Journal of Alloys and Compounds 323–324 (2001) 155–158
www.elsevier.com/locate/jallcom

Lanthanide(III) perchlorate complexes of two 24 membered N_3O_4-donor macrocycles

Emilia Bértolo[a], Rufina Bastida[a,*], David E. Fenton[b], C. Lodeiro[a], Alejandro Macías[a], Adolfo Rodríguez[a]

[a]Departamento de Química Inorgánica, Universidad de Santiago de Compostela, Avda. de las Ciencias s/n, 15706 Santiago de Compostela, Spain
[b]Department of Chemistry, The University, Sheffield S3 7HF, UK

Abstract

Two novel macrocycles, L^1 and L^2, containing a N_3O_4-donor set, have been synthesised, and their complexation potential towards Ln(III) ions have been investigated. The cyclocondensation reaction between 2,6-bis(2-formylphenoxymethyl)pyridine and 1,2-bis(2-aminophenoxy)butane in the absence of metal ions, 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 $NaBH_4$. The interaction of lanthanide(III) ions with both ligands has been investigated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanide(III) complexes; Schiff-base; Oxaazamacrocycle; Template synthesis; Ion-selectivity

1. Introduction

Macrocyclic ligands form stable complexes with lanthanides, offering a wide range of possibilities to explore the special properties of these complexes in areas ranging from medicine to hydrometallurgy [1,2]. We are particularly interested in N_xO_y-donor atom macrocycles as they are expected to form more stable complexes with f-metal ions than the polyaza or polyoxa macrocycles [3,4]. Herein, we present the synthesis and characterisation of two novel 25-membered N_3O_4 macrocycles derived from 2,6-bis(2-formylphenoxymethyl)pyridine and 1,2-bis(2-aminophenoxy)butane. The Schiff-base ligand L^1 has been synthesised by direct reaction and also following a template method, and its coordination ability towards lanthanide(III) ions has been investigated. Moreover the reduction of L^1 to the corresponding saturated ligand L^2 has allowed to investigate the influence of such change on the complexation capacity of the macrocycle as it is converted into a more stable and flexible ligand.

2. Experimental details

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 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. The electronic absorption spectra of the complexes (10^{-4}–10^{-6} M methanol solutions) were measured in the range 220–900 nm using a Hitachi U-3000 and a Perkin–Elmer Lambda 6 spectrophotometers. Emission spectra were recorded on a SPEX F111 Fluorolog spectrofluorimeter.

2,6-Bis(2-formylphenoxymethyl)pyridine [5,6] and 1,2-bis(2-aminophenoxy) butane were prepared according to literature methods [7,8]. Lanthanide(III) perchlorates were commercial products (from Johnson–Matthey) used without further purification. Solvents were of reagent grade purified by the usual methods.

CAUTION: Perchlorates are potentially explosive.

2.1. Synthesis of L^1 in absence of metal ions. General procedure

A solution of 1,2-bis(2-aminophenoxy)butane (1 mmol)

---

*Corresponding author. Fax: +34-81-597-525.
E-mail address: qibastid@usc.es (R. Bastida).

0925-8388/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0925-8388(01)01109-4

in absolute ethanol (50 cm^3) was added dropwise to a refluxing solution of 2,6-bis(2-formylphenoxymethyl)pyridine (1 mmol) in the same solvent (50 cm^3). The solution was gently refluxed with magnetic stirring for ca. 2.5 h. The colour changed to yellow and a yellow powder precipitated. The product was filtered off, washed with absolute ethanol and dried in vacuo.

L^1: Yield 75%. *Anal.* Calc. for $C_{37}H_{33}N_3O_4.H_2O$: C, 73.8; N, 6.9; H 5.8%. Found: C 73.4; N, 6.2; H 6.3%. Melting point: 172°C. FAB: $[L^1+H]^+$ 584. IR: $\nu(CN)_{imi}$ 1621 cm^{-1}; $\nu(C=C)_{ar}$, $\nu(C=N)_{py}$ 1595, 1492 cm^{-1}.

2.2. 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 absolute ethanol (50 cm^3) was added a solution of $Ln(ClO_4)_3.xH_2O$ (Ln=La, Ce, Pr, Sm, Gd) (1 mmol) in the same solvent (10 cm^3), and then an ethanolic solution (50 cm^3) of 1,2-bis(2-aminophenoxy)butane (1 mmol) was added dropwise. The colour of the solution changed to yellow, and refluxing was continued for a further 3 h. The reaction produced firstly an unidentified precipitate which was removed by filtration. The filtrate was then concentrated to ca. 10 cm^3 and an equal volume of diethyl ether was slowly infused into the solution producing powdery precipitates. The yellow products were filtered off, washed with absolute ethanol or methanol (ca. 5 cm^3) and dried in vacuo. Microanalytical data are given in Table 1. The complexes are air-stable yellow solids, soluble in acetonitrile, chloroform, dimethylformamide and dimethylsulfoxide, moderately soluble in ethanol and methanol and insoluble in diethyl ether and hexane.

2.3. Synthesis of L^2. General procedure

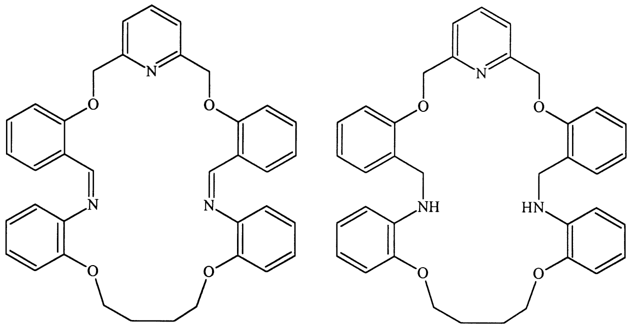
L^1 L^2

Fig. 1. Macrocycles L^1 and L^2.

This ligand was prepared following a method previously reported for similar macrocycles [9,10], by direct reaction between 1,2-bis(2-aminophenoxy)butane and 2,6-bis(2-formylphenoxymethyl)pyridine, followed by in situ reduction with sodium tetrahydroborate.

L^2: Yield 38%. *Anal.* Calc. for $C_{37}H_{33}N_3O_4.H_2O$: C, 73.3; N, 6.9; H 6.5%. Found: C 73.5; N, 6.7; H 6.7%. Melting point: 152°C. FAB: $[L+H]^+$ 588. IR: $\nu(NH)$ 3434 cm^{-1}; $\nu(C=C)_{ar}$, $\nu(C=N)_{py}$ 1599, 1510 cm^{-1}. ^1H and ^{13}C NMR data (in $CDCl_3$) are presented in Fig. 2, Table 2.

2.4. Synthesis of lanthanide(III) perchlorate complexes of L^2 – General procedure

To a refluxing solution of L^2 (0.1 mmol) in absolute ethanol (15 cm^3) was added dropwise a solution of the hydrated lanthanide perchlorates of La(III), Ce(III), Pr(III), Nd(III), Eu(III) or Er(III) (0.1 mmol) dissolved in the same solvent (10 cm^3). The resulting colourless solution was refluxed ca. 5 h. and then allowed to cool. The volume of the solution was reduced to ca. 10 cm^3 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 white solids, air-stable, soluble in acetonitrile, chloroform, dimethylformamide, dimethylsulfoxide, ethanol and methanol, and insoluble in hexane and diethyl ether.

Table 1
Analytical, yield, molar conductance (in DMF) and infrared data (in KBr) for the complexes $LnL^1(ClO_4)_3.xH_2O$ and $LnL^2(ClO_4)_3.xH_2O$

Complex	Analysis (%)[a]			Yield (%)	Λ_M ($\Omega^{-1}mol^{-1}cm^2$)	IR (cm^{-1})		
	C	N	H			$\nu(C=N)_{imi}$	$\nu(C=N)_{py}$ $\nu(C=C)_{ar}$	$\nu(ClO_4)$
$CeL^1(ClO_4)_3.4H_2O$	40.6 (40.6)	3.5 (3.8)	4.0 (3.7)	43	149	1631	1602; 1495	1144; 1115; 1086; 1042; 627
$PrL^1(ClO_4)_3.2EtOH$	44.1 (44.0)	3.9 (3.7)	4.2 (4.0)	32	157	1640	1601; 1496	1144; 1115; 1087; 625
$SmL^1(ClO_4)_3.H_2O$	42.8 (43.0)	3.9 (4.0)	3.1 (3.2)	49	161	1639	1602; 1494	1144; 1114; 1086; 1042; 627
$CeL^2(ClO_4)_3.8H_2O$	37.6 (37.9)	3.4 (3.5)	4.4 (4.5)	25	149	–	1600; 1495	1144; 1118; 1090; 636; 625
$PrL^2(ClO_4)_3.12H_2O$	35.9 (35.7)	3.3 (3.3)	4.7 (4.9)	38	154	–	1601; 1496	1147; 1121; 1090; 636; 626

[a] Calculated values in parentheses.

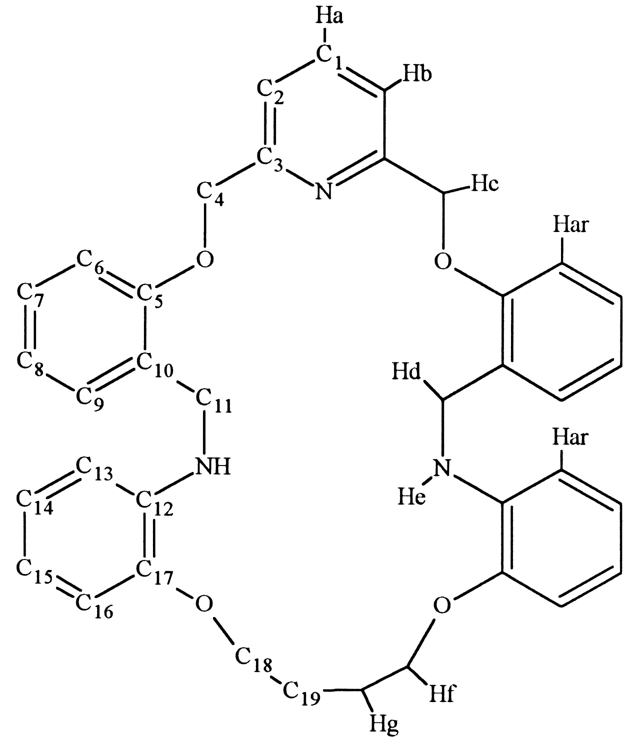

Fig. 2. ^{1}H and ^{13}C NMR assigments for L^2.

3. Results and discussion

3.1. Macrocycles L^1 and L^2

We have found that in the reaction between 2,6-bis(2-formylphenoxymethyl)pyridine and 1,2-bis(2-aminophenoxy)butane the [1+1] Schiff-base macrocycle L^1 is formed as the majority product. The in situ reduction with sodium tetrahydroborate of L^1 provides the corresponding reduced macrocyclic ligand L^2 in a good yield. Both ligands were characterised by elemental analysis, FAB mass spectrometry, IR and NMR spectroscopy.

Table 2
^{1}H and ^{13}C NMR data (500 MHz) in $CDCl_3$ for L^2[a]

Assignment	Shift (δ ppm)	Integration	Assignment	Shift (δ ppm)
H_a	7.52 (t)	1H	C_1	137.4
H_b	7.36 (d)	2H	C_2	119.8
H_{ar}	7.32 (d)	2H	C_3; C_5	157.5; 157.0
	7.24 (m)	2H	C_{17}	146.5
	6.96 (m)	4H	C_{10}; C_{12}	138.4; 127.9
	6.88 (t)	2H	C_7; C_9	131.0; 128.8
	6.80 (d)	2H	C_6; C_8	121.2; 121.1
	6.68 (d)	2H	C_{13}; C_{14}	116.3; 112.4
	6.60 (t)	2H	C_{15}; C_{16}	110.7; 110.5
H_c	5.25 (s)	4H	C_4	70.2
H_e	5.22 (s)	2H	–	–
H_d	4.50 (s)	4H	C_{11}	45.4
H_f	3.70 (s)	4H	C_{18}	67.8
H_g	1.30 (m)	4H	C_{19}	25.8

[a] d=doublet; m=multiplet; t=triplet; s=singlet.

The FAB mass spectra of both macrocycles play an important role in confirming the monomeric [1+1] nature of the ligands. They show the highest molecular weight peaks at m/z 584 and 588, corresponding to $[L^1+H]^+$ and $[L^2+H]^+$ respectively. The IR spectrum of L^1 clearly shows the imine band at 1621 cm^{-1} but also exhibit the carbonyl band at ca. 1687 cm^{-1}, indicating formation of acyclic as well as cyclic products. The spectrum of the reduced ligand L^2 features a secondary amine N–H stretching at 3434 cm^{-1} and no imine band at ca. 1621 cm^{-1}. Both spectra exhibit bands at ca. 1600 and 1480 cm^{-1} as expected for the aromatic and pyridine rings vibrations [11].

The ^{1}H NMR spectrum of L^1 (in $CDCl_3$) is complicated and shows more signals than expected; however, it clearly shows a peak at 9.1 ppm corresponding to the imine protons. When recording 24 h and 48 h later the complexity of the spectrum increases, may be due to the hydration and hydrolysis of imine bonds [12]. The ^{1}H NMR spectrum (in $CDCl_3$) of L^2 shows the absence of the signal attributable to the imine protons and the appearance of a new singlet signal at 5.22 ppm corresponding to the NH amine protons; the latter was confirmed by deuterium exchange when D_2O was added. The spectrum was recorded after 24 h. and 48 h. and no change was observed, demonstrating the greater stability of the ligand compared with L^1. The ^{13}C spectrum of L^2 features 19 signals, as expected for the symmetry of the macrocycle. The assignment of the signals has been made using NMR techniques (COSY, DEPT-135, HMQC).

3.2. Metal complexes of L^1 and L^2

Perchlorate complexes of both ligands have been obtained in a good yield. In the case of L^1, a template method has been successfully employed in the synthesis of analytically pure compounds formulated as $LnL^1(ClO_4)_3.xH_2O$ (Ln=Ce, Sm) or $PrL^1(ClO_4)_3.2EtOH$. The reaction between equimolar amounts of L^2 and the hydrated lanthanide perchlorates gives analytically pure products $LnL^2(ClO_4)_3.xH_2O$ (Ln=Ce or Pr). Attempts to obtain the corresponding [1:1, Ln:L] complexes with Ln=La or Gd (in the case of L^1) and Ln=La, Nd, Eu or Er (for the ligand L^2) were unsuccessful. The yield, analytical, conductivity and IR data for the complexes are presented in Table 1.

The molar conductivities of the complexes in dimethylformamide are in the range reported for 2:1 electrolytes in this solvent [13], suggesting that one perchlorate counterion must be co-ordinated, at least in dmf, and also most likely in the solid state. The FAB mass spectra feature in all cases peaks at m/z 584 and 588 as the most intense ones, confirming the stability of the macrocycles in the metal complexes. All spectra show peaks at higher molecular weights, that in some cases have also been assigned.

The IR spectra of all complexes were recorded in KBr. The absence of carbonyl and amine bands in the di-iminic complexes, together with the appearance of an imine band at 1631–1640 cm^{-1}, indicates that cyclocondensation has occurred; this band is shifted to higher wavenumbers respect to that of the free ligand, suggesting coordination *via* the imine nitrogen atoms. As in the case of L^2, the IR spectra of its complexes also show the absence of bands assignable to the iminic groups. The absorption bands attributable to the stretching mode for the N–H vibrations are hidden by the presence of a broad band at ca. 3430 cm^{-1} due to the presence of water molecules in the complexes [14]. The absorptions of the counterions provide some useful structural information. The absorption bands in the regions 1120 (ν_3) and 630 (ν_4) cm^{-1} are assignable to the asymmetric Cl–O stretching mode and the symmetric Cl–O bending mode respectively: the broadening and splitting of these bands suggest the presence of coordinated perchlorate groups in the complexes [15].

The UV/visible spectra of the metal complexes of $PrL^1(ClO_4)_3.3EtOH$ and $SmL^1(ClO_4)_3.H_2O$ were recorded using $10^{-4}-10^{-6}$ M methanol solutions. The spectra were recorded immediately after preparation of the solutions and again after 1 day and 1 week, and they were found to be reproducible. They both show two strong, broad absorption bands at 267 and 252 nm, corresponding to the $\pi-\pi^*$ transitions of the pyridine, benzene rings, and iminic groups [16]. The low definition showed by the spectrum of L^1 prevented from comparing it to those of the complexes. Room temperature emission spectra were recorded using 10^{-6} M methanol solutions. The spectrum of the Sm(III) complex was recorded following excitation at 267 nm, which resulted in a low fluorescent emission. It was not possible to observe an antenna effect [17] and the luminescent quantum yield could not be calculated because of the low residual intensity of the emission.

4. Conclusions

The cyclocondensation reaction between 2,6-bis(2-formylphenoxymethyl)pyridine and 1,2-bis(2-aminophenoxy)butane yields the Schiff-base macrocycle L^1, which, on reaction with $NaBH_4$, is readily reduced to the more flexible macrocycle L^2 (Fig. 1). The spectroscopic data suggest that L^1 is formed as the major product, but also show the presence of impurities due to the formation of acyclic products and/or unreacted dicarbonilic precursor. The integrity of the macrocycle L^2 in solution has been confirmed by NMR studies. Mononuclear lanthanide complexes have been prepared from both macrocycles in a good yield. The replacement of the N–H groups of the reduced ligand may provide a wide range of new functionalized derivatives showing more encapsulating properties.

Acknowledgements

We thank A Xunta de Galicia (PGIDT99PXI20902B) for financial support.

References

[1] C.F.G. Geraldes, in: NMR in Supramolecular Chemistry, Kluwer Academic Publishers, 1999, p. 133.

[2] J.-C.G. Bunzli, G.R. Choppin (Eds.), Lanthanide Probes in Life, Chemical and Earth Sciences, Elsevier, Amsterdam, 1989, Chapter 5.

[3] F. Avecilla, R. Bastida, A. de Blas, D.E. Fenton, A. Macías, A. Rodríguez, T. Rodríguez-Blas, S. García-Granda, R. Córzo-Suárez, J. Chem. Soc., Dalton Trans. (1997) 409.

[4] M. Vicente, C. Lodeiro, H. Adams, R. Bastida, A. de Blas, D.E. Fenton, A. Macías, A. Rodríguez, T. Rodríguez-Blas, Eur. J. Inorg. Chem. (2000) 1015.

[5] E. Buhleier, W. Werner, F. Vögtle, Justus Liebigs Ann. Chem. (1979) 537.

[6] A. Bailey, D.E. Fenton. J.F. Kitchen, T.H. Lilley, M.G. Williams, P.A. Tasker, A.L.J. Leong, L.F. Lindoy, J. Chem. Soc., Dalton Trans. (1991) 627.

[7] R.D. Cannon, B. Chiswell, L.M. Venanzi, J. Chem. Soc., Sect. A (1967) 1277.

[8] P.A. Tasker, E.B. Fleischer, J. Am. Chem. Soc. 92 (1970) 7072.

[9] P.G. Grimsley, L.F. Lindoy, H.C. Lip, R.J. Smith, J.T. Baker, Aust. J. Chem. 30 (1977) 2095.

[10] E. Bértolo, R. Bastida, A. de Blas, D.E. Fenton, A. Macías, A. Rodríguez, T. Rodríguez-Blas, A. Villar, Z. Naturforsch. 53b (1998) 1445.

[11] S.M. Peng, G.C. Gordon, V.L. Goedken, Inorg. Chem. 17 (1978) 119.

[12] K.K. Abid, D.E. Fenton, Inorg. Chim. Acta 95 (1984) 119.

[13] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.

[14] K. Nakamoto, in: Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th Edition, Wiley Interscience, 1997.

[15] L. De Cola, D.L. Smailes, L.M. Vallarino, Inorg. Chem. 25 (1986) 1729.

[16] E. Pretsch, T. Clerc, J. Seibl, W. Simon, in: Tables of Spectral Data For Structure Determination of Organic Compounds, 2nd Edition, Springer-Verlag, 1989.

[17] N. Sabbatini, S. Perathoner, V. Balzani, B. Alpha, J.-M. Lehn, in: V. Balzani, D. Reidel (Eds.), Supramolecular Photochemistry, Reidel Publishing Company, 1987, p. 187.