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Lanthanide(III) Nitrate Complexes of Two 17 Membered N_3O_2-Donor Macrocycles

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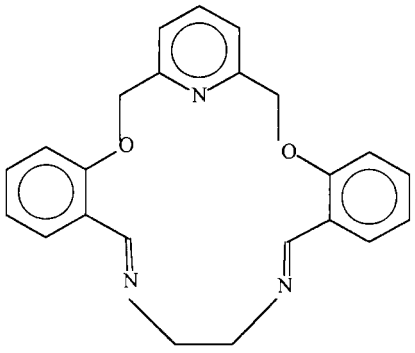
Abstract. The interaction of lanthanide(III) ions with two N_3O_2-macrocycles, L^1 and L^2, derived from 2,6-bis(2-formylphenoxymethyl)pyridine and 1,2-diaminoethane has been investigated. Schiff-base macrocyclic lanthanide(III) complexes $LnL^1(NO_3)_3 \cdot xH_2O$ (Ln = Nd, Sm, Eu or Lu) have been prepared by direct reaction of L^1 and the appropriate hydrated lanthanide nitrate. The direct reaction between the diamine macrocycle L^2 and the hydrated lanthanide(III) nitrates yields complexes $LnL^2(NO_3)_3 \cdot H_2O$ only for Ln = Dy or Lu. The reduction of the Schiff-base macrocycle decreases the complexation capacity of the ligand towards the Ln(III) ions. The complexes have been characterised by elemental analysis, molar conductivity data, FAB mass spectrometry, IR and, in the case of the lutetium complexes, ^{1}H NMR spectroscopy.

Key words: lanthanide(III) complexes, Schiff-base, oxaazamacrocycle, ion selectivity.



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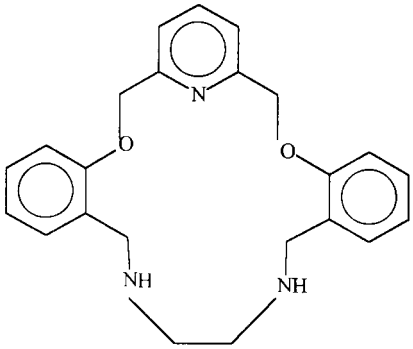

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1. Introduction

Recognition of the importance and usefulness of complexes containing macrocyclic ligands has led to a considerable effort being invested in developing synthetic routes for these compounds [1–6]. Studies on complexes of Schiff-base macrocyclic ligands with different ring size, and number and nature of donor atoms for coordination with a variety of metal centers have been published [7–11]. Macrocyclic ligands form stable complexes with lanthanides and hence they serve as a springboard to explore the coordination chemistry of these metal ions. These complexes are currently attracting much attention because of their special properties in areas ranging from medicine to hydrometalurgy [12–16]. We are particularly interested in N_xO_y-donor atom macrocycles which exhibit hard and soft base character as they are expected to form more stable complexes with f-metal ions than the polyaza or polyoxa macrocycles. The study now reported is part of our investigations on lanthanide(III) complexes with several N_xO_y-donor macrocyclic ligands containing pyridine or furan head units and aromatic lateral units [17–25]. As Schiff-base ligands can be hydrolytically sensitive, they can be reduced to the corresponding saturated macrocycles, allowing us to investigate the influence of such changes on the complexation capacity of the macrocycles as they are converted into more stable and flexible ligands. Herein, we present the synthesis and characterisation of lanthanide nitrate complexes with two 17-membered N_3O_2 donor-atom macrocycles derived from 2,6-bis(2-formylphenoxymethyl)pyridine and 1,2-diaminoethane.

2. Experimental

2.1. METHODS

Elemental analyses were carried out by the University of Santiago de Compostela Microanalytical Service on Carlo Erba 1108 and Leco CNHS-932 microanalysers. IR spectra were recorded as KBr discs or fluorolube mulls using Mattson Cygnus 100, Bio-Rad FTS 135 and FTS 175 C spectrometers. NMR spectra were recorded using a Bruker WM-300 spectrometer. 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.

2.2. CHEMICALS AND STARTING MATERIALS

2,6-Bis(2-formylphenoxymethyl)pyridine was prepared according to the literature method [26]. Lanthanide(III) nitrates were commercial products (from Aldrich and Johnson-Matthey) used without further purification. Solvents were of reagent grade purified by the usual methods.

2.3. SYNTHESIS OF L^1

1,2-Diaminoethane (1 mmol) in methanol (50 cm^3) was added to a refluxing solution of 2,6-bis(2-formylphenoxymethyl)pyridine (1 mmol) in the same solvent (50 cm^3). A white solid developed immediately. The reaction mixture was refluxed for ca. 0.5 h. and then underwent a hot filtration. The white precipitate was washed with methanol and dried under vacuum. The ligand was characterised by microanalysis, FAB m.s, IR and ^{1}H NMR spectroscopy. Yield: 68%. IR (KBr disc) (cm^{-1}): ν(C=N)$_{imi}$ 1641; ν(C=N)$_{py}$ 1600, 1450. *Anal.* Calc. for $C_{23}H_{21}N_3O_2$: C: 74.4; H: 11.3; N: 5.7%. Found: C: 74.3; H: 11.1; N: 5.4%.

H^1 NMR (in $CDCl_3$) (δ, ppm): 3.8 (4H, s, CH_2CH_2), 5.1 (4H, s, CH_2O), 6.9–7.8 (11H, m, aromatics), 8.6 (2H, s, CH=N). Mass spectrum (positive-ion FAB): m/z 372 $[L^1+H]^+$. The compound is air stable, moderately soluble in chloroform, dimethylformamide and dimethylsulfoxide, and insoluble in ethanol, methanol, acetonitrile and diethyl ether.

2.4. SYNTHESIS OF L^2

This ligand was synthesised as previously described in the literature [27, 28] *via* Mn(II)-templated cyclocondensation of the precursors followed by an *in situ* reductive demetallation of the manganese(II) Schiff-base complex by $NaBH_4$. The "one pot" synthesis was proved to be more effective than the isolation of the diimine intermediate. The ligand was characterised by microanalysis, FAB m.s, IR and ^{1}H NMR spectroscopy. Yield: 35%. IR (KBr disc) (cm^{-1}): ν(NH) 3340, ν(C=N)$_{py}$ 1600, 1450. *Anal.* Calc. for C_{23} $H_{25}N_3O_2.H_2O$: C: 70.2; H: 10.7; N: 6.9%. Found: C: 70.4; H: 10.1; N: 6.3%. H^1 NMR (in $CDCl_3$) (δ, ppm): 1.9 (2H, broad, NH), 2.7 (4H, s, CH_2CH_2), 3.8 (4H, s, CH_2—N), 5.1 (4H, s, CH_2O), 6.9–7.2 (11H, m, aromatics). Mass spectrum (positive-ion FAB): m/z 376 $[L^2 + H]^+$. The compound is air stable, soluble in ethanol, methanol, acetonitrile, chloroform, dimethylformamide and dimethylsulfoxide, and insoluble in diethyl ether.

2.5. SYNTHESIS OF LANTHANIDE(III) COMPLEXES OF L^1. GENERAL PROCEDURE

To a refluxing suspension of L^1 (0.5 mmol) in chloroform (25 cm^3) was added dropwise the appropriate hydrated lanthanide nitrate (0.5 mmol) dissolved in absolute ethanol (5 cm^3). The resulting reaction mixture was refluxed until clear (ca. 1.5 h) and then allowed to cool. The volume of the solution was reduced to ca. 3 cm^3 and the same volume of diethyl ether was added to aid precipitation. The complexes were filtered off, washed with cold ethanol and dried under vacuum. Microanalytical data are given in Table I. The complexes are air stable, soluble in chloroform, dimethylformamide and dimethylsulfoxide, moderately soluble in acetonitrile, and insoluble in diethyl ether.

Table I. Analytical, yield and molar conductance data (in DMF) for the complexes $LnL^1(NO_3)_3 \cdot xH_2O$ and $LnL^2(NO_3)_3 \cdot xH_2O$

	Ln	x	Analysis (%)[a] C	N	H	Yield (%)	Λ_M (Ω^{-1} mol^{-1} cm^2)
L^1							
	Nd*	–	40.7 (40.8)	10.5 (10.5)	4.0 (4.1)	37	159.4
	Sm	–	39.6 (39.0)	11.3 (11.8)	2.6 (2.9)	19	157.4
	Eu	8	32.6 (32.3)	9.4 (9.8)	4.2 (4.3)	28	173.4
	Lu	6	32.7 (32.8)	10.3 (10.0)	3.8 (3.9)	32	141.1
L^2							
	Dy	1	37.7 (37.2)	11.5 (11.3)	3.7 (3.6)	25	141.6
	Lu	1	37.4 (37.5)	11.2 (11.4)	3.8 (3.4)	38	142.3

[a] Calculated values in parentheses.
* Crystallises with 2 EtOH.

2.6. SYNTHESIS OF LANTHANIDE(III) COMPLEXES OF L^2. GENERAL PROCEDURE

To a refluxing solution of L^2 (0.5 mmol) in absolute ethanol (20 cm^3) was added an ethanolic solution of the corresponding hydrated lanthanide nitrate (0.5 mmol, 5 cm^3). The reaction mixture was refluxed until a white precipitate appeared (ca. 1.5 h). The reaction mixture was filtered hot, and the product was washed with a small amount of cold ethanol and dried under vacuum. Microanalytical data are given in Table I. The complexes are air stable, soluble in chloroform, dimethylformamide and dimethylsulfoxide, moderately soluble in acetonitrile, and insoluble in diethyl ether.

3. Results and Discussion

3.1. MACROCYCLES L^1 AND L^2

In previous papers, we have reported that in some cases the use of 2,6-bis(2-formylphen-
oxymethyl)-pyridine as the dicarbonyl precursor for amine condensation leads to Schiff-base macrocycles in the absence of templating agents [22, 29]. In other cases the direct reaction between the dicarbonyl and diamine precursors yields a mixture of acyclic as well as cyclic products, and no pure compounds can be isolated [25].

In this work, we have found that in the reaction between 2,6-bis(2-formylphenoxymethyl)pyridine and 1,2-diaminoethane in methanol, the [1 + 1] Schiff-base macrocycle is formed as the major product. The macrocyclic ligand was character-

ised by elemental analysis, FAB mass spectrometry, IR and ^{1}H NMR spectroscopy. The FAB mass spectrum of L^1 plays an important role in confirming the monomeric [1+1] (dicarbonyl and diamine) nature of the ligand. The most intense peak corresponds to $[L^1+H]^+$, at m/z 372. The IR spectrum of the ligand clearly shows the imine band at 1641 cm^{-1} and the absence of bands due to formyl or amine stretches, indicating the formation of a cyclic product. It also exhibits bands at 1600 and 1450 cm^{-1} as expected for the two highest-energy pyridine-ring vibrations [30]. The ^{1}H NMR spectrum of the ligand in $CDCl_3$ shows a single peak at ca. 8.6 ppm corresponding to the imine protons, but no signals corresponding to the formyl or amine protons are present.

An *in situ* reductive demetallation of the Mn(II) complex of L^1 with sodium borohydride, proved to be successful for the synthesis of the corresponding reduced macrocycle L^2. This synthesis has been previously described in the literature [27, 28]. The ligand was characterised by elemental analysis, FAB mass spectrometry, IR and ^{1}H NMR spectroscopy.

3.2. METAL COMPLEXES OF L^1

The reactions between equimolar amounts of L^1 and hydrated lanthanide nitrates in chloroform/ethanol under the conditions described in the Experimental Section gave analytically pure products $LnL^1(NO_3)_3 \cdot xH_2O$ (Ln = Nd, Sm, Eu or Lu). Attempts to obtain the corresponding [1 : 1, Ln : L^1] complexes for Ln = La, Ce, Pr, Gd or Tb were unsuccessful. Under the experimental conditions used we have found that L^1 was unable to make complexes with the lanthanide nitrates following a template method, so a non-template approach was used to synthesise them.

The molar conductivities of the compounds in dimethylformamide are in the range reported for 2 : 1 electrolytes in this solvent [31]. This suggests that one ion must be co-ordinated, at least in DMF, and also most likely in the solid state. The yield, analytical and conductivity data for the complexes are presented in Table I.

The FAB mass spectra (Table II) show in all cases a peak at m/z 372 corresponding to the free dimine macrocycle as the most intense one. The spectra of the complexes of Nd, Sm and Eu also contain peaks attributable to the molecular ions $[NdL^1]^+$, $[SmL^1(NO_3)_2]^+$ and $[EuL^1(NO_3)_2]^+$.

The IR spectra of the complexes are listed in Table II. The absorptions due to the imine bond at 1648–1659 cm^{-1} are shifted to higher wavenumbers with respect to the free ligand, suggesting coordination via the imine nitrogen atoms. All spectra exhibit medium to strong bands at ca. 1600 and 1450 cm^{-1} corresponding to the pyridine-ring vibrations [30].

The absorptions of the counterions provide some useful structural information. The absorption bands in the regions 1466–1458 (ν_5), 1311–1294 (ν_1) and 758–753 (ν_2) cm^{-1} suggest the presence of coordinated nitrate groups [32, 33]. The two highest frequency bands are separated by ca. 165 cm^{-1}. The magnitude of this separation indicates a strong interaction of the oxygen atoms of the nitrates with

Table II. Infrared and FAB mass spectral data for the complexes $LnL^1(NO_3)_3 \cdot xH_2O$ and $LnL^2(NO_3)_3 \cdot xH_2O$

		IR (cm^{-1})				FAB	
	Ln	ν_{imine}	ν(NH)	ν_{py}	$\nu(NO_3)$	Peak	Assignment
L^1							
	Nd	1648	–	1601	1458; 1294; 753	372	$[L^1 + H]^+$
						515	$[NeL^1]^+$
	Sm	1659	–	1601	1458; 1302; 758	372	$[L^1 + H]^+$
						647	$[SmL^1(NO_3)_2]^+$
	Eu	1659	–	1604	1466; 1311; 756	372	$[L^1 + H]^+$
						648	$[EuL^1(NO_3)_2]^+$
	Lu	1654	–	1602	1458; 1300; 755	372	$[L^1 + H]^+$
L^2	Dy	–	3426	1594	1456; 1300; 756	376	$[L^2 + H]^+$
	Lu	–	3426	1594	1456; 1302; 756	611	$[LuL^2(NO_3)]^+$
						376	$[L^2 + H]^+$

the lanthanide ions, typical of bidentate coordination [34, 35]. When the spectra are recorded as KBr discs, an intense band at ca. 1384 cm^{-1} suggests the presence of ionic nitrates [36], however, in fluorolube this band disappears indicating that a bromide ion can displace a nitrate anion [20]. The ^1H NMR spectrum of the lutetium complex was run in $CDCl_3$ and gave the expected simple spectrum, indicating the integrity of the complex in that solvent. The spectrum is very similar to that of the free macrocycle, and there are no significant shiftings of the signals.

3.3. METAL COMPLEXES OF L^2

Complexation reactions of L^2 with the hydrated lanthanide nitrates were carried out in order to investigate the coordination capability of these more flexible and hydrolytically stable ligands towards the Ln(III) ions. Analytically pure products $[LnL^2][NO_3]_3 \cdot xH_2O$ (Ln = Dy or Lu) have been isolated from the reaction between the diamine macrocycle L^2 and the corresponding lanthanide nitrate. The yield, analytical and conductivity data are listed in Table I. All the efforts to prepare complexes of L^2 with the hydrated lanthanide nitrates of La, Ce, Sm, Eu, Gd or Tb were unsuccessful. The microanalytical data for these ions were in accordance with a [1:2, Ln:L^2] stochiometry, but no pure products could be isolated.

The molar conductivities for the complexes in dimethylformamide fall in the range reported for a 2 : 1 electrolyte in this solvent [31]. The FAB mass spectra show in both cases a peak at m/z 376 corresponding to the free ligand. The spectrum of the lutetium complex also shows a small peak at 611 attributable to the fragment $[LuL^2(NO_3)]^+$. The IR spectra of the complexes are assigned as shown in

Table II. The IR data are consistent with the presence of the reduced macrocycle in the complex. The IR spectra of both complexes show secondary amine stretches at 3426 cm^{-1} for the dysprosium complex and 3436 cm^{-1} for the lutetium complex which are shifted to higher wavenumbers relative to that of the free macrocycle. The absorption bands at ca. 1594 and 1450 cm^{-1} due to the pyridine ring vibrations are present. The presence of bands at ca. 1456, 1301 and 756 cm^{-1}in the spectra clearly identify these species as containing coordinated nitrate groups [32, 33]. The intense band at 1384 cm^{-1} in the KBr spectra disappears when the spectra were recorded in fluorolube. The H^1 NMR spectrum of the lutetium complex in $CDCl_3$ indicates the integrity of the complex in that solvent by giving a simple spectrum; the spectrum is very similar to that of the free macrocycle.

4. Conclusions

The direct reaction in low dilution conditions between 2,6-bis(2-formylphenoxymethyl)pyridine and 1,2-diaminoethane was found to be more effective in the synthesis of the Schiff-base macrocycle instead of the template method using lanthanide(III) ions. However, for the synthesis of the corresponding diamine macrocycle an *in situ* reductive demetallation of the Mn(II) Schiff-base macrocyclic complex was proved to be more successful. Some stable lanthanide(III) complexes were prepared by direct reaction between the appropriate metal salt and macrocycles L^1 or L^2, respectively. The results showed that the reduction of the Schiff-base macrocycle decreases the complexation capacity of the ligand and it increases its selective complexation towards the Ln(III) ions.

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