



## Lanthanide(III) Complexes with Pyridine Head Macrocyclic Ligands

EMILIA BERTOLO<sup>1</sup>, RUFINA BASTIDA<sup>1\*</sup>, DAVID E. FENTON<sup>2</sup>, CARLOS LODEIRO<sup>1</sup>, ALEJANDRO MACIAS<sup>1</sup> and ADOLFO RODROGUEZ<sup>1</sup>

<sup>1</sup>Departamento de Química Inorgánica, Universidad de Santiago de Compostela, Avda. das Ciencias s/n, 15782 Santiago de Compostela, Spain; <sup>2</sup>Department of Chemistry, University of Sheffield S3 7HF, UK

(Received 23 July 2002; in final form: 25 September 2002)

**Key words:** lanthanide(III) complex, oxazamacrocycle, pyridine head, Schiff-base

### Abstract

The ability of lanthanide(III) ions to form stable complexes with three different macrocyclic ligands, L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup>, has been investigated. The Schiff base macrocycle L<sup>1</sup> and its corresponding reduced ligand L<sup>2</sup> are derived from 2,6-bis(2-formylphenoxy)methylpyridine and diethylenetriamine; the reduced ligand L<sup>3</sup> is derived from 2,6-diformylpyridine and N,N-bis(3-aminopropyl)methylamine. Lanthanide nitrate complexes of L<sup>1</sup> and L<sup>2</sup> have been prepared by direct reaction between each ligand and the appropriate hydrated lanthanide nitrate; attempts to obtain the corresponding perchlorate complexes have been unsuccessful. All nitrate complexes of L<sup>1</sup> give the expected [1:1, Ln:L<sup>1</sup>] stoichiometry; however, complexes obtained with L<sup>2</sup> show a [2:1, Ln:L<sup>2</sup>] stoichiometry. Finally, complexation reactions with L<sup>3</sup> have been carried out in order to investigate the coordination capability of this small and flexible ligand towards the Ln(III) ions.

### Introduction

In recent years, macrocyclic complexes with lanthanide ions are attracting considerable attention, since they have potential applications in a number of areas such as medicine, biochemistry or photochemistry [1–4]. Macrocyclic Schiff bases are of special interest, provided that they can selectively chelate particular metal ions according to the number, type and position of their donor atoms, the ionic radius of the metal ion or the coordinating properties of the counterions involved in the reaction [5, 6]. Moreover, due to the sensitivity of the Schiff-base ligands towards hydrolysis, reduction to the corresponding saturated macrocycles provides a more flexible coordination environment and thus allows investigating the influence of such changes on their complexation capacity.

One aim of our research group is the study of N<sub>x</sub>O<sub>y</sub>-donor atom macrocyclic ligands, since they are expected to form stable complexes with *d* and *f* metal ions with suitable properties for either theoretical studies or practical applications [7, 8]. Herein, we present the study of the complexation capability towards lanthanide(III) ions of three macrocyclic ligands, named L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup>. Both the Schiff base macrocycle L<sup>1</sup> and its corresponding reduced ligand L<sup>2</sup> are 20-membered N<sub>4</sub>O<sub>2</sub> donor-atom macrocycles derived from 2,6-bis(2-formylphenoxy)methylpyridine and diethylenetriamine. L<sup>3</sup> is a 14-membered N<sub>4</sub> macrocycle derived from 2,6-diformylpyridine and N,N-bis(3-aminopropyl)methylamine. The three macrocycles are depicted in Figure 1.

### Experimental

#### Instrumentation and materials

Elemental analyses were carried out by the University of Santiago de Compostela Microanalytical Service on Carlo Erba 1108 and Leco CNHS-932 microanalysers. Infrared spectra were recorded as KBr discs or using NaCl windows, using Mattson Cygnus 100, Bio-Rad FTS 135 and Bio-Rad FTS 175 C spectrometers. Proton NMR spectra were recorded using Bruker WM-250 and WM-500 spectrometers. Positive ion FAB mass spectra were recorded on a Kratos MS50TC spectrometer using a 3-nitrobenzyl alcohol (MNBA) matrix. Conductivity measurements were carried out in 10<sup>-3</sup> mol dm<sup>-3</sup> methanol or N,N-dimethylformamide solutions at 25 °C using a WTW LF-3 conductometer.

Lanthanide(III) nitrates and perchlorates were commercial products from Johnson-Matthey and Aldrich (**CAUTION:** perchlorates are potentially explosive and should be handled with care). N,N-bis(3-aminopropyl)methylamine and diethylenetriamine were supplied by Fluka. 2,6-Diformylpyridine [9, 10] and 2,6-Bis(2-formylphenoxy)methylpyridine [11] were prepared according to the literature methods. Solvents were of reagent grade purified by the usual methods.

#### Synthesis of L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup>

L<sup>1</sup> and L<sup>2</sup>, derived from 2,6-bis(2-formylphenoxy)methylpyridine and diethylenetriamine, were synthesised following a method previously described in the literature [12]. To a refluxing solution of 2,6-bis(2-formylphenoxy)methylpyridine

\* Author for correspondence: E-mail: qibastid@usc.es

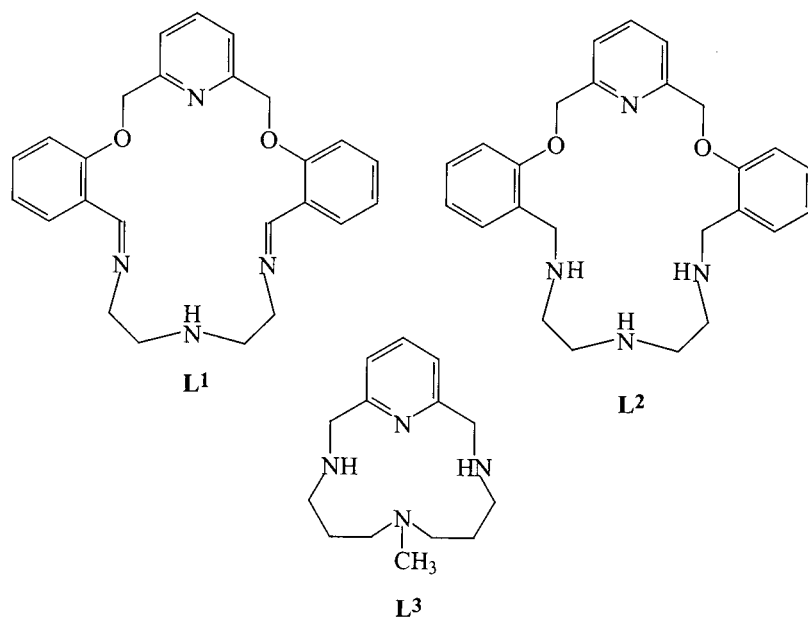


Figure 1. Ligands  $\text{L}^1$ ,  $\text{L}^2$  and  $\text{L}^3$ .

(3.0 mmol), dissolved in methanol (150 cm<sup>3</sup>), was added dropwise a solution of diethylenetriamine (3.0 mmol) in 50 cm<sup>3</sup> of the same solvent. The resulting colourless solution was refluxed *ca.* 2 h., filtered and then allowed to cool; this led to the formation of a white solid, that was filtered, dried in vacuo and recrystallised in methanol-chloroform (50% v/v). The corresponding reduced ligand  $\text{L}^2$  was prepared by direct reaction between 2,6-bis(2-formylphenoxy)methylpyridine and diethylenetriamine in methanol, followed by *in situ* reduction with sodium tetrahydroborate.  $\text{L}^3$  was prepared as described by N. W. Alcock and co-workers [13, 14], by *in situ* reductive demetallation of the corresponding Schiff base Cu(II) perchlorate complex. The three ligands were characterised by microanalysis, FAB mass spectrometry, IR and <sup>1</sup>H NMR spectroscopy; the crystal structure of  $\text{L}^3$  has been published recently by Lodeiro and co-workers [15].

$\text{L}^1$ : Yield 73%. IR (KBr, cm<sup>-1</sup>) 1638 (C=N)<sub>imi</sub>, 3431 (NH), 1600 and 1490 ((C=N)<sub>py</sub>, (C=C)<sub>ar</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, in ppm):  $\delta$  = 8.8 (s, 2H, C=NH), 7.9 (t, 1H, Py), 7.7 (d, 2H, Py); 7.3–6.6 (m, 8H, Ph), 5.2 (s, 4H, PyCH<sub>2</sub>O), 3.8 (broad s, 4H, —CH<sub>2</sub>—NH), 3.0 (broad s, 4H, C=N—CH<sub>2</sub>), 2.0 (s, 1H, NH). MS (positive-ion FAB): *m/z* 415 [ $\text{L}^1$ ]<sup>+</sup>. Anal.: Calcd. For C<sub>25</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>·H<sub>2</sub>O: C, 69.4; N, 12.9; H, 6.4. Found: C, 69.3; N 12.7; H, 6.3. The ligand is air stable, soluble in chloroform, dimethylformamide and dimethylsulfoxide, moderately soluble in acetonitrile, absolute ethanol and dichloromethane, and insoluble in methanol, hexane and diethylether.

$\text{L}^2$ : Yield 59%. IR (KBr, cm<sup>-1</sup>) 3431 (NH), 1590 and 1492 ((C=N)<sub>py</sub>, (C=C)<sub>ar</sub>);  $\delta$  = 1667 (NH) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, in ppm) 7.9 (t, 1H, Py), 7.5 (d, 2H, Py), 7.1–6.9 (m, 8H, Ar), 4.9 (s, 4H PyCH<sub>2</sub>O), 4.4 (s, 2H Ar—CH<sub>2</sub>—NH), 4.3, 3.2, 3.0, (three broad s, 12H, CH<sub>2</sub>—CH<sub>2</sub>); 2.9 (s, 1H, (CH<sub>2</sub>)<sub>2</sub>—NH—(CH<sub>2</sub>)<sub>2</sub>). Positive-ion FAB mass spectrum *m/z* = 419 [ $\text{L}^2$ ]<sup>+</sup>. Anal.: Calcd. for C<sub>25</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>·2H<sub>2</sub>O:

C, 66.0; N 12.3; H 7.4. Found: C, 66.1; N, 12.3; H, 7.3. The ligand is air stable, soluble in acetonitrile, methanol, absolute ethanol, chloroform, dimethylformamide and dimethylsulfoxide, and insoluble in hexane and diethylether.

$\text{L}^3$ : Yield 85%. IR (KBr, cm<sup>-1</sup>) 3454 (NH), 1597 and 1459 (C=N)<sub>py</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub> in ppm) 7.5 (t, 1H, Py), 6.9 (d, 2H, Py), 3.8 (s, 4H, Py—CH<sub>2</sub>), 2.9 (broad s, 2H, NH), 2.5 (t, 4H, NH—CH<sub>2</sub>), 2.3 (t, 4H, —CH<sub>2</sub>—NCH<sub>3</sub>), 1.9 (s, 3H, —CH<sub>3</sub>), 1.7 (t, 4H, CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>). Positive-ion FAB mass spectrum: *m/z* = 249 [ $\text{L}^3$ ]<sup>+</sup>. Anal.: Calc. for C<sub>14</sub>H<sub>24</sub>N<sub>4</sub>·2H<sub>2</sub>O: C, 59.2; N, 19.7; H, 9.9. Found: C, 59.8; N, 19.9; H, 9.3. The ligand is air stable, soluble in water, acetonitrile, methanol, absolute ethanol, chloroform, dimethylformamide and dimethylsulfoxide, and insoluble in hexane, petroleum ether and diethylether.

#### Synthesis of lanthanide(III) complexes of $\text{L}^1$ and $\text{L}^2$ . General procedure

To a refluxing solution of  $\text{L}^1$  or  $\text{L}^2$  in 10 cm<sup>3</sup> of the appropriate solvent (chloroform for  $\text{L}^1$  and ethanol for  $\text{L}^2$ ) was added dropwise a solution of 0.5 mmol of the corresponding lanthanide perchlorate in absolute ethanol (10 cm<sup>3</sup>). The resulting solution was refluxed for *ca.* 3–4 h.; during that period its colour slowly changed to yellow. The solution was then allowed to cool and finally concentrated to *ca.* 5 cm<sup>3</sup>, which led to the formation of a yellow precipitate; in some cases, a small amount of diethyl ether (*ca.* 2 cm<sup>3</sup>) was added to aid precipitation. The precipitate was washed with a small amount of cold ethanol and dried under vacuum. Microanalytical data are given in Table 1.

For  $\text{L}^1$ , the reaction was attempted with the nitrates of La(III), Ce(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III) Yb(III) and Lu(III), as well as the perchlorates of La(III), Ce(III), Pr(III) and Gd(III). The complexes synthesised are air stable, soluble in dimethylformamide and dimethylsulfoxide, moderately soluble in ethanol, methanol

Table 1. Analytical, yield and molar conductance data (in DMF for L<sup>1</sup> and L<sup>2</sup>, and methanol for L<sup>3</sup>) for the complexes with L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup>

	Analysis* %			Yield (%)	$\Delta_M^{**}$
	C	N	H		
LaL <sup>1</sup> (NO <sub>3</sub> ) <sub>3</sub> ·EtOH	41.6 (41.3)	12.3 (12.4)	4.3 (4.1)	34	123
CeL <sup>1</sup> (NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	35.2 (35.3)	11.9 (11.5)	3.9 (4.4)	45	159
SmL <sup>1</sup> (NO <sub>3</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	37.0 (37.2)	12.1 (12.1)	4.5 (4.0)	54	152
TbL <sup>1</sup> (NO <sub>3</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	36.2 (36.9)	12.0 (12.0)	3.8 (3.9)	52	114
Ce <sub>2</sub> L <sup>2</sup> (NO <sub>3</sub> ) <sub>6</sub> ·12H <sub>2</sub> O	23.5 (23.3)	10.3 (10.8)	3.9 (4.2)	10	186
Gd <sub>2</sub> (NO <sub>3</sub> ) <sub>6</sub> ·9H <sub>2</sub> O	23.5 (23.6)	11.8 (11.0)	3.9 (3.7)	21	175
Tb <sub>2</sub> L <sup>2</sup> (NO <sub>3</sub> ) <sub>6</sub> ·10H <sub>2</sub> O	23.6 (23.3)	10.3 (10.8)	3.9 (3.8)	18	179
Dy <sub>2</sub> L <sup>2</sup> (NO <sub>3</sub> ) <sub>6</sub> ·EtOH	27.5 (27.9)	11.9 (12.0)	3.7 (3.1)	14	182
LaL <sup>3</sup> (NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	24.8 (24.7)	14.2 (14.3)	4.7 (5.2)	53	84
EuL <sup>3</sup> (NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	23.6 (24.2)	14.3 (14.1)	5.4 (5.2)	66	95
GdL <sup>3</sup> (NO <sub>3</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	23.8 (23.4)	14.0 (13.7)	4.8 (5.3)	87	88
TbL <sup>3</sup> (NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	24.1 (24.6)	13.8 (14.3)	4.4 (4.9)	56	80
HoL <sup>3</sup> (NO <sub>3</sub> ) <sub>3</sub> ·3.5H <sub>2</sub> O	25.2 (25.4)	14.9 (14.8)	4.6 (4.7)	85	94
ErL <sup>3</sup> (NO <sub>3</sub> ) <sub>3</sub> ·5.5H <sub>2</sub> O	24.2 (24.0)	13.8 (13.9)	4.6 (5.3)	65	81
TmL <sup>3</sup> (NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	21.8 (22.0)	12.8 (12.8)	4.9 (5.5)	79	96
LaL <sup>3</sup> (ClO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	21.4 (21.2)	6.9 (7.1)	4.4 (4.5)	48	121
SmL <sup>3</sup> (ClO <sub>4</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	22.1 (21.8)	7.7 (7.3)	4.6 (4.2)	51	112
GdL <sup>3</sup> (ClO <sub>4</sub> ) <sub>3</sub> ·0.5H <sub>2</sub> O	23.7 (23.6)	7.4 (7.8)	3.7 (3.5)	77	116
HoL <sup>3</sup> (ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	22.4 (21.9)	7.7 (7.3)	4.2 (3.9)	80	105
ErL <sup>3</sup> (ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	21.9 (21.9)	7.6 (7.3)	4.0 (3.9)	58	90

\* Calculated values are given in parenthesis.

\*\* 25 °C, 10<sup>-3</sup> M ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ).

and chloroform, and insoluble in acetonitrile, diethyl ether and hexane.

In the case of L<sup>2</sup> the reaction was attempted with the nitrates of La(III), Ce(III), Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III), and the perchlorates of La(III), Ce(III), Pr(III) and Sm(III). The complexes obtained are air stable, soluble in chloroform, dimethylformamide and dimethylsulfoxide, moderately soluble in acetonitrile, methanol and absolute ethanol and insoluble in hexane and diethylether.

#### Synthesis of lanthanide(III) complexes of L<sup>3</sup>. General procedure

L<sup>3</sup> (0.15 mmol) was dissolved in methanol (35 cm<sup>3</sup>), and 0.15 mmol of the appropriate hydrated lanthanide nitrate or perchlorate, dissolved in methanol (15 cm<sup>3</sup>), were added dropwise. The resulting solution was to a vigorously stirred during ca. 72 h., and then concentrated to one third of the original volume; this led to the formation of a microcrystalline powder that was isolated and dried under vacuum. In some cases, a small amount of diethyl ether was slowly infused to aid precipitation. Microanalytical data are given in Table 1.

For L<sup>3</sup>, the reaction was attempted with the nitrates of Y(III), La(III), Eu(III), Gd(III), Tb(III), Ho(III), Er(III) or Tm(III), and the perchlorates of La(III), Ce(III), Sm(III), Gd(III), Ho(III) or Er(III). The complexes are air stable, soluble in acetone, methanol, acetonitrile, water and dichloromethane, moderately soluble in absolute ethanol, dimethylformamide, and insoluble in diethyl ether and cyclohexane.

## Results and discussion

### Microanalytical and molar conductivity data

Yield, microanalytical and molar conductivity data for the complexes characterised with the three ligands are presented in Table 1. Reaction between equimolar amounts of the Schiff base macrocyclic ligand L<sup>1</sup>, and hydrated lanthanide nitrates gave analytically pure products formulated as LaL<sup>1</sup>(NO<sub>3</sub>)<sub>3</sub>·EtOH or LnL<sup>1</sup>(NO<sub>3</sub>)<sub>3</sub> · xH<sub>2</sub>O (Ln=Ce(III), Sm(III) or Tb(III)). This reaction was also attempted with the hydrated nitrates of Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Yb(III) and Lu(III), but only free macrocycle and unreacted metal salt were recovered.

Complexation reactions between the reduced ligand L<sup>2</sup> and the hydrated lanthanide nitrates and perchlorates were carried out in order to investigate the coordination capability of this more flexible and hydrolytically stable ligand towards the Ln(III) ions. All complexes isolated with L<sup>2</sup> respond to the formula Ln<sub>2</sub>L<sup>2</sup>(NO<sub>3</sub>)<sub>6</sub> · xH<sub>2</sub>O (Ln=Ce(III), Gd(III), Tb(III) or Dy(III)); reaction with the hydrated nitrates of La(III), Sm(III) or Eu(III) did not yield the expected macrocyclic complex. Remarkably, reduction of the azomethine groups leads to a change on the stoichiometry of the complexes, suggesting that the increase of the ligand flexibility influences its capability to host more than one metal ion.

In addition, the complexation reactions were also performed with the hydrated perchlorates of La(III), Ce(III), Pr(III) and Gd(III) for L<sup>1</sup>, and La(III), Ce(III), Pr(III) and Sm(III) in the case of L<sup>2</sup>. It is noteworthy that it has not been possible to obtain complexes of L<sup>1</sup> and L<sup>2</sup> with lanthanide

perchlorates, even changing the experimental conditions or the solvent used. In the absence of a crystal structure, crucial to elucidate the coordinative environment of the metal ion in the molecule, we must be careful when attempting to explain the inability of both ligands to form stable complexes with lanthanide(III) perchlorates. It is possible that the  $L^1$  and  $L^2$  on their own are not able to respond to the high coordinative requirements of the lanthanide ions; the involvement of nitrate groups in the coordination sphere of the metal ion may increase the stability of the macrocyclic complex and thus facilitate its formation. Since perchlorate groups are weaker complexing agents towards lanthanide ions, these counterions might not be able to stabilise the corresponding macrocyclic complex.

With regard to  $L^3$ , complexation reactions with hydrated Ln(III) nitrate and perchlorates have been carried out in order to investigate the coordination capability of this small and flexible ligand towards the Ln(III) ions. Analytically pure products  $\text{LnL}^3(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (Ln=La(III), Eu(III), Gd(III), Tb(III), Ho(III), Er(III) or Tm(III)) and  $\text{LnL}^3(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$  (Ln=La(III), Sm(III), Gd(III), Ho(III) or Er(III)) have been isolated and characterised; under the experimental conditions employed, reactions with Ce(III) perchlorate and Y(III) nitrate have been unsuccessful, since only free macrocycle and unreacted metal salt were recovered.

Molar conductivity data for complexes with  $L^1$  and  $L^3$ , measured in dimethylformamide (for  $L^1$ ) or methanol (for  $L^3$ ), are in the range reported for 1:1–2:1 electrolytes in this solvent [16]; this suggests the existence of coordinated counterions, at least in these solvents, and also most likely in the solid state. On the other hand, the values obtained in dimethylformamide for the complexes with  $L^2$  are higher, in the range of those reported for 2:1–3:1 electrolytes. Molar conductivity measurements for each complex were recorded 15 m, 30 m, 1 h and 2 h after preparation of the sample; in the case of complexes with  $L^1$  and  $L^2$ , a significant increase in the values was observed for all cases, suggesting displacement of counterions from the coordination sphere by solvent molecules; no significant effect was observed for  $L^3$  complexes.

#### Mass spectral results

The FAB mass spectra show in all cases a peak corresponding to the protonated ligand as the most intense one, at  $m/z$  415 ( $L^1$ ), 419 ( $L^2$ ) or 249 ( $L^3$ ); this confirms the stability of the three ligands in their complexes. All spectra show peaks at higher molecular mass, that in some cases have been assigned to different molecular fragments. For  $L^1$ , the spectrum of the La(III) complex shows a peak at  $m/z$  677, corresponding to the fragment  $[\text{LaL}^1(\text{NO}_3)_2]^+$ . In the case of  $L^2$ , the spectrum of the Gd(III) complex shows peaks at  $m/z$  436 and 732, corresponding to the fragment  $[\text{L}^2(\text{H}_2\text{O}) + \text{H}]^+$  and  $[\text{Gd}_2\text{L}^2]^+$  respectively; moreover, in the Tb(III) complex it is possible to observe a peak at  $m/z$  853, corresponding to the species  $[\text{Tb}_2\text{L}^2\text{NO}_3(\text{H}_2\text{O})_3]^+$ . With regard to  $L^3$ , the spectra of the nitrate complexes of La(III), Gd(III), Tb(III) and Er(III) show a peak attributable to the molecular

ion  $[\text{LnL}^3(\text{NO}_3)_2]^+$  at  $m/z$  512, 531, 532 and 541 respectively; the spectrum for the Eu(III) complex features a peak at  $m/z$  650, attributable to the molecular fragment  $[\text{Eu}(\text{L}^3)_2]^+$ , formed under FAB conditions. Unfortunately, even though the spectra of the perchlorate complexes show peaks at  $m/z$  higher than that of  $L^3$  protonated (at 249), they cannot be assigned to any particular molecular fragment.

#### IR spectra

The IR spectra play an important role in confirming the stability of the ligands in their macrocyclic complexes. The spectra for the complexes with  $L^1$  show a medium band at 1632–1640  $\text{cm}^{-1}$  attributable to the azomethine group, and the absence of bands corresponding to carbonyl groups confirms the stability of the ligand in the metal complexes. In addition, the spectra for the complexes of  $L^2$  and  $L^3$  do not show bands attributable to the azomethine or carbonyl groups, confirming again the stability of both reduced ligands in their complexes. For  $L^1$  and  $L^2$ , bands attributable to  $\nu(\text{NH})$  cannot be observed due to the existence of a broad band at *ca.* 3450  $\text{cm}^{-1}$  assignable to the stretching and bending modes of water; however, bands at *ca.* 1665  $\text{cm}^{-1}$ , attributable to  $\delta(\text{NH})$ , can be observed in the spectra for Ce(III) and Sm(III) complexes with  $L^1$  and the Ce(III) complex with  $L^2$  [17]. All spectra exhibit medium to strong bands at *ca.* 1600 and 1490  $\text{cm}^{-1}$  as expected for the two highest-energy  $\nu(\text{C}=\text{N})_{\text{py}}$  and  $\nu(\text{C}=\text{C})_{\text{ar}}$  vibrations [18].

The absorptions of the nitrate counterions provide some useful structural information. The presence of strong absorption bands at 1459–53 ( $\nu_5$ ), 1297–1304 ( $\nu_1$ ) and 756–760 ( $\nu_3$ )  $\text{cm}^{-1}$  indicates the presence of coordinated nitrate groups [19, 20]. The two highest frequency bands are separated by *ca.* 160  $\text{cm}^{-1}$ . The magnitude of this separation indicates a strong interaction of the oxygen atoms of the nitrates with the lanthanide ions, typical of bidentate coordination [21]. When the spectra are recorded as KBr discs, one very intense band at *ca.* 1383  $\text{cm}^{-1}$ , characteristic of ionic nitrate, is observed, in Fluorolube this band disappears indicating that bromide ion can displace a co-ordinated nitrate [22].

The IR spectra of the perchlorate complexes with  $L^3$  show absorption bands at *ca.* 1120 ( $\nu_3$ ) and 630 ( $\nu_4$ )  $\text{cm}^{-1}$ , assignable to the asymmetric Cl—O stretching mode and the asymmetric Cl—O bending-mode, respectively [23, 24]. Both exhibit considerable splitting due to the reduced symmetry of the coordinated species, suggesting the presence of coordinated perchlorates in the complex [25]; the  $\nu_3$  band has three maxima at *ca.* 1120, 1087 and 1100  $\text{cm}^{-1}$ , and the lower-energy band also shows splitting with two maxima at 636 and 627  $\text{cm}^{-1}$ . However, in the absence of crystal structure determinations, our information is not enough to allow the assignment of definitive molecular geometries.

#### NMR spectra

The  $^1\text{H}$  NMR spectra for the diamagnetic La(III) nitrate complexes of  $L^1$  and  $L^3$ , as well as the La(III) perchlorate complex with  $L^3$  were recorded immediately after dissol-

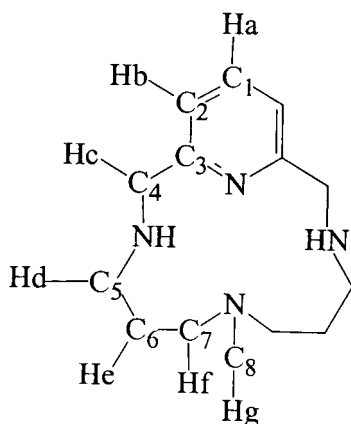


Figure 2. Proton and carbon assignment for the NMR spectra of  $\text{LaL}^3(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (500 MHz,  $\text{DMSO-d}_6$ ).

Table 2.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR data for the complex  $\text{LaL}^3(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (500 MHz,  $\text{DMSO-d}_6$ )

Assignment	$\delta$ (ppm)	Assignment	$\delta$ (ppm)
H <sub>a</sub>	7.90 (t, 1H)	C <sub>1</sub>	138.2
H <sub>b</sub>	7.35 (d, 2H)	C <sub>2</sub>	121.9
H <sub>c</sub>	4.20 (s, 4H)	C <sub>4</sub>	50.7
H <sub>d</sub>	2.90 (t, 4H)	C <sub>5</sub>	45.2
H <sub>e</sub>	1.80 (t, 4H)	C <sub>6</sub>	23.9
H <sub>f</sub>	2.40 (t, 4H)	C <sub>7</sub>	54.4
H <sub>g</sub>	2.50 (s, 3H)	C <sub>8</sub>	40.0
		C <sub>3</sub>	153.6

ution of the samples in DMSO, and gave the expected simple spectrum, confirming the integrity of the three ligands in the metal complexes. The spectrum for the complex  $\text{LaL}^1(\text{NO}_3)_3 \cdot \text{EtOH}$  is very similar to that of the free macrocycle, and there is no significant shifting of the signals. This suggests that competition between the DMSO molecules and the macrocyclic ligands for the lanthanide ion could result in removal of the metal ion from the ligand, which could be eventually followed by ligand breakdown; however, the latter must be discarded, since the spectra obtained after 12 h, 24 h or even several days were similar to the initial ones, demonstrating the stability of the ligand in DMSO solution.

On the contrary, signals in the spectra of the La(III) perchlorate and nitrate complexes with  $\text{L}^3$  are slightly shifted towards low field when compared to those of the free ligand, probably due to coordination effects of the metal ion. Again, the spectra obtained after 12 h, 24 h or several days were similar to the initial ones. The complex  $\text{LaL}^3(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was studied by  $^{13}\text{C}$ , homonuclear COSY 45, HMQC and DEPT-135; the proton and carbon assignment presented in Figure 2 and Table 2. The  $^{13}\text{C}$  NMR spectrum for the complex shows 8 signals, as expected for the number of non-equivalent C atoms in  $\text{L}^3$ .

## Conclusions

The interaction of lanthanide(III) ions with the Schiff-base macrocycle  $\text{L}^1$  and the reduced ligands  $\text{L}^2$  and  $\text{L}^3$  has been investigated.  $\text{L}^1$  and  $\text{L}^2$  derive from 2,6-bis(2-formylphenoxymethyl)pyridine and diethylenetriamine. Macrocyclic lanthanide(III) complexes of these two ligands have been prepared by direct reaction between the corresponding ligand and the appropriate hydrated lanthanide nitrate; under the experimental conditions described in the experimental section it has not been possible to isolate the corresponding perchlorate complexes. All nitrate complexes of  $\text{L}^1$  give the expected  $[1:1, \text{Ln}:\text{L}^1]$  stoichiometry; however, when the complexation reactions have been carried out with  $\text{L}^2$ , all complexes obtained show a  $[2:1, \text{Ln}:\text{L}^2]$  stoichiometry. In addition, mononuclear Ln(III) complexes with  $\text{L}^3$ , derived from 2,6-diformylpyridine and N,N-bis(3-aminopropyl)methylamine, have been successfully isolated and characterised, showing the possibility of obtaining stable Ln(III) complexes with this small macrocycle.

## Acknowledgements

We thank La Xunta de Galicia (PGIDT01PXI20901PR) for financial support.

## References

- G.F. de Sá, O.L. Malta, C. de Mello Donegá, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, and E.F. da Silva Jr.: *Coord. Chem. Rev.* **196**, 165 (2000).
- E. Constable: *Coordination Chemistry of Macrocyclic Compounds*, Oxford University Press, Oxford (1999).
- C.F.G. Geraldes: *NMR in Supramolecular Chemistry*, Kluwer Academic Publishers, Dordrecht, p. 133 (1999).
- Yu. A. Zolotov (ed): *Macrocyclic Compounds in Analytical Chemistry*, in J.D. Winefordner (series ed.), *A Series of Monographs on Analytical Chemistry and its Applications*, Vol. 143, Wiley-Interscience, New York (1997).
- B. Dietrich, P. Viout, and J.-M. Lehn: *Macrocyclic Chemistry*, VCH Verlagsgesellschaft, Weinheim (1993).
- P. Guerriero, S. Tamburini, and P.A. Vigato: *Coord. Chem. Rev.* **17**, 139 (1995).
- E. Bertolo, R. Bastida, D.E. Fenton, C. Lodeiro, A. Macías, and A. Rodríguez: *J. Alloy Compd.* **323/324**, 155 (2001).
- M. Vicente, C. Lodeiro, H. Adams, R. Bastida, A. de Blas, D.E. Fenton, A. Macías, A. Rodríguez, and T. Rodríguez-Blas: *Eur. J. Inorg. Chem.* 1015 (2000).
- D. Jerchel and H.E. Heck: *Justus Liebigs Ann. Chem.* **613**, 180 (1958).
- P. Moore, N.W. Alcock, R.G. Kingston, and C. Perpoint: *J. Chem. Soc., Dalton Trans.* 2543 (1987).
- L.P. Battaglia, A. Bonamartini Corradi, and M. Mangia: *Inorg. Chim. Acta* **42**, 191 (1980). N.A. Bailey, D.E. Fenton, S.J. Kitchen, T.H. Lilley, M.G. Williams, P.A. Tasker, A.J. Leong, and L.F. Lindoy: *J. Chem. Soc., Dalton Trans.* 627 (1991).
- B. Najera: PhD. thesis, University of Sheffield, Sheffield (1998).
- N.W. Alcock, P. Moore, and H.A.A. Omar: *J. Chem. Soc., Dalton Trans.* 985 (1986)
- N.W. Alcock, K.P. Balakrishnan, and P. Moore: *J. Chem. Soc., Chem. Commun.* 1731 (1985).
- C. Lodeiro, R. Bastida, A. Macías, A. Rodríguez, and A. Saint-Maurice: *Acta Cryst.* **C56**, e255–e256 (2000).
- W.J. Geary: *Coord. Chem. Rev.* **7**, 81 (1971).
- K. Nakamoto: *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley Interscience, New York (1978).

18. S.M. Peng, G.C. Gordon, and V.L. Goedken: *Inorg. Chem.* **17**, 119 (1978).
19. J.R. Ferraro: *J. Inorg. Nucl. Chem.* **10**, 319 (1959).
20. V.A. Aruma and V. Alexander: *Inorg. Chim. Acta* **249**, 319 (1996).
21. S. James, D.S. Kumar, and V. Alexander: *J. Chem. Soc. Dalton Trans.* 1773 (1999).
22. F. Avecilla, R. Bastida, A. de Blas, D.E. Fenton, A. Macías, A. Rodríguez, T. Rodríguez-Blas, S. García-Granda, and R. Corzo-Suarez: *J. Chem. Soc., Dalton Trans.* 409 (1997).
23. A.J. Hathaway and A.E. Underhill: *J. Chem. Soc.* 3091 (1961).
24. S.F. Pavkovic and D.W. Meek: *Inorg. Chem.* **4**, 1091 (1965).
25. L. De Cola, D.L. Smailes, and L.M. Vallarino: *Inorg. Chem.* **25**, 1729 (1986).