Lanthanide(III) Complexes of Two Novel N₃O₄-donor Macrocycles Derived from 3,6-Dioxa-1,8-Octanediamine

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Abstract

Two novel N_3O_4 macrocycles, L^1 and L^2, have been synthesised, and their complexation potential towards Ln(III) ions has been investigated. Direct cyclocondensation between 2,6-bis(2-formylphenoxymethyl)pyridine and 3,6-dioxa-1,8-octanediamine yields the macrocycle L^1 as the main product. The diamine macrocycle L^2 is formed by reaction of the diamine and dicarbonyl precursors followed by an *in situ* reduction with $NaBH_4$. Series of Ln(III) complexes have been obtained for both ligands, by direct synthesis between L^1 or L^2 and different Ln(III) hydrated nitrates or perchlorates; however, attempts to synthesise the corresponding Ln(III) complexes with L^1 following a template method have been unsuccessful. All complexes obtained with L^1 give a [2:1, Ln:L^1] stoichiometry. The reduction of the diiminic bonds increases the flexibility of the macrocycle and leads to a change in the stoichiometry; all complexes obtained with L^2 show a [3:1, Ln:L^2] relation.

Introduction

Lanthanide ions and their complexes are extraordinarily effective catalysts for the hydrolytic cleavage of phosphate ester bonds, including those of DNA and RNA [1, 2]. The challenge lies in designing ligands with the appropriate characteristics: for example, a ligand must bind to the metal ion strongly, so that it can be attached to a sequence-specific recognition agent. Macrocyclic ligands are of great interest, since they can bind metal ions with a high degree of thermodynamic stability and/or kinetic inertness. Schiff-base macrocyclic ligands were among the first examples of Ln(III) complexes developed as nucleases; Morrow *et al.* [3] showed that Schiff base Ln(III) complexes could hydrolyse RNA bonds catalytically. More recently, Zhu *et al.* have reported the synthesis of lanthanide dinuclear complexes which can catalyse the hydrolysis of plasmid DNA [4]

Our group is interested in the study of macrocycles containing nitrogen and oxygen as donor atoms, and their reactivity towards lanthanide ions. In previous papers, we have already reported the ability of N_xO_y-macrocycles derived from 2,6-bis(2-formylphenoxymethyl)pyridine to obtain highly stable complexes with lanthanide ions [5, 6]. We now present the synthesis and characterisation of two novel 23-membered N_3O_4 macrocycles, L^1 and L^2, derived from 2,6-bis(2-formylphenoxymethyl)pyridine and 3,6-dioxa-1,8-octanediamine (see Figure 1). The Schiff-base ligand L^1 has been synthesised by direct reaction between the dicarbonilic and diaminic precursors. The corresponding saturated ligand L^2, more flexible and more stable against hydrolysis, has been obtained by reduction of L^1 in absence of any metal ion. The coordination ability of both ligands towards lanthanide(III) ions has been investigated, and series of di and tri nuclear Ln(III) complexes have been obtained.

Experimental

Elemental analyses were carried out by the University of Santiago de Compostela Microanalytical Service on a Carlo Erba 1108 and a Leco CNHS-932 microanalysers. IR spectra were recorded, in NaCl windows or as KBr discs, using a Bio-Rad FTS 135 and a FTS 175 C spectrophotometers. NMR spectra were recorded using a Bruker DPX-250 and a AM-500 spectrometers. Positive ion FAB mass spectra were recorded on a Kratos MS50TC spectrometer using a 3-nitrobenzyl alcohol matrix. Melting points were carried out using a BÜCHI melting point apparatus. Conductivity measurements were carried out in *ca.* 10^{-3} mol dm^{-3} N,N-dimethylformamide solutions at 20 °C, using a WTW LF-3 conductometer.

2,6-Bis(2-formylphenoxymethyl)pyridine [7, 8] was prepared according to literature methods. 3,6-Dioxa-1,8-octanediamine (Merck), and lanthanide(III) perchlorates and nitrates (Johnson-Matthey), were commercial products, used without further purification. Solvents were of reagent grade purified by the usual methods. CAUTION: Perchlorates are potentially explosive.

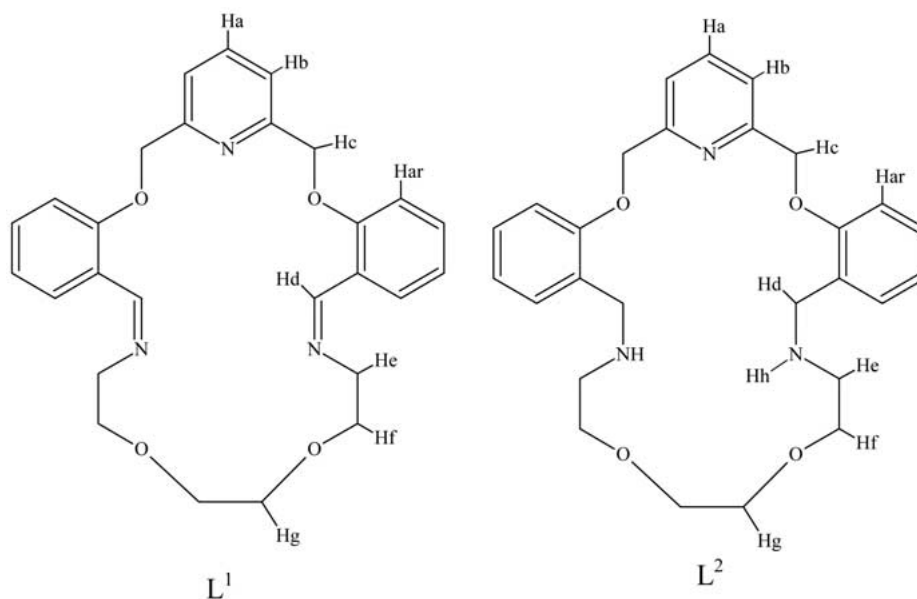* Author for correspondence. E-mail: qibastid@usc.es

Figure 1. Ligands L^1 and L^2, with the proton assignation for the NMR discussion.

Synthesis of L^1 and L^2. General procedure

L^1 was prepared by direct reaction between the di-carbonilic and diaminic precursors. A solution of 3,6-dioxa-1,8-octanediamine (1 mmol) in acetonitrile (50 cm³) was added dropwise to a refluxing solution of 2,6-bis(2-formylphenoxymethyl)pyridine (1 mmol) in the same solvent (75 cm³). The solution was gently refluxed with magnetic stirring for *ca.* 3 h, during which the colour changed slowly to yellow. The solution was allowed to cool and then concentrated to 5 cm³; careful addition of diethyl ether (*ca.* 5 cm³) produced a yellow powder. The product was filtered off, washed with absolute ethanol and dried in vacuo.

L^2 was prepared following a method previously reported for similar macrocycles [5], by direct reaction between 3,6-dioxa-1,8-octanediamine and 2,6-bis(2-formylphenoxymethyl)pyridine, followed by *in situ* reduction with sodium tetrahydroborate. L^2 was isolated as colourless oil, and dried in vacuo. Both ligands are air stable, soluble in acetone, acetonitrile, chloroform, dimethylformamide, dimethylsulfoxide, ethanol and methanol, and insoluble in diethyl ether and hexane.

L^1: Yield 72%. Anal. Calc. for $C_{27}H_{29}N_3O_4 \cdot H_2O$: C, 67.9; N, 8.8; H 6.5%. Found: C 67.3; N, 8.5; H 6.2%. Melting point: 180 °C. FAB: $[L^1 + H]^+$ 460. IR: $\nu(CN)_{imi}$ 1639 cm⁻¹; $\nu(C=C)_{ar}$, $\nu(C=N)_{py}$ 1597, 1488 cm⁻¹.

L^2: Yield 45%. Anal. Calc. for $C_{27}H_{33}N_3O_4 \cdot 3H_2O$: C, 62.6; N, 8.1; H 7.5%. Found: C 62.9; N, 8.0; H 7.8%. FAB: $[L^2 + H]^+$ 464. IR: $\nu(NH)$ 3335 cm⁻¹; $\delta(NH)$ 1665 cm⁻¹; $\nu(C=C)_{ar}$, $\nu(C=N)_{py}$ 1594, 1490 cm⁻¹.

Template synthesis of L^1 in the presence of metal ions. General procedure

To a refluxing solution of 2,6-bis(2-formylphenoxymethyl) pyridine (1 mmol) in acetonitrile (40 cm³) was added a solution of 1 mmol of $Ln(X)_3 \cdot xH_2O$ (X = ClO_4^-; Ln = La(III), Ce(III), Pr(III); X = NO_3^-; Ln = La(III), Nd(III), Sm(III), Gd(III)) in the same solvent (10 cm³); after heating for *ca.* 30 minutes, an acetonitrile solution (50 cm³) of 3,6-dioxa-1,8-octanediamine (1 mmol) was added dropwise. The colour changed slowly to yellow, and refluxing was continued for a further 2–3 h. The solution was allowed to cool and then concentrated to *ca.* 10 cm³, and an equal volume of diethyl ether was slowly infused into the solution producing powdery precipitates. It has not been possible to identify any of these products. Further attempts to synthesise complexes of L^1 with lanthanide(III) salts, by changing the conditions employed were always unsuccessful.

Direct synthesis of lanthanide(III) complexes with L^1. General procedure

To a refluxing solution of L^1 (0.1 mmol) in acetonitrile (20 cm³) was added dropwise a solution of 0.1 mmol of the corresponding hydrated lanthanide perchlorate (La(III), Ce(III), Pr(III), Gd(III), Sm(III) or Er(III)) or nitrate (La(III), Ce(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) or Lu(III)) dissolved in the same solvent (10 cm³). The resulting yellow solution was refluxed during 3-4 h and then allowed to cool. The volume was reduced to *ca.* 10 cm³ and the same volume of diethyl ether was added to aid precipitation. The complexes were filtered off, washed with a little cold ethanol and dried under vacuum. Microanalytical data are given in Table 1. The complexes were isolated as yellow solids, air-stable, soluble in acetonitrile, chloroform, dimethylformamide, dimethylsulfoxide, ethanol and methanol, and insoluble in hexane and diethyl ether.

Table 1. Analytical, molar conductance (in DMF) and FAB (in mnba) data for the complexes with L^1 and L^2

| | Analysis* % | | | Δ_M** | FAB data | |
	%C	%N	%H		Assignment	Peak
$La_2L^1(ClO_4)_6$	24.8 (24.3)	3.0 (3.1)	2.4 (2.1)	210	$[L]^+$	460
$La_2L^1(NO_3)_6.9H_2O$	25.3 (25.5)	9.8 (9.9)	3.1 (3.7)	190	$[L]^+$	460
					$[La_2L]^+$	737
$Ce_2L^1(NO_3)_6.4H_2O$	27.5 (27.4)	10.9 (10.6)	3.5 (3.1)	180	$[L]^+$	460
$Sm_2L^1(NO_3)_6.10H_2O$	24.1 (24.7)	9.3 (9.6)	3.5 (3.7)	185	$[L]^+$	460
$Eu_2L^1(NO_3)_6.7H_2O$	25.1 (25.7)	10.1 (9.9)	3.8 (3.4)	170	$[L]^+$	460
$Gd_2L^1(NO_3)_6.14H_2O$	23.6 (23.2)	8.9 (9.0)	4.2 (4.1)	196	$[L]^+$	460
					$[Gd_2L(NO_3)_4]^+$	1023
$Tb_2L^1(NO_3)_6.7H_2O$	25.8 (25.4)	9.5 (9.8)	4.0 (3.4)	183	$[L]^+$	460
$Dy_2L^1(NO_3)_6.6H_2O$	25.5 (25.6)	9.3(9.9)	3.9 (3.2)	195	$[L]^+$	460
					$[Dy_2L(NO_3)]^+$	849
$La_3L^2(ClO_4)_9$	18.7 (18.2)	2.6 (2.3)	2.5 (1.8)	205	$[L]^+$	464
$Gd_3L^2(ClO_4)_9$	17.3 (17.7)	2.5 (2.3)	1.8 (1.8)	200	$[L]^+$	464
$La_3L^2(NO_3)_9.9H_2O$	20.4 (20.2)	10.4 (10.5)	3.5 (3.2)	180	$[L]^+$	464
					$[La_2L(NO_3)_3]^+$	927
					$[La_3L(NO_3)_6]^+$	1252
$Sm_3L^2(NO_3)_9.10H_2O$	19.3 (19.2)	10.1 (10.1)	3.4 (3.2)	189	$[L]^+$	464
					$[SmL]^+$	613
					$[Sm_2L(NO_3)_7(H_2O)_2]^+$	1390
$Dy_3L^2(NO_3)_9.10H_2O$	19.5 (19.2)	9.8 (9.9)	3.2 (3.1)	185	$[L]^+$	464
$Gd_3L^2(NO_3)_9.10H_2O$	19.4 (19.3)	9.9 (10.0)	3.3 (3.2)	179	$[L]^+$	464
					$[Gd_3L(H_2O)_3]^+$	991
					$[Gd_3L(NO_3)_7(H_2O)]^+$	1389

* Calculated values are given in parentheses.
**25 °C, 10^{-3} M (Ω^{-1} cm$_2$mol^{-1}).

Direct synthesis of lanthanide(III) complexes with L^2. General procedure

An ethanolic solution (10 cm^3) of 0.1 mmol of the corresponding hydrated lanthanide perchlorate (La(III), Ce(III), Pr(III), Gd(III), Sm(III) or Er(III)) or nitrate (La(III), Ce(III), Sm(III), Eu(III), Gd(III) or Lu(III)) was added dropwise to a refluxing solution of L^2 (0.1 mmol) in absolute ethanol (20 cm^3). The resulting colourless solution was refluxed during 3–4 h, during which a white turbidity began to form. The solution was allowed to cool and the volume was reduced to *ca.* 10 cm^3. In some cases, a white solid precipitated directly from the solution; in other cases, a small amount of diethyl ether was added to aid precipitation. The complexes were filtered off, washed with a little cold ethanol and dried under vacuum. Microanalytical data are given in Table 1. The complexes were isolated as yellow solids, air-stable, soluble in acetonitrile, chloroform, dimethylformamide, dimethylsulfoxide and methanol, moderately soluble in ethanol, and insoluble in hexane and diethyl ether.

Results

Elemental analysis data, molar conductivities and mass spectral results

Reaction between 2,6-bis(2-formylphenoxymethyl)pyridine and 3,6-dioxa-1,8-octanediamine yields the [1 + 1] Schiff-base macrocycle L^1 as the main product. The corresponding reduced macrocyclic ligand L^2 can be obtained by *in situ* reduction of L^1 with sodium tetrahydroborate. The two ligands were characterised by elemental analysis, FAB mass spectrometry and IR and NMR spectroscopy; data are given in the experimental section.

Under the experimental conditions employed, it has not been possible to isolate Ln(III) complexes with L^1 following a template method. The syntheses have been carried out with the perchlorates of La(III), Ce(III) and Pr(III), and the nitrates of La(III), Nd(III), Sm(III) and Gd(III). Spectroscopic data suggest the formation of the corresponding macrocyclic complexes, but also show impurities due to the presence of unreacted precursors and/or acyclic products.

Complexes of both ligands have been obtained using a direct method; analytical, conductivity and mass spectrometry data are presented in Table 1. For L^1, analytically pure compounds formulated as $La_2L^1(ClO_4)_6$ and $Ln_2L^1(NO_3)_6.xH_2O$ (Ln = La(III), Ce(III), Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III)), have been isolated and characterised. Also, reaction between equimolecular amounts of L^2 and the hydrated Ln(III) salts yields complexes formulated as $Ln_3L^2(ClO_4)_9$ (Ln = La(III) and Gd(III)) and $Ln_3L^2(NO_3)_9.xH_2O$ (Ln = La(III), Sm(III), Gd(III) and Dy(III)). In order to discard that the stoichiometries obtained were due to unreacted metal salt, the complexes were washed with small amounts of absolute ethanol, methanol or acetonitrile; recrystallisation in different solvents was also

conducted. In none of the cases it was possible to observe a change in the stoichiometry. All complexes present fairly high molar conductivity values in dimethylformamide, in the range reported for 2 : 1–3 : 1 electrolytes in this solvent [9].

The FAB mass spectra confirm the monomeric [1 + 1] nature of L^1 and L^2, by featuring the molecular ion peaks at m/z 460 and 464, which correspond to $[L^1 + H]^+$ and $[L^2 + H]^+$ respectively. These two peaks also appear in the spectra of the complexes, confirming the stability of both macrocycles in the metal complexes. All spectra show peaks at higher molecular weights, which in some cases have also been assigned to di and trinuclear species; results are presented in Table 1.

Infrared spectroscopy

The spectra of L^1 and its complexes, registered as KBr discs, clearly show a band attributable to imine groups at *ca.* 1639 cm^{-1}, and the absence of bands attributable to carbonyl and/or amine groups. The spectrum of the reduced ligand L^2, registered in NaCl windows, features bands assignable to secondary amine N–H stretching and bending modes at *ca.* 3335 and 1665 cm^{-1} respectively, and no bands attributable to imine bonds can be observed. In the spectra of the complexes, the absorption band attributable to the stretching mode is hidden by a broad band at *ca.* 3400 cm^{-1}, due to the presence of water molecules in the complexes [10]. The spectra for the complexes of L^2 with Sm(III) and Gd(III) feature bands attributable to the N–H bending mode, at 1653 and 1663 cm^{-1} respectively. For the perchlorate complexes, the broadening and splitting of the absorption bands at *ca.* 1100 (v_3) and *ca.* 630 (v_4) cm^{-1}, assignable to the asymmetric Cl–O stretching and symmetric Cl–O bending modes respectively, suggest the presence of coordinated perchlorate groups [11]. For the nitrate complexes, the presence of strong absorption bands at *ca.* 1451 (v_5), 1300 (v_1), 826 (v_3), and 754 (v_3) cm^{-1} indicates the presence of coordinated nitrate groups [12, 13]. The magnitude of the separation between $v_5 - v_1$ is typical of bidentate coordination [14].

NMR spectroscopy

Figure 1 shows the proton assignation, so the following discussion can be followed more easily. A complete NMR study of both ligands (^{1}H, ^{13}C, DEPT, COSY-45, HMQC) was performed. Spectra were collected immediately after sample preparation, and 24, 48 and 72 hours later; no difference was observed, showing the integrity of the ligands in solution. The ^{1}H NMR spectrum for L^1 (in CD$_3$CN) clearly shows a peak at 8.7 ppm, corresponding to the imine protons. The ^{1}H NMR spectrum of L^2 (in CDCl$_3$) does not feature a signal attributable to the imine protons. Two new signals appear at 3.85 and 2.20 ppm, corresponding to H_d and H_h respectively; the latter was confirmed by D$_2$O exchange. The ^{13}C spectrum of L^1 features 14 signals, as expected for the symmetry of the macrocycle. The ^{13}C spectrum for L^2 features 27 signals, one for each C in the macrocycle, suggesting that the reduction of the iminic bonds leads to an increase in the ligand flexibility. The increase in the number of signals has

already been observed in another macrocyclic ligand also derived from 2,6-bis(2-formylphenoxymethyl)pyridine [15].

^{1}H NMR spectra of La$_2$L^1(ClO$_4$)$_6$, La$_2$L^1(NO$_3$)$_6$.9H$_2$O, La$_3$L^2(ClO$_4$)$_9$ and La$_3$L^2(NO$_3$)$_9$.9H$_2$O were recorded in CD$_3$CN; a spectrum of L^2 was recorded in CD$_3$CN for comparative reasons. The spectra for the complexes with L^1 are not very informative due to the low resolution of the signals. The spectra for the complexes with L^2 show some differences in the positions of the signals with respect to those of the free ligand. The peak attributable to H_c, that appears at 5.2 ppm in the spectrum of the free ligand (in CD$_3$CN), is shifted to 5.4 ppm in the spectrum of the complexes. The peaks attributable to the aliphatic part of the ligand (H_d, H_e, H_f, and H_g) are also shifted to lower field, between 0.2–0.5 ppm depending on the signal. The shift is particularly significant for H_d (from 3.8 to 4.3 ppm) and H_e (from 2.6 to 3.1 ppm).

Discussion

The absence of crystal structures does not allow us to determine the exact structure of the metal complexes. The high metal : ligand ratios (2 : 1 for L^1 and 3 : 1 for L^2) do not seem unreasonable considering that the ligands present both a sufficiently large macrocyclic cavity and enough donor atoms to potentially host more than one metal ion. It also appears that the increased flexibility of the macrocyclic skeleton, due to the reduction of the di-iminic bonds, influences greatly the coordination capacity of the ligand, allowing it to host an additional cation. The synthesis of dinuclear lanthanide complexes with macrocycles is well documented in the literature [16, 17]. The formation of trinuclear complexes is more infrequent, but examples can also be found [18]. It is worth mentioning that a higher number of complexes have been isolated using nitrate as counterion. This suggests that the additional help provided by the involvement of nitrate groups in the coordination sphere of the metal ion may play a key role in the formation of the complex. The influence of the counterion has been already observed by our research group in other macrocycles derived from 2,6-bis(2-formylphenoxymethyl)pyridine and an aliphatic amine [5]. Without a crystal structure, it is impossible to know the exact role of the water molecules in the nitrate complexes, and the reason why they are not present in the perchlorate complexes; they could be crystallisation water.

There are different alternatives for the structure of di and trinuclear macrocyclic complexes. One possibility is that all metal ions are coordinated to the macrocyclic ligand. Dinuclear complexes have already been reported with a ligand derived from 3,6-dioxa-1,8-octanediamine and 2,6-diformyl-*p*-cresol [19, 20]; the corresponding macrocycle results from a [2 + 2] condensation, and the crystal structures of the complexes feature both metallic ions coordinated to the macrocyclic ligand. On the other hand, it is also possible that one metallic ion (or two, in the case of the trinuclear complexes) is coordinated to the macrocycle, while the rest are part of a complex anion [21]. In our case, the mass spectra show the existence of fragments $[Ln_2L^1(NO_3)_x]^+$ and $[Ln_3L^2(NO_3)_x]^+$, which seems more in accordance with the

first structural possibility. For that reason, we suggest that the most likely structures are those where all metallic ions are coordinated to the macrocyclic ligand.

The ^{1}H NMR spectra of the complexes with L[2] show the shift of some peaks to lower field when compared to that of the free ligand; this could indicate that the adjacent donor atoms may be involved in the coordinative sphere of the metallic ion. Since protons H_c are affected, one lanthanide ion could be coordinated to the N_{py}, and the O atoms next to the pyridine head. The peaks attributable to the aliphatic part of the ligand are also shifted, which suggests that the other two metal ions are coordinated to the NH groups and possibly to the O atoms of the ethylene bridge. The ligand is highly flexible, and it is impossible to know if the coordination is endo and/or exocyclic. The other coordination positions would be occupied by anions, possibly acting as bidentate, and perhaps water molecules.

Conclusions

The cyclocondensation reaction between 2,6-bis(2-formylphenoxymethyl)pyridine and 3,6-dioxa-1,8-octanediamine yields the Schiff-base macrocycle L[1], which, on reaction with NaBH$_4$, is readily reduced to the more flexible macrocycle L[2]. Attempts to synthesise Ln(III) complexes with L[1] following a the template method have been unsuccessful. However, series of Ln(III) complexes have been obtained by direct synthesis between L[1] or L[2] and different Ln(III) hydrated nitrates or perchlorates. All complexes obtained with L[1] give a [2:1, Ln:L[1]] stoichiometry. The reduction of the diiminic bonds increases the flexibility of the macrocycle and leads to a change in the stoichiometry; all complexes obtained with L[2] show a [3:1, Ln:L[2]] relation. Although in absence of crystal structures it is not possible to establish the real structure of the macrocyclic complexes, careful examination of the spectroscopic data suggests that all metallic ions are coordinated to the macrocyclic ligand. Finally, it is noteworthy that more complexes have been obtained when using nitrate as the counterion, showing the important role of the counterion in the synthesis of the corresponding metal complex.

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