been assessed by SEM and EDX analyses. The peaks due to the barium and chlorine, clearly detectable in the acyclic [Ba(H₂L')](ClO₄)₂ and cyclic [Ba(H₂L_A)](ClO₄)₂ complexes and evidencing a 1:2 Ba:Cl ratio, completely disappear after the reaction with guanidine sulfate. H₂L_A is a yellow solid, stable in air, very soluble in chloroform and moderately soluble in other organic

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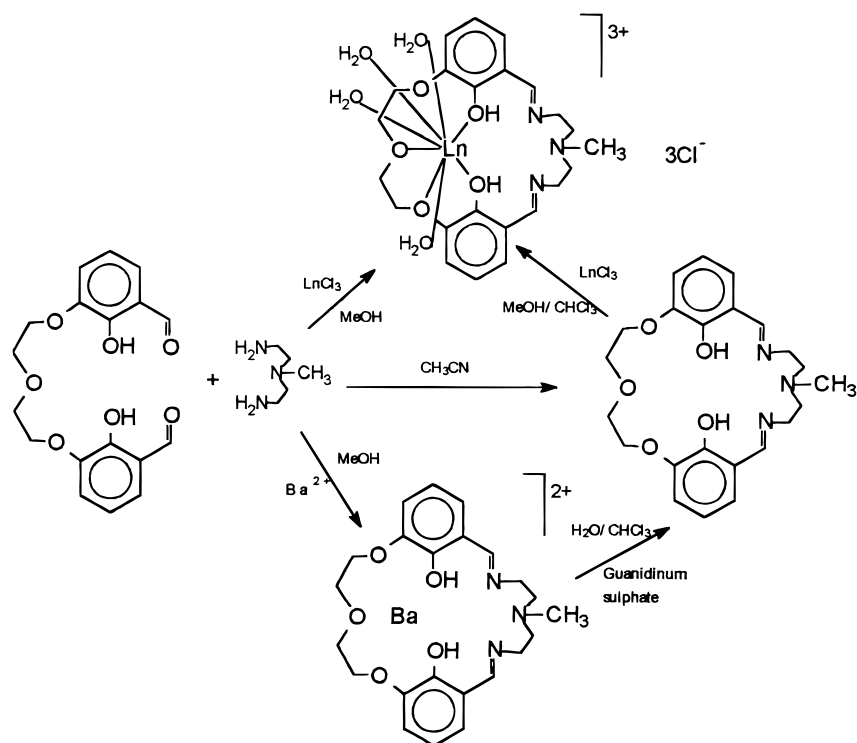
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Scheme 1



solvents. Its infrared spectrum shows a strong peak at 1634 cm^{-1} due to $\nu(\text{C}=\text{N})$ while no bands due to $\text{C}=\text{O}$ or NH_2 groups have been detected. The ^1H NMR spectrum of H_2L_A in CDCl_3 shows the following peaks (ppm): 8.19 (CH iminic protons), 6.96–6.54 (aromatic protons), 4.20, 3.95, 3.63 (methylene protons), and 2.32 (methyl protons). Its mass spectrum shows the parent peak, $[\text{MH}]^+$, at the appropriate m/z value.²⁴ These data is consistent with the [1+1] cyclic nature of this Schiff base ligand and confirms that the self-condensation and the template reaction followed by a demetalation process give rise to the same product. H_2L_A reacts with $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ in methanolic/chloroform solution and in a 1:1 molar ratio to form the yellow complex $[\text{La}(\text{H}_2\text{L}_A)(\text{H}_2\text{O})_4]\text{Cl}_3$. Moreover, by condensation of the diformyl $\text{H}_2\text{L}'$ and amine 1,5-diamino-3-azamethylpentane precursors, in the presence of the appropriate rare earth hydrate chloride as templating agents, the same macrocyclic complexes have been synthesized (Scheme 1). The template reaction, which affords nearly quantitative yields, has been used to prepare the whole series of rare earth $\text{Ln}(\text{III})$ complexes. The crude products have been recrystallized from *n*-propyl or isopropyl alcohol to produce $[\text{Ln}(\text{H}_2\text{L}_A)(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot n\text{H}_2\text{O}$. The chlorine:lanthanide ratio of 3:1 was established by scanning electron microscopy SEM and EDX analyses. The magnetic moments, at room temperature, of the complexes other than lanthanum(III), yttrium(III), and lutetium(III) correspond to those of the free ions, indicating that they behave as isolated paramagnetic centers.

The IR spectra of $[\text{Ln}(\text{H}_2\text{L}_A)(\text{H}_2\text{O})_4]\text{Cl}_3$ show a strong $\nu(\text{C}=\text{N})$ band in the range $1653\text{--}1660\text{ cm}^{-1}$ slightly affected by the change of the metal ion. Upon coordination there is a shift of this absorption toward higher wavelengths ($\Delta\nu = 19\text{--}26\text{ cm}^{-1}$) to suggest that the iminic bonds have a stronger double bond character with respect to the free ligand. It is likely that this is caused by the coordination of the lanthanum(III) into the crown-

like site, which reduces the strength of the hydrogen bonds between the phenolic O–H and the imino nitrogen. This is consistent with a concomitant shift ($\Delta\nu = 17\text{--}24\text{ cm}^{-1}$) toward lower wavelengths observed for the bands associated with $\nu(\text{C}=\text{O})$, particularly that in the range $1227\text{--}1234\text{ cm}^{-1}$ with respect to the ligand ($\nu(\text{C}=\text{O})$ at 1251 cm^{-1}). FAB mass spectra show peaks at m/z value corresponding to the ions $[\text{M} - \text{Cl}]^+$, $[\text{M} - \text{Cl} - \text{HCl}]^+$ and $[\text{M} - \text{Cl} - 2\text{HCl}]^+$, these fragmentation products being diagnostic of the proposed formulation.²⁴

The prepared complexes are stable not only in air but also in methanol or ethanol, where they have been shown to have moderate solubility. Conversely, in the strong coordinating solvent DMSO a demetalation process takes place with the consequent formation of $\text{Ln}(\text{DMSO})_n(\text{Cl})_3$ and H_2L_A . For the whole series of $[\text{Ln}(\text{H}_2\text{L}_A)(\text{H}_2\text{O})_4]\text{Cl}_3$ complexes a detailed structural characterization by ^1H and ^{13}C NMR spectroscopy is reported further on.

Crystal Structures. Crystals of $[\text{Ln}(\text{H}_2\text{L}_A)(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot (\text{H}_2\text{O})_n$ ($\text{Ln} = \text{Ce}, \text{Dy}, \text{and Lu}$; for Ce and Dy, $n = 1$; for Lu, $n = 3$) were obtained from slow evaporation of *n*-propanol solutions. The ORTEP representation of the crystal structures of the Ce, Dy, and Lu complexes are shown in Figures 1 and 2. To improve clarity, the ionic chlorine atoms and the uncoordinated water molecules have been omitted. The structures consist of discrete $[\text{Ln}(\text{L})(\text{H}_2\text{O})_4]^{3+}$ cations and three Cl^- counterions with one (in the Ce and Dy complexes) and three (in the Lu complex) water molecules trapped in the lattice. The cerium and dysprosium complexes are isomorphous.

Each central metal ion is located in the O_2O_3 crown-like site of the macrocyclic ligand and reaches the coordination number of nine by bonding five oxygen atoms from the ligand and four oxygen atoms from water molecules. The oxygen atoms O(3), O(4), and O(5), are etheric, whereas O(1) and O(2) are phenolic. The coordination geometry of the title complexes is influenced by the dimensions of the central metal ion and by the degree of freedom of the donor oxygen atoms. The size of the lutetium

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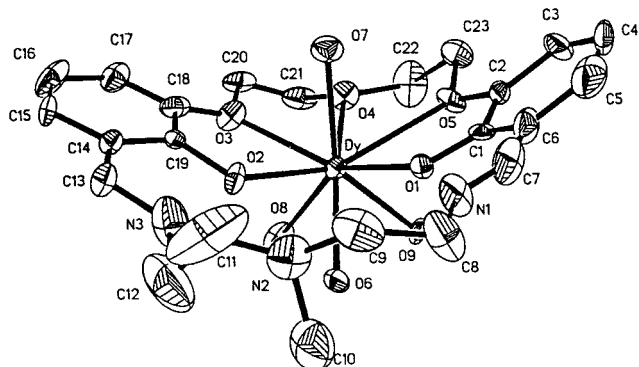


Figure 1. ORTEP diagram of $[\text{Dy}(\text{H}_2\text{L}_\text{A})(\text{H}_2\text{O})_4]^{3+}$ cation showing the atom-labeling scheme. Uncoordinated water molecules and chlorine ions are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. The cerium complex presents an identical drawing. The carbon atoms around the N(2) are introduced at 50% of probability to reduce the disorder.

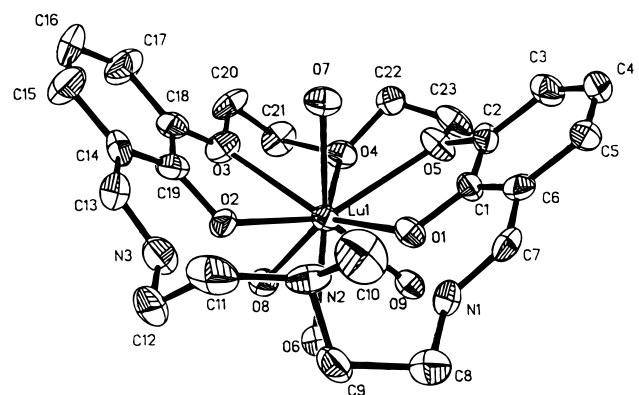


Figure 2. ORTEP diagram of $[\text{Lu}(\text{H}_2\text{L}_\text{A})(\text{H}_2\text{O})_4]^{3+}$ cation showing the atom-labeling scheme. Uncoordinated water molecules and chlorine ions are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

ion (ionic radii 0.85 Å), when compared to those of the other two ions (ionic radii 1.034 Å for Ce; 0.908 Å for Dy) is probably more suitable for a stable complex with the ligand in the O₂O₃ coordination site.

Five possible coordination polyhedra with nine vertices are known; of them the most stable is the tricapped trigonal prism which shows slightly higher stability than the capped square antiprism^{25,26}. Both these geometries are found in several lanthanide complexes with the same coordination number and similar ligands,^{10a,27,28} with a slight predominance of the trigonal prism. The coordination geometry of the lutetium compound is well described as either a distorted square monocapped antiprism, with the O(5) atom as the cap, or as a distorted tricapped trigonal prism with the O(3), O(5), and O(6) atoms as caps.

The coordination geometry of the cerium and dysprosium complexes is better described as a distorted square monocapped antiprism. In fact, considering it to be a tricapped trigonal prism, severe distortions have to be taken into account.

The reduced dimensions of the lutetium ion cause the position of the benzene wings, in the butterfly shape adopted by the cyclic ligand, to be more folded thereby forming a dihedral angle

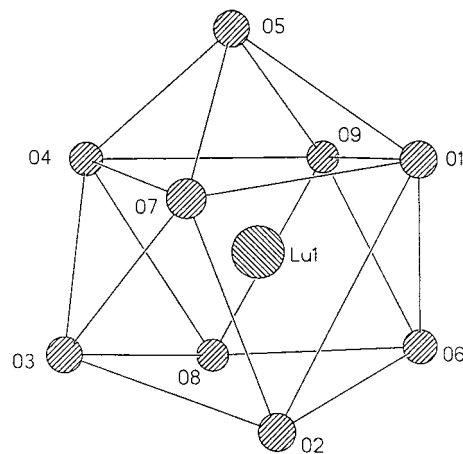


Figure 3. Shape of the coordination polyhedron for the lutetium complex.

Table 3. Representative Torsion Angles (deg) for the Lanthanide Complexes $[\text{Ln}(\text{H}_2\text{L}_\text{A})]^{3+}$

	central metal ion		
	Ce	Dy	Lu
O(3)–C(20)–C(21)–O(4)	–51	–46	–51
C(21)–O(4)–C(22)–C(23)	167	161	–179
O(4)–C(22)–C(23)–O(5)	54	46	–49
C(7)–N(1)–C(8)–C(9)	132	130	128
N(1)–C(8)–C(9)–N(2)	2	58	–60
C(8)–C(9)–N(2)–C(10)	55	62	–55
C(10)–N(2)–C(11)–C(12)	–50	–53	–174
C(9)–N(2)–C(11)–C(12)	–178	–174	–49
N(2)–C(11)–C(12)–N(3)	–72	–80	–59
C(11)–C(12)–N(3)–C(13)	–125	–127	–92

of 97.8°. Whereas, in the cerium and dysprosium complexes the angles are 53.6 and 53.0°, respectively, with a flatter disposition of the ligand around the metals. This causes a noticeable dissimilarity between the M–O (etheric) bond distances and the torsion angles of the ligand (O–C–C–O and N–C–C–N) present in the complexes. The conformation of the torsion angles O(3)–C(21)–C(22)–O(4) and O(4)–C(23)–C(24)–O(5) are *g*[–] and *g*⁺ for the Ce and Dy compounds, respectively, and *g*[–] and *g*[–] in the Lu complex. The M–(O) (etheric) bond distances decrease with the reduction of the dimensions of the central ions with a similar behavior in the Ce and Dy complexes. The decrease of the ionic radius in the case of lutetium is such that the constraints, to which the oxygen atoms O(3) and O(5) are subjected, are predominant with consequent steric hindrance in the coordination of the O(4) to the central ion. The contact distance O(3)···O(5), for example, is remarkably lower (4.07(1) Å) in the lutetium complex than in the cerium and dysprosium complexes (4.63(1) and 4.44(1) Å, respectively).

Comparable differences are present in the conformation of the torsion angles of the ligand chain not involved in the coordination; the conformations of the torsion angles N(1)–C(8)–C(9)–N(2) and N(2)–C(11)–C(12)–N(3) are *g*[–] and *g*⁺ respectively for both Ce and Dy complexes but are *g*[–] and *g*[–] for the analogues in the Lu complex. A consequence of these differences is an alteration in the direction of the methyl group C(10)H₃ bonded to the N(2) atom; where it points to the concave part of the molecule in the lutetium complex and in the opposite direction in the other two complexes. The hydrogen bonding network in the crystal structure of these complexes is remarkable and involves the three chlorine anions and all the coordinated and uncoordinated water molecules.

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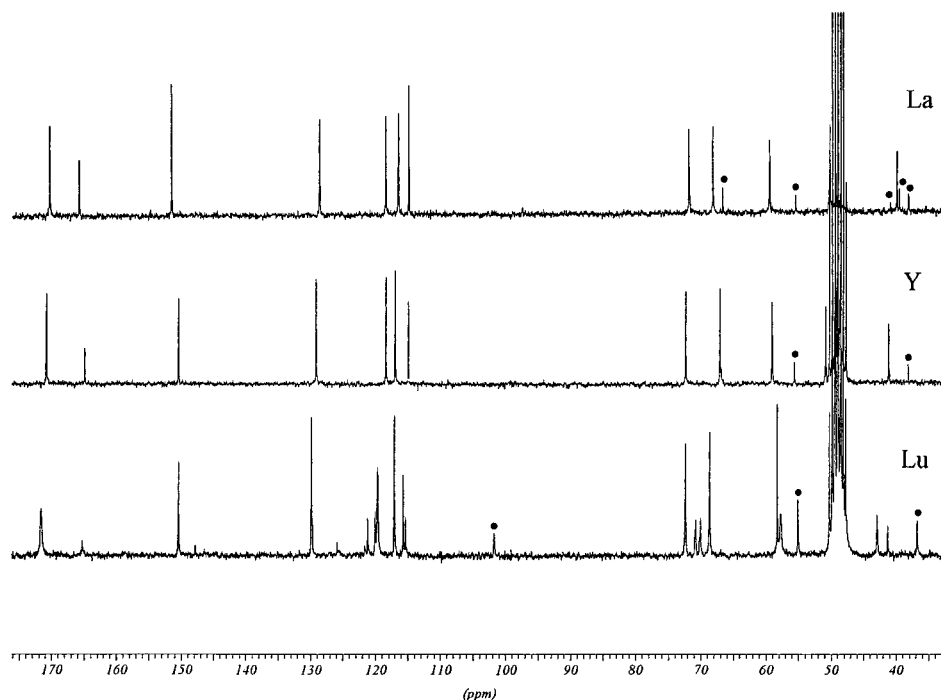


Figure 4. 200 MHz ^{13}C NMR spectra in CD_3OD of $[\text{Ln}(\text{H}_2\text{L}_A)(\text{H}_2\text{O})_4]\text{Cl}_3$ ($\text{Ln} = \text{La}, \text{Y}, \text{Lu}$) at 298 K. The resonances labeled with ● refer to impurities.

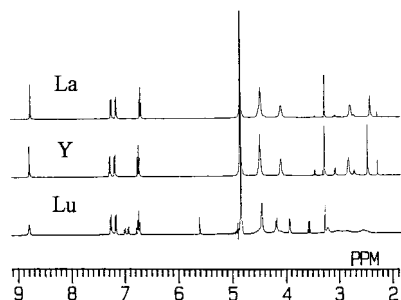


Figure 5. 400 MHz ^1H NMR spectra in CD_3OD of $[\text{Ln}(\text{H}_2\text{L}_A)(\text{H}_2\text{O})_4]\text{Cl}_3$ ($\text{Ln} = \text{La}, \text{Y}, \text{Lu}$) at 298 K.

Solution Structure and Dynamics. Spectra of Diamagnetic Complexes. The NMR spectra were recorded in 0.1 M solutions of CD_3OD where the $[\text{Ln}(\text{H}_2\text{L}_A)]^{3+}$ complexes showed good solubility. In the solid state, the conformational requirements of the diether bridges and the ethylenediamine groups result in a complex structure of low symmetry where all the carbon atoms (23) are chemically and magnetically different. The ^{13}C NMR spectra of the diamagnetic La^{3+} , Y^{3+} , and Lu^{3+} complexes at 298 K are shown in Figure 4. The spectra of the La^{3+} and Y^{3+} derivatives consist of only twelve resonances, five in the aliphatic region and seven in the chemical shift range of 115–171 ppm. Clearly, this spectral degeneracy indicates that a dynamic process is occurring in solution on the NMR time scale which averages the signals of pairs of atoms. More information is gained from the proton spectra, reported in Figure 5. Once more, the spectra of the La^{3+} and Y^{3+} derivatives are very similar and consist of eight resonances: a singlet at low field (relative intensity 1; ≈ 8.7 ppm) for the imino protons, three multiplets in the aromatic region (1:1:1; 6.7–7.5 ppm), a broad singlet (4; ≈ 4.5 ppm), two broad triplets (2:2; 2.8–4.3 ppm), and a singlet (1.5; ≈ 2.5 ppm) easily attributable to the methyl group. The complete assignment of the peaks has been possible on the basis of a 2D NOESY experiment for $[\text{La}(\text{H}_2\text{L}_A)]^{3+}$. At 298 K and by using a mixing time τ_m of 220 ms cross-peaks

were detected between the methyl group and the resonance at 2.82 ppm and between the imino protons peak and the aromatic resonance at 7.37 ppm, thus allowing the discrimination between the proton pairs 2–3 and 5–6. Finally, a heteronuclear 2D COSY experiment at 298 K provided the basis for the assignment of the ^{13}C NMR spectra. The high flexibility of the macrocycle in methanolic solution at room temperature is clearly revealed by the presence in the proton spectra of two triplets (A_2B_2 pattern) for the ethylenediamine groups and of a singlet for the diether bridges originating from a fast conformational interchange. In conclusion, the NMR spectra are consistent with the presence in solution of a time-averaged planar structure of the complexes of symmetry C_{2v} , resulting from a rapid rearrangement of the ligand about the metal ion. The most likely process involves conformational changes of the ethylenic groups (proton pairs 5–6 and 8–9) accompanied by a twisting motion of the two wings about the binary symmetry axis passing through the central O atom of the crown site, the metal ion and the $\text{N}-\text{CH}_3$ group. Then, the overall process can be described as an interchange between two enantiomeric forms to give an averaged planar structure. On the other hand, the NMR spectra do not provide precise information about the coordination scheme of the lanthanide ion and the question remains whether the coordination polyhedron found in the solid state is maintained in solution or not. In principle, the metal ion could occupy the adjacent N_3O_2 coordination site or be involved in a fast exchange between the two compartments.

The room-temperature proton and carbon NMR spectra of $[\text{Lu}(\text{H}_2\text{L}_A)]^{3+}$ show evident differences in the number and line width of the resonances in respect to the corresponding spectra of La^{3+} and Y^{3+} complexes. For instance the proton 5 is splitted in two broad multiplets and the methyl ^1H resonance appears collapsed in the baseline. In the ^{13}C NMR spectrum this latter group displays two almost equally intense resonances. Such behavior could arise from an increasing stereochemical rigidity of the complexes along the lanthanide series and from the presence of two (or more) isomeric species in slow exchange

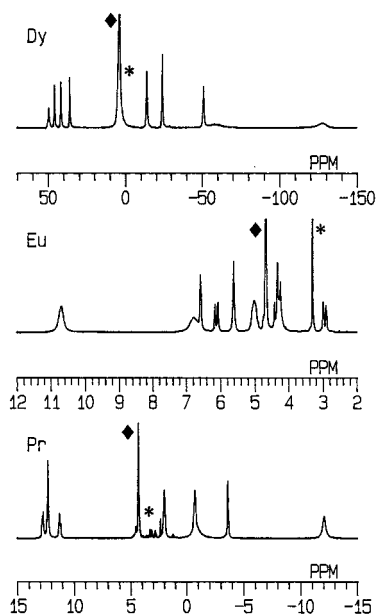


Figure 6. 90 MHz ¹H NMR spectra in CD₃OD of [Ln(H₂L_A)(H₂O)₄]-Cl₃ (Ln = Pr, Eu, Dy) at 355 K. The resonances labeled with * and ♦ refer to methanol and water protons, respectively.

or it could be ascribed to the occurrence of a structural change across the series as a result of the lanthanide contraction.^{29,30}

To address these questions we have investigated the proton spectra of the complexes with the paramagnetic ions and we will return later to reconsider the spectral properties of [Lu(H₂L_A)]³⁺.

Spectra of Paramagnetic Complexes. The ¹H NMR spectra were recorded at 2.4 T in CD₃OD for the paramagnetic [Ln(H₂L_A)]³⁺ complexes, where Ln = Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), and Yb(III). Representative spectra are shown in Figure 6. At 298 K the proton spectra of the paramagnetic lanthanide chelates from Ce(III) to Tm(III) present eight resonances (nine effectively observed only for the complexes of Sm(III), Er(III), and Tm(III)), with large differences in terms of chemical shift range (ranging from about 8 ppm for Sm(III) to more than 300 ppm for Dy(III); Table 4) and line widths. This simple observation represents an indication that the fast intramolecular rearrangement found for the La and Y complexes with H₂L_A is maintained along the lanthanide series from Ce to Tm. The 8 peaks present a relative area ratio of 1:1:1:1:1.5:2:2:2 and on this basis a straightforward distinction of the aromatic and imino protons (relative intensity 1) from the ethylenic (2) and the methyl group (1.5) can be made. With the exceptions of Sm, Er, and Tm complexes a ninth resonance, integrating to 2H and corresponding to a CH₂ group, cannot be observed at room temperature because of its extensive line broadening.

The proton spectra of the complexes of the lighter lanthanides (Ce–Eu) not only are characterized by relatively small paramagnetic shifts, but also show a limited line broadening of the resonances which allows the detection of the coupling pattern of the aromatic protons and the assignment of the imino proton. The remaining four signals (three at temperatures below 330 K), corresponding to the four ethylenic proton pairs, can be grouped into two different sets according to their relative line

broadening.³¹ The differences in the relative line broadening reflects different metal-proton distances, the broader peaks being associated with the proton nuclei of the ligand closer to the lanthanide ion. In fact, two mechanisms contribute to the paramagnetic transverse relaxation rate ($R_{2p} = \Delta\nu_{1/2}$) of the protons near a lanthanide ion other than Gd, namely the dipolar and Curie-spin contributions,³¹ respectively:

$$\pi\Delta\nu_{1/2} = R_{2p} = \frac{4}{15} \frac{\mu_B^2 \gamma_H^2 g_J^2}{r_{LnH}^6} J(J+1)\tau_S + \frac{7}{5} \frac{\omega_H^2 \mu_B^4 g_J^4}{r_{LnH}^6 (3kT)^2} J^2(J+1)^2\tau_R \quad (1)$$

where ω_H is the proton Larmor frequencies, τ_S is the electron spin relaxation time (of the order of 0.1 ps) and τ_R is the reorientational correlation time (about 80 ps at 300 K). According to eq 1, the line width of a given peak is markedly magnetic field dependent and exhibits also a dependence from the inverse sixth power of the corresponding proton–metal distance. From the X-ray structure of [Dy(H₂L_A)]³⁺ we calculate for the protons 4, 5, 6, 8, and 9 the distance values of 6.10, 5.67, 6.03, 4.07 and 3.59 Å, respectively. Thus, in the solid state the protons 4, 5, and 6 are located at a rather similar distance from the metal ion, considerably longer than that for protons 8 and 9. In solution, for the [Tb(H₂L_A)]³⁺ complex, at 90 MHz and 333 K, the imino proton 4 has a $\Delta\nu_{1/2} = 96$ Hz, whereas the four peaks of relative intensity 2 at –13.4, –25.0, –25.6, and –122.8 ppm present a line width at half height of 68, 390, 73, and 323 Hz, respectively. Thus, we may safely assign to protons 5 and 6 the peaks at –13.4 and –25.6 ppm and to protons 8 and 9 the resonances at –122.8 and –25.0 ppm. Analogous considerations enable us to distinguish aromatic protons 2 and 3. The ratio between the relaxation rates of a pair of protons do not reproduce quantitatively the ratio of the inverse sixth power of the distances, as expected on the basis of eq 1, probably because the stereochemical nonrigidity of the complexes in solution results in an “average” structure in the NMR spectra. The discrepancy between solution and solid-state distance data could also arise from a possible contribution of the scalar coupling to the measured line width, not resolved in this case ($40 \leq \Delta\nu_{1/2} \leq 393$ Hz). However, this possibility can be ruled out since very similar results are obtained by a quantitative evaluation of the Curie-spin contribution to R_{2p} (eq 1) through measurement of the magnetic field dependence of the line width (at 90, 200, 270, and 400 MHz).³¹ These results, further confirmed from the corresponding observations in the case of the complexes from Ce to Tm, show that in methanolic solution the complexes maintain the same type of coordination polyhedron found in the solid state, being the metal ion located in the crown-like site, and suggest an high degree of isostructurality along the lanthanide series.

A further proof of the spectral assignment and more structural information may be gained from an analysis of the lanthanide-induced shifts (δ_p).^{29,30,32} As a result of through-space (dipolar) and through-bond (contact) interactions between the electronic spin on the Ln(III) ion and the nuclear spins of the macrocyclic ligand nuclei, the resonance of a given proton is markedly shifted from the position observed in a corresponding diamagnetic environment (for example, the analogous La, Y, or Lu complexes):

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Table 4. Experimental ^1H NMR Chemical Shifts (ppm) for the $[\text{Ln}(\text{H}_2\text{L}_A)]^{3+}$ Complexes in CD_3OD at 2.1 T and 303 K (Peak Nomenclature Corresponds to Chart 1)

Ln	1	2	3	4	5	6	7	8	9
La	6.82	7.29	7.37	8.90	4.23	2.90	2.55	4.61	4.61
Ce	9.75	9.75	9.75	11.45	2.17	-0.35	-1.50	-7.37	-
Pr	11.71	13.01	13.31	12.54	1.41	-1.31	-5.34	-14.50	-
Nd	9.86	11.41	10.44	11.67	4.01	1.95	-0.063	-0.98	-
Sm	7.44	7.80	8.16	9.20	2.50	2.50	1.89	4.01	4.01
Eu	3.94	2.45	5.79	6.38	5.24	4.46	6.65	12.05	-
Tb	26.56	42.52	46.30	67.56	-19.76	-33.38	-51.92	-155.3	-
Dy	39.01	48.52	52.80	58.66	-20.45	-30.87	-68.13	-	-
Ho	26.02	26.02	28.64	34.26	-2.49	-8.56	-25.09	-54.89	-
Er	-2.25	-2.25	4.23	8.66	19.78	19.78	28.2	75.70	35.33
Tm	-14.80	-14.80	-14.80	-12.07	26.67	30.11	46.14	121.90	54.49
Y	6.76	7.20	7.30	8.79	4.12	2.85	2.47	4.51	4.51

Table 5. Computed Values for Dipolar (G_n) and Contact (F_n) Terms of the Isotropic Paramagnetic Proton Shifts for the Paramagnetic $[\text{Ln}(\text{H}_2\text{L}_A)]^{3+}$ Complexes Using Eq 3

	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8
F_n	0.156	0.058	-0.073	-0.314	-0.115	-0.125	-0.071	-0.133
G_n	-0.396	-0.413	-0.409	-0.442	0.329	0.457	-0.716	1.971
AF_n^a	0.28	0.12	0.16	0.18	0.18	0.16	0.07	0.09
	Ce	Pr	Nd	Eu	Tb	Dy	Ho	Er
AF_m^a	0.06	0.17	0.60	0.53	0.08	0.09	0.22	0.20

^a Agreement factors as defined in eq 5.

$$\delta_p = \delta^{\text{dip}} + \delta^{\text{con}} \quad (2)$$

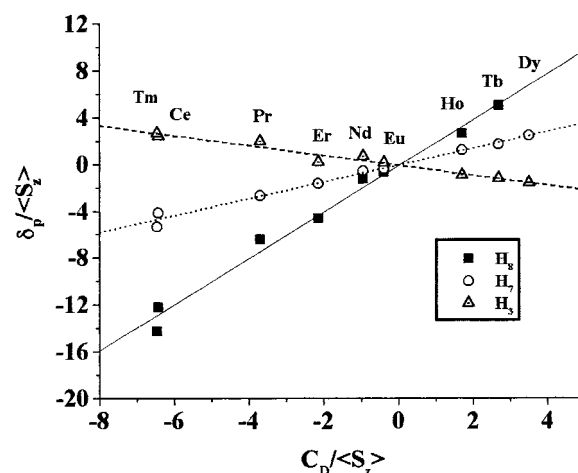
The dipolar contribution contains the information on the position in space of the ligand nuclei, whereas the contact term depends on the unpaired spin density on the same nuclei and therefore provides information on the bonding. The overall isotropic paramagnetic shift contains these two contributions and is given by

$$\delta_p = F_n \langle S_z \rangle_m + G_n C_m^{\text{D}} \quad (3)$$

where F_n depends only on the observed nucleus and is independent of the lanthanide, $\langle S_z \rangle_m$ describes the influence of the lanthanide on the scalar shifts and this value has been computed,³³ G_n contains the geometric information inherent in the location in space of the nucleus observed, and C_m^{D} is a lanthanide dependent term whose theoretical values can be found in the literature.³⁴ The isotropic shift δ_p can be separated according to the structure-independent method by Reilley *et al.* where eq 3 is rearranged into the linear form given by eq 4

$$\frac{\delta_p}{\langle S_z \rangle_m} = \frac{G_n C_m^{\text{D}}}{\langle S_z \rangle_m} + F_n \quad (4)$$

which is particularly suited for the lanthanide complexes where normally the dipolar contribution is largely prevalent ($G_n/F_n \gg 1$). Under the condition that the complexes are *isostructural*, we should obtain a *linear* plot of $\delta_p/\langle S_z \rangle_m$ against $G_n C_m^{\text{D}}/\langle S_z \rangle_m$ for a particular nucleus n of the ligand in corresponding complexes across the entire lanthanide series. This procedure has been applied to protons 1–8 in nine $[\text{Ln}(\text{H}_2\text{L}_A)]^{3+}$ complexes. The results for some representative proton nuclei (H_3 , H_7 , and H_8) are shown in Figure 7 which illustrates clearly the good linearity of the plots, with no apparent break near the middle of the series, as often observed. Thus, significant structural changes across the Ln(III) series (from Ce to Tm) can be safely excluded. Least-square values for F_n and G_n are

**Figure 7.** Separation of contact and dipolar paramagnetic shifts for representative protons of $[\text{Ln}(\text{H}_2\text{L}_A)]^{3+}$ complexes according to eq 4.

listed in Table 5. Furthermore, in the table are reported agreement factors evaluated for each nucleus (AF_n)³² and for each lanthanide ion (AF_m)³⁵ according to the following equations:

$$\text{AF}_n = \sqrt{\frac{\sum_m (\delta_{nm}^{\text{obs}} - \delta_{nm}^{\text{calc}})^2}{\sum_m (\delta_{nm}^{\text{obs}})^2}}, \quad \text{AF}_m = \sqrt{\frac{\sum_n (\delta_{nm}^{\text{obs}} - \delta_{nm}^{\text{calc}})^2}{\sum_n (\delta_{nm}^{\text{obs}})^2}} \quad (5)$$

The data of the Sm(III) complex have not been included in the analysis because of the large errors associated with this metal ion, which induces very little paramagnetic isotropic shifts. The agreement factors (AF_n) reported in Table 5 are rather good ($0.07 < \text{AF}_n < 0.28$) and similar to published data for Ln-dipicolinate complexes.³⁶

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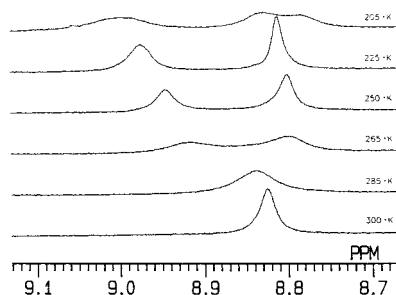


Figure 8. 400 MHz ^1H VT NMR spectra in CD_3OD for the imino protons of $[\text{Lu}(\text{H}_2\text{L}_\text{A})(\text{H}_2\text{O})_4]\text{Cl}_3$.

The AF_m factors are comprised in the range 0.08–0.60 and compare rather well with those obtained by an analogous procedure on related complexes.³⁶ The large values associated with the complexes of Nd and Eu probably reflects the inaccuracy of the method used for the separation of the contact and dipolar shifts, as discussed by Kemple and Piguet.^{35,36} As it is often the case for Ln(III) complexes, the contact contribution to the paramagnetic shift is small and nearly negligible for protons 5–7 ($-0.125 < F_\text{n} < -0.071$), to further indicate that the nitrogen atoms are not involved in the bonding to the metal ion. The large contact shift calculated for the aromatic protons could be the result of the insufficient quality of the evaluation of this term, even though significant contact contributions have been observed even at atoms that are several bonds removed.³⁷ This is particularly evident in systems with π -electron delocalization.

Conversely, the largest geometric factor G_n is calculated for H_8 as a result of a short Ln–H distance, thus confirming the analysis of the relaxation data.

Spectra of Yb(III) and Lu(III) Complexes. Remarkably different spectral features are found in the case of the heavier Yb(III) and Lu(III) derivatives. The 90 MHz ^1H NMR spectrum of $[\text{Yb}(\text{H}_2\text{L}_\text{A})]^{3+}$ at 25 °C cover a chemical shift range of about 70 ppm (from –5 to 65 ppm) and consists of a large number of broad and unresolved peaks, partially superimposed, that at higher temperature accounts for more than 20 resonances of different intensities. Clearly, a dynamic process is taking place over the entire temperature range investigated (0–55 °C) and this likely involves the interconversion of at least two different species. The marked line broadening even in the limiting spectrum at high-temperature prevents from further analysis. The NMR spectra of the Lu(III) complex are more informative. In particular, the 100.6 MHz $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum at 25 °C shows 2 different resonances for the methyl group, with relative intensity ratio of 0.7:1, to point out the presence in solution of two species. This is confirmed by a ^1H – ^{13}C 2D COSY experiment and supported by the presence of 7 peaks in the aromatic region (there were four for La(III) and Y(III) complexes) and of exceedingly broad peaks for both the imino carbon C_4 and C_{10} , probably resulting from an exchange process. At –15 °C the interconversion process is frozen out and the doubling of the peaks results more evident. Particularly clear is the behavior of the peak corresponding to H_4 in the VT 400 MHz proton spectra, reported in Figure 8. At room temperature and above a single resonance is observed at 8.8 ppm, as found in the case of the other diamagnetic derivatives. By lowering

the temperature the peak markedly broadens, disappears into the baseline (near 0 °C) and splits in two lines (–10 °C) that progressively sharpen down to –40 °C. Below this latter temperature each resonance at 8.98 and 8.81 ppm, respectively, broadens again and eventually splits in two lines in the low temperature limiting spectrum. An analogous behavior (but less clearly depicted owing to the extensive superposition of the spectral lines) can be observed in the aromatic and aliphatic regions of the proton spectra. These data are consistent with the presence in solution of two interconverting isomeric species, each one characterized by a limited number of proton and carbon resonances in the NMR spectra and thus fluxional on the NMR time scale. The isomerization process can be frozen out near –10 °C, whereas another process is still taking place, likely a conformational equilibrium of the ethylenic groups which removes the signal degeneracy in the NMR spectra.

An hypothesis about the nature of the two isomeric forms observed in the NMR spectra of the Yb and Lu complexes is not possible on the basis of the available data. However, we may notice that a hindered inversion of the N(2) atom (Figure 2) could originate two species differing in the relative orientation of the methyl group, yet maintaining the same number of resonances as a result of an analogous dynamic behavior. This could be an effect resulting from the increased stereochemical rigidity often observed for the complexes with the heavier lanthanides, as a consequence of their smaller ionic size. A particularly clear example supporting this view has been recently reported for the Ln(III) complexes of *N,N,N',N'*-tetraethylpyridine-2,6-dicarboxamide.³⁸ Solution NMR data indicate that the complexes of the heavier Ln(III) ions (Er–Lu) are kinetically inert and display a D_3 triple-helical geometry, whereas the lighter ions (La–Tb) produce complexes endowed with a D_{3h} structure originating from fast $\text{P} \leftrightarrow \text{M}$ helical interconversion. In both this example and in our case steric constraints in the coordination polyhedron are induced by the larger cations which cause a weakening of some Ln-donor atoms bonds and a more flexible structures.

Conclusions

The mononuclear lanthanide complexes $[\text{Ln}(\text{H}_2\text{L}_\text{A})(\text{H}_2\text{O})_4]\text{Cl}_3$ provide an interesting series of compounds characterized by an identical or a very similar crystal structure consisting of a coordination polyhedron better described as a distorted monocapped square antiprism.

A detailed NMR study has allowed a complete assignment of the proton resonances for both diamagnetic and paramagnetic species. The overall pattern of the NMR spectra are consistent with the maintenance in solution of the coordination features found in the solid state, although a high degree of stereochemical nonrigidity represents a common property of the complexes across the lanthanide series. The exclusive preference of all the 4f metal ions for the O_2O_3 instead of the N_3O_2 compartment offers new possibilities for the preparation of pure, heterodinuclear complexes. Studies are currently in progress along this direction in order to synthesize new magnetic probes or devices based on the peculiar molecular recognition properties of the macrocycle reported in this work.

Acknowledgment. We thank Mr. A. Aguiari and Mrs. O. Biolo for technical assistance, Progetto Strategico–CNR Tecnologie Chimiche Innovative and MURST (S.A., M.B.) for

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financial support. This work was carried out under the EU-BIOMED II-MACE Project (S.A., M.B.).

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures of $[\text{Ce}(\text{H}_2\text{L}_A)(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot \text{H}_2\text{O}$, $[\text{Dy}$ -

$(\text{H}_2\text{L}_A)(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot \text{H}_2\text{O}$, and $[\text{Lu}(\text{H}_2\text{L}_A)(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ are available free of charge via the Internet at <http://pubs.acs.org>.

IC980715R