DALTON

Complexes of lanthanide(III) ions with macrocyclic ligands containing pyridine head units*

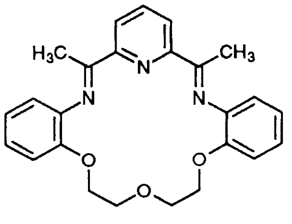
Rufina Bastida,[a] Andrés de Blas,[b] Pilar Castro,[a] David E. Fenton,[c] Alejandro Macías,[a] Rita Rial,[a] Adolfo Rodríguez[a] and Teresa Rodríguez-Blas[b]

[a] *Departamento de Química Inorgánica, Universidad de Santiago de Compostela, Avda. de las Ciencias s/n, 15706 Santiago de Compostela, Spain*
[b] *Departamento de Química Fundamental e Industrial, Universidad de La Coruña, Campus de la Zapateira s/n, 15071 La Coruña, Spain*
[c] *Department of Chemistry, The University, Sheffield S3 7HF, UK*

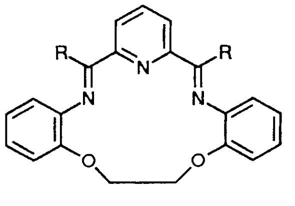
Lanthanide(III) salts were found to act as templates for the cyclic condensation of organic dicarbonyl compounds with primary diamines to yield complexes of macrocyclic Schiff-base ligands in moderate to good yield. Three types of macrocyclic lanthanide(III) complexes were obtained: (*i*) mononuclear complexes of an 18-membered sexidentate N_3O_3 macrocycle derived from the reaction of 2,6-diacetylpyridine with 1,5-bis(2-aminophenoxy)-3-oxapentane; (*ii*) mononuclear complexes of 15-membered pentadentate N_3O_2 macrocycles derived from the reactions of 2,6-diacetyl- or 2,6-diformyl-pyridine with 1,2-bis(2-aminophenoxy)ethane. The complexes were characterised by elemental analyses, molar conductivity, mass, IR and ^{1}H NMR spectroscopy and thermogravimetric and magnetic measurements.

The use of transition-metal or alkaline-earth-metal cations to control the stereochemistry of reactions involving the formation of imine groups is well known and is frequently applied to the synthesis of complexes of macrocyclic ligands.[1–4] The possibility of using lanthanide(III) ions in the template synthesis of Schiff-base macrocycles, on the basis of the similarity of their ionic radii with those of the alkaline-earth-metal cations, has been proposed and a number of reports have been published.[5–8] Most efforts to date have focused on '1 + 1' or '2 + 2' macrocycles containing aromatic head units and aliphatic lateral units. In contrast, little has been reported on lanthanide macrocycles having aromatic head units and rigid, aromatic lateral units.[9–16]

We are interested in the synthesis of lanthanide(III) complexes with mixed N_xO_y donor-atom macrocycles containing aromatic, head and lateral units. We have recently reported the template synthesis of lanthanide(III) complexes of a N_3O_3 sexidentate macrocycle.[17] In this paper we describe the results of an extension of the investigation to the lanthanide(III)-promoted synthesis of the related macrocycles L^1–L^3 derived from 2,6-diacetyl- and 2,6-diformyl-pyridine, respectively, which also contain nitrogen and oxygen donor atoms, in order to elucidate the possible influence of the dicarbonyl precursors, the change in the aliphatic bridge length, and of the counter ion (NO_3^- or ClO_4^-) on the chemical selectivity and complex syntheses.



L^1



L^2 R = Me
L^3 R = H

Experimental

Elemental analyses were carried out on a Carlo Erba 1108 elemental analyser. The IR spectra were recorded as KBr discs using a Perkin-Elmer 1330 spectrometer, ^{1}H NMR spectra on a Bruker WM 250 spectrometer and FAB mass spectra using a Kratos MS 50 TC mass spectrometer and a 3-nitrobenzyl alcohol matrix. Magnetic moments were determined at room temperature on an IMC vibrating-sample magnetometer model 1660 digital measurement system. Conductivity measurements were carried out in 10^{-3} mol dm^{-3} dimethylformamide solutions at 20 °C using a WTW LF-3 conductivimeter. Thermograms were obtained with a Perkin-Elmer ATG-7 thermogravimetric system (heating rate 20 °C min^{-1}, nitrogen atmosphere).

2,6-Diformylpyridine was prepared according to the literature method,[18,19] 1,5-bis(2-aminophenoxy)-3-oxapentane and 1,2-bis(2-aminophenoxy)ethane by reduction of the corresponding dinitro precursors using a similar procedure to that described previously.[20,21] 2,6-Diacetylpyridine, lanthanide(III) nitrates and perchlorates were commercial products from Aldrich and Alfa laboratories used without further purification. Solvents were of reagent grade purified by the usual methods. **CAUTION**: Reactions involving perchlorates were carried out in small quantities (1 mmol) and with screen protection, because they are potentially explosive.

Condensation between 2,6-diacetylpyridine and 1,5-bis(2-aminophenoxy)-3-oxapentane in the absence of metal ions

2,6-Diacetylpyridine (1 mmol) was dissolved in hot absolute ethanol (100 cm^3). The diamine (1 mmol) dissolved in absolute ethanol (25 cm^3) was slowly added. The solution was gently refluxed with magnetic stirring for *ca.* 4 h, changing to yellow-green; no precipitate appeared. When the solution was evaporated on a rotary evaporator a brown oily compound was obtained, but no identifiable product could be isolated.

---

* *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Reaction of 2,6-diacetylpyridine and 1,5-bis(2-aminophenoxy)-3-oxapentane in the presence of lanthanide(III) ions

General procedure for [LnL^1][NO$_3$]$_3$. To a refluxing solution of 2,6-diacetylpyridine (1 mmol) in absolute ethanol (25 cm^3) was added a solution of the hydrated lanthanide nitrate (1 mmol) (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu) in the same solvent (50 cm^3). The solution was gently refluxed with magnetic stirring for *ca.* 30 min and an ethanolic solution (50 cm^3) of the diamine (1 mmol) added dropwise. Refluxing and stirring were maintained for *ca.* 4 h and then the solution was concentrated to half of the initial volume using a Dean–Stark apparatus. Fine powdery products were obtained, filtered off, washed with ethanol and dried *in vacuo*. For the synthesis of the complexes of Sm, Dy and Ho it was necessary to catalyse the reaction by adding *ca.* 5 drops of triethyl orthoformate. The microanalytical data and characteristics of the compounds are given in Table 1.

Complexes of Ho, Er, Tm, Yb and Lu prepared by this procedure did not provide satisfactory analyses. The complexes appear to be air stable, and are soluble in dimethylformamide, dimethyl sulfoxide, acetonitrile and methanol and insoluble in dichloromethane, carbon tetrachloride and water.

General procedure for [LnL^1][ClO$_4$]$_3$. To a refluxing solution of 2,6-diacetylpyridine (1 mmol) in absolute ethanol (25 cm^3) was added a solution of the hydrated lanthanide perchlorate (1 mmol) (Ln = La, Ce, Pr, Nd, Eu, Gd, Tb, Ho or Er) in the same solvent (15 cm^3). Stirring and heating was maintained during the addition of 1,5-bis(2-aminophenoxy)-3-oxapentane (1 mmol) dissolved in absolute ethanol (15 cm^3); the mixture was then refluxed for *ca.* 12 h and cooled to room temperature. The solid was isolated by decanting the solution and stirred with anhydrous diethyl ether (15 cm^3), decanted again and dried *in vacuo*. The microanalytical data and characteristics of the lanthanum and cerium complexes are given in Table 1. The products obtained in the reactions with the nitrates of Pr, Nd, Eu, Gd, Tb, Ho or Er had infrared spectra similar to those of the other complexes but gave unsatisfactory analytical results, hence are not listed in Table 1. A number of attempts were made to purify the products in suitable solvents, but no analytically pure materials were obtained. The compounds appear to be less air stable than the nitrate complexes and their solubility is comparable with that of the nitrate complexes.

Condensation between 2,6-diacetylpyridine and 1,2-bis(2-aminophenoxy)ethane in the absence of metal ions

To a warm solution of 2,6-diacetylpyridine (1 mmol) in absolute ethanol (150 cm^3) was added dropwise a solution of 1,2-bis(2-aminophenoxy)ethane in absolute ethanol (50 cm^3). The solution was gently refluxed with magnetic stirring for *ca.* 4 h, and then evaporated to *ca.* 50 cm^3 using a Dean–Stark apparatus. On cooling, an off-white product crystallised and was filtered off, washed with ethanol and dried *in vacuo*.

Reaction of 2,6-diacetylpyridine and 1,2-bis(2-aminophenoxy)ethane in the presence of lanthanide(III) ions

General procedure for [LnL^2][ClO$_4$]$_3$. To a warm solution of 2,6-diacetylpyridine (1 mmol) in absolute ethanol (30 cm^3) was added a solution of the hydrated lanthanide perchlorate (1 mmol) (Ln = La, Ce, Pr, Nd, Gd, Ho or Er) in absolute ethanol (10 cm^3). The solution was stirred and heated while an ethanolic solution (25 cm^3) of the diamine (1 mmol) was added slowly and then refluxed for 4 h. The precipitated solid complex was filtered off, washed with ethanol and dried *in vacuo*. The complexes appear to be air stable, are soluble in dimethylformamide, acetonitrile and dimethyl sulfoxide and insoluble in methanol, dichloromethane, chloroform and water.

Condensation between 2,6-diformylpyridine and 1,2-bis(2-aminophenoxy)ethane in the absence of metal ions

Ethanolic solutions of 2,6-diformylpyridine (1 mmol in 35 cm^3) and 1,2-bis(2-aminophenoxy)ethane (1 mmol in 25 cm^3) were mixed and refluxed with stirring for *ca.* 10 h. The dialcohol addition product crystallised out as fine needles on cooling, and was recrystallised from ethanol.

Reaction of 2,6-diformylpyridine and 1,2-bis(2-aminophenoxy)ethane in the presence of lanthanide(III) ions

General procedure. The [LnL^3][ClO$_4$]$_3$ complexes (Ln = La, Ce, Pr, Nd, Gd, Tb, Ho or Er) were prepared by an analogous procedure to that described above for [LnL^2][ClO$_4$]$_3$ but using 2,6-diformylpyridine. No identifiable products precipitate initially from solution and the volume of the filtrates was reduced to *ca.* 10 cm^3 using a rotary evaporator. A small quantity of diethyl ether was slowly infused into the filtrates producing powdery precipitates. The lanthanum complex prepared using this procedure did not give satisfactory analysis.

The complexes appear to be air stable, soluble in dimethyl sulfoxide, dimethylformamide, methanol and acetonitrile, and insoluble in chloroform, dichloromethane and water. The cerium complex was insoluble in methanol and acetonitrile and soluble in chloroform and dichloromethane.

Results and Discussion

Complexes of L^1

We have found that in the reaction between 2,6-diacetylpyridine and 1,5-bis(2-aminophenoxy)-3-oxapentane in absolute ethanol an unidentifiable viscous oil was obtained. Cook and Fenton[22] have reported that a template method using only Sr^{II} was found to provide a useful route to the formation of the metal diimine macrocyclic complex. However there is no obvious reason why only strontium, of all the alkaline-earth metal cations, should form a complex with this macrocycle. We have prepared complexes of this 18-membered macrocycle by the template method using lanthanide(III) ions as a metal template. These results show that the metal ion is essential to the macrocycle synthesis.

Lanthanide(III) complexes. Reactions between equimolar amounts of 2,6-diacetylpyridine, 1,5-bis(2-aminophenoxy)-3-oxapentane, and hydrated lanthanide nitrates or perchlorates under the conditions described (see Experimental section) gave yields between 24 and 73 and *ca.* 23% of analytically pure products [LnL^1][NO$_3$]$_3$·xH$_2$O (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy) and [LnL^2][ClO$_4$]$_3$·xEtOH (Ln = La or Ce) respectively. We were unable to obtain analytically pure products in the reactions attempted with the nitrates of Ho, Er, Tm, Yb or Lu and the perchlorates of Pr, Nd, Eu, Gd, Tb, Ho or Er.

All the complexes were characterized by elemental analyses (C, H, N), molar conductivity, magnetic moment measurements, thermal analyses, mass and IR spectroscopy. The analytical and conductivity data are presented in Table 1. The conductivity data in dimethylformamide (dmf) for the [LnL^1][NO$_3$]$_3$·xH$_2$O complexes are in the range reported[23] for 2:1 electrolytes in this solvent. These data suggest that one nitrate ion is co-ordinated, at least in dmf; such co-ordination is also most likely in the solid state. For the lanthanum and cerium perchlorate complexes the molar conductance values measured in MeCN are between those for 1:1 and 2:1 electrolytes.

Thermogravimetric analyses show that the lanthanide nitrate complexes have high thermal stability. All exhibit similar diagrams due to their similar structures. The TGA curves show in most cases stages betwen 50 and 200 °C, indicating that the complexes contain small solvent molecules. The complexes have

Table 1 Analytical, yield and molar conductance (in dmf) data for the complexes $[LnL^1][NO_3]_3{\cdot}xH_2O$ and $[LnL^1][ClO_4]_3$

		Analysis (%)[a]				
Ln	x	C	N	H	Yield (%)	Λ/Ω^{-1} cm^2 mol^{-1}
$[LnL^1][NO_3]_3{\cdot}xH_2O$						
La	—	40.70 (40.55)	11.80 (11.35)	2.80 (3.40)	43.7	181.3
Ce	6.5	34.95 (34.60)	10.65 (9.70)	3.35 (4.40)	26.3	172.5
Pr	4.5	36.20 (36.50)	10.85 (10.20)	3.75 (4.15)	32.4	182.8
Nd	5.5	34.40 (35.55)	10.40 (9.90)	3.70 (4.25)	73.3	175.9
Sm	2.5	37.70 (37.70)	10.85 (10.55)	3.45 (3.75)	31.6	110.6
Eu	1	38.40 (38.95)	10.20 (10.90)	3.35 (3.50)	24.6	172.2
Gd	1	39.70 (38.65)	10.00 (10.80)	4.15 (3.50)	24.8	164.3
Tb	1	38.90 (38.60)	10.75 (10.80)	4.40 (3.45)	70.0	179.9
Dy	4	35.55 (35.95)	10.45 (10.05)	3.95 (3.95)	41.4	165.3
$[LnL^1][ClO_4]_3$						
La		35.45 (35.20)	4.30 (4.95)	2.30 (2.95)	22.6	210.6
Ce[b]		36.15 (36.05)	4.85 (4.65)	3.50 (3.45)	21.9	200.2

[a] Calculated values in parentheses. [b] The compound crystallises with 1 molecule of ethanol.

Table 2 Infrared, FAB mass spectral data and magnetic moments for the complexes $[LnL^1][NO_3]_3{\cdot}xH_2O$ and $[LnL^1][ClO_4]_3$

	IR (cm^{-1})			Mass spectrometry (FAB)		
Ln	ν(C=N) imine	ν_{py}	$\nu(NO_3^-)$	*m/z*	Assignment	μ/μ_B
$[LnL^1][NO_3]_3{\cdot}xH_2O$						
La	1620	1580, 1480, 610	1440, 1380, 1300, 1240, 820, 760, 740	678	$[LaL(NO_3)_2]^+$	—
Ce	1620	1580, 1480, 610	1440, 1380, 1300, 1240, 820, 760, 740	679	$[CeL(NO_3)_2]^+$	3.04
Pr	1620	1580, 1480, 610	1440, 1380, 1300, 1240, 810, 760, 740	680	$[PrL(NO_3)_2]^+$	3.71
Nd	1620	1580, 1480, 610	1440, 1380, 1300, 1240, 820, 760, 740	683	$[NdL(NO_3)_2]^+$	3.44
Sm	1620	1580, 1480, 610	1450, 1380, 1320, 1250, 820, 770, 740	691	$[SmL(NO_3)_2]^+$	1.70
Eu	1620	1580, 1480, 610	1460, 1380, 1300, 820, 760	692	$[EuL(NO_3)_2]^+$	3.54
Gd	1620	1580, 1480, 610	1450, 1380, 1300, 1260, 820, 740	697	$[GdL(NO_3)_2]^+$	7.40
Tb	1620	1580, 1480, 610	1450, 1380, 1300, 1240, 820, 740	698	$[TbL(NO_3)_2]^+$	—
Dy	1620	1580, 1480, 610	1450, 1380, 1300, 1250, 810, 750, 740	703	$[DyL(NO_3)_2]^+$	—
$[LnL^1][ClO_4]_3$			$\nu(ClO_4^-)$			
La	1660	1580, 1480, 420	1145, 1100, 1080, 630, 620	752	$[LaL(ClO_4)_2]^+$	—
Ce	1660	1580, 1480, 420	1140, 1100, 1080, 630, 620	753	$[CeL(ClO_4)_2]^+$	2.86

no clearly defined melting point and begin to decompose between 280 and 310 °C. The total weight loss of the lanthanum complex was found to be 80.9% which is close to the calculated value of 79.5% (considering the product of decomposition to be La_2O_3).

The magnetic moments of all the lanthanide(III) complexes, recorded in Table 2, show little deviation from the theoretical values for the tripositive lanthanide ions[24] and those previously reported,[25,26] suggesting that the 4f electrons do not participate in bond formation in these complexes. The FAB mass spectral data (Table 2) serve the important function of confirming the monomeric [1 + 1] (dicarbonyl and diamine) nature of the complexes. The most intense peaks correspond to $[LnL^1(NO_3)_2]^+$ or $[LnL^1(ClO_4)_2]^+$, respectively.

The IR spectra (Table 2) of the nitrate complexes show a moderate-intensity absorption at *ca.* 1620 cm^{-1} attributable to the imine ν(C=N)[27] but no bands are observed for the free carbonyls or primary diamines indicating that complete condensation has occurred. Both perchlorate complexes have similar IR spectra exhibiting ν(C=N) as a moderately strong band at *ca.* 1660 cm^{-1}. The water present in the majority of the complexes (broad absorption band at *ca.* 3450 cm^{-1}) is probably lattice and/or co-ordinated water. All the spectra exhibit medium-to-strong bands at *ca.* 1580 and 1480 cm^{-1} as expected for the two highest-energy pyridine-ring vibrations. The low-frequency pyridine modes are observed at *ca.* 610 and 420 cm^{-1} suggesting co-ordination of the pyridine nitrogen.[28]

Information regarding the possible bonding modes of the nitrate and perchlorate anions may also be obtained from the IR spectra, and their assignments were made by comparison to the literature values. The presence of bands in the spectra of the nitrate complexes at *ca.* 1380 and 820 cm^{-1} indicate that ionic nitrate groups are present.[29,30] Also, the two most intense nitrate absorptions associated with the asymmetric stretch appear at *ca.* 1450 cm^{-1} (ν_5) and 1300 cm^{-1} (ν_1) and clearly identify these species as containing co-ordinated nitrate groups.[31] For the lanthanum and cerium perchlorate complexes the ν_3 (asymmetric Cl–O stretching mode) and ν_4 (asymmetric Cl–O bending mode) bands of the ClO_4^- group occurring at *ca.* 1080 and 620 cm^{-1} are split and noticeably broadened. The broadening or splitting of these bands suggests some interaction of at least one of the ClO_4^- anions with the metal.[32,33] It has not been possible to grow crystals of the complexes suitable for structure determination and absolute assignment of the anion disposition must remain tentative since it is difficult to present an unambiguous assignment on IR arguments alone. It is, however, possible to suggest that these compounds possess similar structures to those proposed for complexes with the analogous macrocycle derived from 2,6-diformylpyridine.[17] The ^1H NMR spectrum of the diamagnetic $[LaL^1][NO_3]_3$ complex was run in $(CD_3)_2SO$ and CD_3CN. The spectrum in $(CD_3)_2SO$ is complicated and indicates that different types of products are present. In this solvent there is likely to be competition between the solvent and the ligand for the lanthanide. This could result in removal of the metal from the macrocycle, followed by ligand breakdown. However, immediately after dissolution in CD_3CN the expected simple spectrum was obtained: δ 8.4–8.6 (m, 3 H, C_5H_3N), 7.6–7.2 (m, 8 H, C_6H_4), 4.5 (m, 4 H, $C_6H_4OCH_2$), 4.3 (m, 4 H, OCH_2CH_2) and 2.8 (s, 6 H, CH_3). The spectrum obtained after *ca.* 24 h was complicated, similar to that in $(CD_3)_2SO$, which indicates that the complex is susceptible to decomposition in solution.

Table 3 Analytical, yield and molar conductance (in dmf) data for the complexes $[\mathrm{LnL^2}][\mathrm{ClO_4}]_3\cdot x\mathrm{H_2O}\cdot y\mathrm{EtOH}$

			Analysis (%) *				
Ln	x	y	C	N	H	Yield (%)	Λ/Ω^{-1} cm^2 mol^{-1}
La	—	2	35.25 (36.00)	4.40 (4.65)	3.65 (3.65)	33.5	160.8
Ce	—	1	35.15 (35.05)	4.25 (4.90)	3.85 (3.15)	28.8	124.7
Pr	—	5.5	38.35 (38.35)	3.65 (3.95)	4.70 (5.05)	16.3	157.4
Nd	2	3	36.00 (35.25)	4.00 (4.25)	4.85 (4.35)	12.3	173.0
Gd	5	—	30.85 (30.10)	4.20 (4.60)	3.75 (3.40)	85.2	139.2
Ho	7	—	28.65 (28.75)	3.80 (4.35)	3.75 (3.65)	56.8	210.6
Er	4	—	30.70 (30.40)	4.75 (4.60)	3.40 (3.20)	63.1	191.7

* Calculated values in parentheses.

The ^{1}H NMR spectrum of the lanthanum perchlorate complex was run in $(\mathrm{CD_3})_2\mathrm{SO}$ and $\mathrm{CD_3CN}$; unfortunately it was complicated and not very informative.

Complexes of L^2

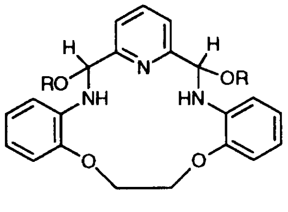
The reaction of 2,6-diacetylpyridine and 1,2-bis(2-aminophenoxy)ethane in 1 : 1 ratio in absolute ethanol gives an off-white crystalline material. This product gives bands at 3440, 3350 and 1700 cm^{-1} in the IR spectrum, which can be attributed to $\nu(\mathrm{NH_2})$ and $\nu(\mathrm{C{=}O})$ stretches indicating that cyclisation has not occurred. The FAB mass spectrum shows peaks at *m/z* 245 and 164 corresponding to the free diamine and dicarbonyl precursors. No peak at *m/z* 389 corresponding to the monomeric acyclic derivative is present. However, lanthanide(III) complexes of the 15-membered $\mathrm{N_3O_2}$ macrocycle L^2 were prepared *via* template condensation of 2,6-diacetylpyridine with 1,2-bis(2-aminophenoxy)ethane in absolute ethanol in the presence of $\mathrm{Ln(ClO_4)_3}\cdot x\mathrm{H_2O}$ (Ln = La, Ce, Pr, Nd, Gd, Ho or Er). The complexes were characterised by their elemental analyses, molar conductance, magnetic moment measurements, IR spectra and where possible FAB mass spectra. The yields from the reactions, microanalytical and conductivity data are presented in Table 3. The elemental analyses are in keeping with the stoichiometric formulae $[\mathrm{LnL^2}][\mathrm{ClO_4}]_3\cdot x\mathrm{H_2O}\cdot y\mathrm{EtOH}$. The conductivity data in dimethylformamide are in the range reported for 2 : 1 electrolytes in this solvent.[23] The complexes of Ho and Er have values intermediate between those for 2 : 1 and 3 : 1 electrolytes. The magnetic moments of the complexes (Table 4) are also close to the values found for the complexes of macrocycle L^1. For all of the complexes a broad band at *ca.* 3400 cm^{-1} was observed in the IR spectra (Table 4) corresponding to molecules of water or solvent. The absence of any bands which could be assigned to the carbonyl stretching frequency and the presence of a medium-intensity band at *ca.* 1660 cm^{-1} which can be attributed to the imine stretching mode suggests the formation of a macrocycle compound.

Two perchlorate absorptions were observed, one centred at *ca.* 1114 (ν_3) and the other at *ca.* 630 cm^{-1} (ν_4); both showed considerable splitting and the higher-energy band had three well resolved maxima at *ca.* 1143, 1114 and 1087 cm^{-1}. A similar splitting of the ν_3 band has been observed for other lanthanum(III) perchlorate complexes,[34] and it is proposed that this type of splitting indicates the presence of bidentate chelating perchlorate anions. However, as has been stated previously, in the absence of crystal structure determinations our information is insufficient to allow the assignment of definitive molecular geometries.

The FAB mass spectra were not very informative and no clear peaks corresponding to the molecular ion can be observed. The instability of the lanthanum complex solution [$\mathrm{CD_3CN}$ or $(\mathrm{CD_3})_2\mathrm{SO}$] made it impossible to obtain reliable NMR spectra; as a result we are unable to make definitive peak assignments. All of this could be seen as a manifestation of the lower stability of these complexes in comparison with the lanthanum(III) complexes of macrocycle L^1. The extension of the bridge length to five atoms ($\mathrm{CH_2CH_2OCH_2CH_2}$) gives a more flexible ligand, reducing the strain in the macrocycle and increasing the stability of the complexes.

Table 4 Infrared and magnetic data for the complexes $[\mathrm{LnL^2}][\mathrm{ClO_4}]_3\cdot x\mathrm{H_2O}\cdot y\mathrm{EtOH}$

	IR (cm^{-1})			
Ln	ν(C=N) imine	ν_{py}	$\nu(\mathrm{ClO_4^-})$	μ/μ_B
La	1665	1595, 1490	1141, 1116, 1089, 626	—
Ce	1660	1589, 1498	1141, 1116, 1087, 630	1.99
Pr	1660	1597, 1498	1141, 1115, 1086, 630	3.42
Nd	1664	1597, 1496	1141, 1115, 1086, 630	3.33
Gd	1662	1601, 1489	1143, 1114, 1087, 630	7.30
Ho	1658	1604, 1487	1143, 1114, 1085, 630	9.83
Er	1660	1599, 1491	1145, 1116, 1085, 629	9.32



L^4 R = Me, Et or Bu^n

Complexes of L^3

As has been previously reported by Fenton and coworkers[35,36] metal-free macrocycles L^4 were obtained as the alcohol adducts when magnesium salts were used as potential templates. It was also established that those adducts could be prepared in the absence of the metal template. We have found the same effect in the reaction between 2,6-diformylpyridine and 1,3-bis(2-aminophenoxy)ethane in absolute ethanol under the conditions described (see Experimental section).

Metal complexes of the pentadentate macrocycle L^3 have been isolated from the Schiff-base condensation of 2,6-diformylpyridine and 1,3-bis(2-aminophenoxy)ethane in methanol in the presence of perchlorates or nitrates of $\mathrm{Mn^{II}}$ and $\mathrm{Zn^{II}}$ and the crystal structure of the manganese perchlorate complex has been reported.[37] We have investigated the above reaction attempting to introduce $\mathrm{Ln^{III}}$ as the templating cations and also, for comparison with macrocycle L^2, to analyse whether the inductive effect of the methyl groups increasing the ligand donor potential affects the synthesis of the complexes.

The reactions between equimolar amounts of 2,6-diformylpyridine and 1,3-bis(2-aminophenoxy)ethane and hydrated lanthanide perchlorates in refluxing absolute ethanol gave good yields (30–70%) of analytically pure products $[\mathrm{LnL^3}][\mathrm{ClO_4}]_3\cdot x\mathrm{H_2O}\cdot y\mathrm{EtOH}$ (Ln = Ce, Pr, Nd, Gd, Tb, Ho or Er). The yield of the reaction for the cerium complex was only 6%, and the

Table 5 Analytical, yield and molar conductance (in dmf) data for the complexes $[LnL^3][ClO_4]_3 \cdot xH_2O \cdot y$EtOH

			Analysis (%)*				
Ln	x	y	C	N	H	Yield (%)	Λ/Ω^{-1} cm^2 mol^{-1}
Ce	6	2	30.55 (30.55)	4.55 (4.30)	4.60 (4.15)	6.0	260.6
Pr	3	1	30.95 (31.30)	4.70 (4.75)	3.25 (3.30)	49.0	262.6
Nd	4	—	29.35 (29.35)	4.95 (4.90)	3.20 (2.90)	70.5	270.2
Gd	8	1	27.70 (27.90)	4.55 (4.25)	4.20 (3.95)	65.5	286.8
Tb	7	—	27.40 (27.20)	5.00 (4.55)	3.15 (3.35)	43.4	261.2
Ho	14	—	23.90 (23.80)	4.00 (3.95)	4.55 (4.25)	57.9	274.0
Er	8	—	26.60 (26.45)	4.30 (4.40)	3.95 (3.45)	53.9	274.9

* Calculated values in parentheses.

Table 6 Infrared and magnetic data for the complexes $[LnL^3][ClO_4]_3 \cdot xH_2O \cdot y$EtOH

	IR (cm^{-1})			
Ln	ν(C=N) imine	ν_{py}	$\nu(ClO_4^-)$	μ/μ_B
Ce	1662	1597, 1508	1140, 1114, 630	—
Pr	1662	1587, 1494	1141, 1114, 1089, 630	3.42
Nd	1660	1601, 1496	1143, 1114, 1087, 630	3.23
Gd	1622 (br)	1590, 1491	1143, 1113, 1089, 630	7.60
Tb	1662	1597, 1487	1141, 1114, 1089, 630	9.41
Ho	1660	1606, 1487	1143, 1114, 1089, 630	9.58
Er	1656	1604, 1494	1143, 1114, 1089, 630	9.04

majority of the product precipitated initially from the reaction mixture was characterised as the metal-free ethanol-adduct macrocycle, giving a sharp secondary amine ν(NH) band at *ca.* 3390 cm^{-1} in the IR spectrum. This reaction was attempted with the lanthanum(III) ion but was unsuccessful, perhaps due to its larger size. The yields of the reaction, analytical and conductivity data are given in Table 5. In contrast with the L^2 derivatives, the microanalytical data are consistent with a large number of water molecules. The molar conductance values of the complexes measured in dimethylformamide lie in the range reported for 3:1 electrolytes in this solvent,[21] indicating that perchlorate is acting as a weakly co-ordinating anion. As was observed for the complexes of macrocycle L^2, the FAB mass spectra in 3-nitrobenzyl alcohol were not very informative. Most compounds did not show peaks corresponding to the molecular ion, but gave peaks attributable to the diimine macrocycle.

All IR spectra (Table 6) show a very strong and broad band at *ca.* 3370–3390 cm^{-1}, and a moderate-to-weak band at *ca.* 1660 cm^{-1} attributable to the azomethine groups. None showed any absorption at *ca.* 1700 cm^{-1} attributable to ν(C=O) of unchanged carbonyl groups. Bands at *ca.* 1590 and 1487 of pyridine are also present. The ν_3 and ν_4 bands of the ClO_4^- group occurring at *ca.* 1114 and 630 cm^{-1} are split, suggesting some interaction of at least one of the perchlorate anions with the metal. However, the greater intensity of the peak at 1114 cm^{-1} compared with the side peaks at 1140 and 1089 cm^{-1} suggests the coexistence of ionic perchlorate.[34] As we stated previously, the crystal structure of the manganese perchlorate complex $[MnL^3][ClO_4]_2$ has been reported,[37] showing a pentagonal-bipyramidal arrangement of the donor atoms. In this complex the unidentate perchlorate groups are '*trans*' and ν_3 occurs at 1106 and 1040 cm^{-1}. For the lanthanide complexes it is not possible to make a firm structural proposition from the IR data.

Acknowledgements

We thank Dirección General de Investigación Científica y Técnica (PS90-0194) and La Xunta de Galicia (XUGA 20903B94) for financial support.

References

1 N. F. Curtis, *Coord. Chem. Rev.*, 1968, **3**, 3.
2 L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, 1989, chs. 2, 3 and refs. therein.
3 B. Dietrich, P. Viout and J.-M. Lehn, *Macrocyclic Chemistry*, VCH, Weinheim, 1993, ch. 3 and refs. therein.
4 P. Guerriero, S. Tamburini and P. A. Vigato, *Coord. Chem. Rev.*, 1995, **139**, 17.
5 G. Bombieri, *Inorg. Chim. Acta*, 1987, **139**, 21.
6 D. E. Fenton and P. A. Vigato, *Chem. Soc. Rev.*, 1988, **17**, 69.
7 L. M. Vallarino, *J. Less-Common Met.*, 1989, **149**, 121.
8 V. Alexander, *Chem. Rev.*, 1995, **95**, 273.
9 W. Radecka-Paryzek, *Inorg. Chim. Acta*, 1981, **54**, 251.
10 W. Radecka-Paryzek, *Inorg. Chim. Acta*, 1981, **52**, 261.
11 J. de O. Cabral, M. F. Cabral, M. G. B. Drew, F. S. Esho, O. Haas and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1982, 1066.
12 K. K. Abid and D. E. Fenton, *Inorg. Chim. Acta*, 1984, **95**, 119.
13 W. Radecka-Paryzek, *Inorg. Chim. Acta*, 1985, **109**, 21.
14 C. J. Gray and F. A. Hart, *J. Chem. Soc., Dalton Trans.*, 1987, 2289.
15 F. Benetollo, G. Bombieri, L. De Cola, A. Polo, D. L. Smailes and L. M. Vallarino, *Inorg. Chem.*, 1989, **28**, 3447.
16 F. Benetollo, G. Bombieri, K. K. Fonda, A. Polo, J. R. Quaglio and L. M. Vallarino, *Inorg. Chem.*, 1991, **30**, 1345.
17 R. Bandín, R. Bastida, A. de Blas, P. Castro, D. E. Fenton, A. Macías, A. Rodríguez and T. Rodríguez, *J. Chem. Soc., Dalton Trans.*, 1994, 1185.
18 E. P. Papadopoulus, A. Jarrar and C. H. Issidorides, *J. Org. Chem.*, 1966, **31**, 615.
19 D. Jerchel, J. Heider and H. Wagner, *Liebigs Ann. Chem.*, 1958, **613**, 153.
20 P. A. Tasker and E. B. Fleischer, *J. Am. Chem. Soc.*, 1970, **92**, 7072.
21 R. D. Cannon, B. Chiswell and L. M. Venanzi, *J. Chem. Soc. A*, 1967, 1277.
22 D. H. Cook and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 1979, 266.
23 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
24 J. H. Van Vleck and A. Frank, *Phys. Rev.*, 1929, **34**, 494.
25 M. Mohan, J. P. Tandon and N. S. Gupta, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1224.
26 F. A. Hart, *Comprehensive Coordination Chemistry*, eds. R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3, ch. 39, p. 1059.
27 S. C. Cummings and D. H. Busch, *J. Am. Chem. Soc.*, 1970, **92**, 1924.
28 N. S. Gill, R. H. Nuttall and D. E. Scaife, *J. Inorg. Nucl. Chem.*, 1961, **18**, 79.
29 N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 1965, **4**, 804; A. B. P. Lever, E. Mantovani and B. S. Ramaswamy, *Can. J. Chem.*, 1971, **44**, 1957.
30 C. C. Addison and B. B. Gatehouse, *J. Chem. Soc.*, 1961, 3091.
31 W. T. Carnall, S. Siegel, J. R. Ferrano, B. Tani and E. Gebert, *Inorg. Chem.*, 1973, **12**, 560.
32 M. F. Rosenthal, *J. Chem. Educ.*, 1973, **50**, 331.
33 A. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091; S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 1965, **4**, 1091.
34 L. De Cola, D. L. Smailes and L. M. Vallarino, *Inorg. Chem.*, 1986, **25**, 1729.
35 D. H. Cook and D. E. Fenton, *Inorg. Chim. Acta*, 1977, **25**, L95.
36 A. Atkinson, N. A. Bailey, D. E. Fenton, P. D. Hempstead and G. P. Westwood, *J. Inclusion Phenom. Mol. Recogn.*, 1992, **12**, 175.
37 N. W. Alcock, D. C. Liles, M. McPartlin and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1974, 727.

Received 16*th October* 1995; *Paper* 5/06824J