Complexes of Lanthanide Ions with a Schiff-base Macrocyclic Ligand derived from 2,6-Diformylpyridine

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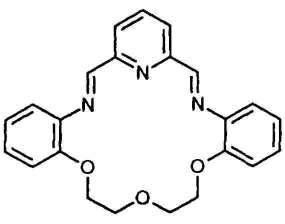
Reaction of 2,6-diformylpyridine with 1,5-bis(2-aminophenoxy)-3-oxapentane in methanol or ethanol in the presence of hydrated $Ln(NO_3)_3$ or $Ln(ClO_4)_3$ (Ln = lanthanide ion) gave complexes of the type $[Ln(NO_3)_3L]$ or $[Ln(ClO_4)_3L]$ where L is the corresponding Schiff-base macrocyclic ligand. In the absence of the metal salt the macrocycle L is not formed. The complexes were characterized by elemental analysis, molar conductivity, mass, IR and ^1H NMR spectroscopy and thermogravimetric and magnetic measurements.

The lanthanide ions were long considered to be a group of elements with rather simple and uninteresting chemistry. More recently, this very 'simplicity' has been the basis of their unusually diverse applications as chemical probes in a broad variety of chemical, biological, geological and environmental systems,[1] and these investigations have often been carried out with the help of macrocyclic ligands.[2,3] Also NMR studies on the water-stable lanthanide complexes have indicated their possible application as shift reagents.[4,5] Other applications of the complexes with macrocyclic ligands could include the extraction and analysis (ion-selective electrodes) of the rare earths.

Schiff bases offer a versatile and flexible series of ligands capable of binding f-metal ions to give complexes with suitable properties for theoretical studies and/or practical applications. 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 several papers have been published.[6,7] In previous papers the template synthesis of complexes of Ca^{II}, Ba^{II}, Sr^{II} (ref. 8) and Pb^{II} (ref. 9) of the 18-membered donor-N_3O_2 macrocyclic ligand L was described. We now report similar syntheses of lanthanide nitrate and perchlorate complexes of L.

Results and Discussion

As has been previously reported,[8] we found that the reaction between 2,6-diformylpyridine and 1,5-bis(2-aminophenoxy)-3-oxapentane in methanol yields a yellow solid which proved to contain a mixture of monomeric and possible polymeric products, and which retained a carbonyl band in the IR spectrum indicating formation of acyclic as well as possible cyclic products. The electron impact (EI) mass spectrum shows peaks at m/z 387 and 403, which can be attributable to the Schiff-base diimine macrocycle L and to the monomeric acyclic derivative respectively. A number of attempts were made to purify the solid, but no analytically pure material was obtained. A template method using Ca^{II}, Ba^{II}, Sr^{II} (ref. 8) and Pb^{II} (ref. 9) as metal template was found to provide a useful route to the formation of the metal diimine macrocycle complex. These results show that the metal ion is essential to the macrocycle synthesis.



L

Nitrate Complexes.—The reactions between equimolar amounts of 2,6-diformylpyridine, 1,5-bis(2-aminophenoxy)-3-oxapentane, and hydrated lanthanide nitrates in refluxing methanol for *ca.* 2 h gave good yields (49–86%) of analytically pure products $[LnL][NO_3]_3$ (Ln = La, Ce, Pr, Nd or Gd). The lanthanum(III) complex crystallizes with 0.5 molecule of solvent as suggested from the microanalytical data. This reaction was also attempted with the lanthanides Tb, Dy, Yb and Lu but although products were obtained the IR spectra and elemental analysis are similar to those of the product obtained by reaction in absence of the metal ion. These results indicate that the heavier lanthanides are not effective templating agents in the formation of this 18-membered ring, perhaps due to their smaller size.[10–12]

All complexes were characterized by elemental analysis (C, H, N), molar conductance, magnetic moment measurements, thermal analyses, mass and IR spectroscopy. The analytical and conductivity data are presented in Table 1. The former are consistent with the formula $[LnL][NO_3]_3 \cdot x MeOH$ [x = 0 or 0.5 (for La)]. The conductivity data in dimethylformamide (dmf) are in the range reported[13] for 2:1 electrolytes in this solvent. This suggests that one nitrate ion must be co-ordinated, at least in dmf, and also most likely in the solid state.

Thermogravimetric analyses show that the lanthanide nitrate complexes have high thermal stability. All the complexes exhibit similar diagrams due to their similar structures. The TGA curves do not have stages up to 340 °C, therefore the complexes do not contain small molecules (water, methanol). The complexes have no clearly defined melting point and begin to decompose in the temperature range 359–392 °C. The total weight loss of the lanthanum complex was found to be 79.3%, which is close to the calculated value of 77.1% (considering the product of decomposition to be La_2O_3). For the other complexes the total weight loss was found to be smaller, between 47 and 56%, close to the calculated value considering the product of decomposition to be $Ln(NO_3)_3$.

The paramagnetic behaviour of lanthanide(III) ions is consistent with the presence of unpaired 4f electrons. Since these electrons are well shielded by the $5s^25p^6$ octet both in their spin and orbital motion, the magnetic moment of a complex should indicate whether they take part in bond formation or not. The magnetic moments of the present lanthanide(III) complexes, recorded in Table 2, show little deviation from the theoretical values for the tripositive lanthanide ions[14] and those reported,[15,16] suggesting thereby that 4f electrons do not participate in bond formation in these complexes.

The absence of carbonyl and amine bands in the IR spectra of the products (Table 2) together with the appearance of an imine band at *ca.* 1615 cm^{-1} indicates that condensation and cyclization has occurred.[17] All the spectra exhibit medium to strong bands at 1593–1603 and 1455–1463 cm^{-1} as expected for the two highest-energy pyridine-ring vibrations. The low-frequency pyridine modes are observed at 630–635 and 423–430 cm^{-1} suggesting co-ordination of pyridine nitrogen.[18]

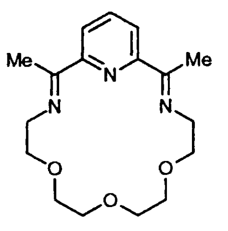
Information about the bonding mode of the nitrate ions may also be obtained from the IR spectra. The free nitrate ion has relatively high symmetry (D_{3h}) and its infrared spectrum consists of three absorption bands at *ca.* 1390, 830 and 720 cm^{-1}. When a nitrate ion becomes co-ordinated in monodentate, bidentate or bridging fashion its effective symmetry is reduced to only C_{2v}. This causes the degeneracies to split and all modes to be infrared active. Hence, it is possible to distinguish between ionic and co-ordinated nitrate groups.[19] In the spectra of all of the complexes the two most intense nitrate absorptions associated with the asymmetric stretch appear at *ca.* 1450 (ν_5) and 1300 cm^{-1} (ν_1) and clearly identify these species as containing co-ordinated nitrate groups. The spectra do not generally allow a clear-cut distinction between mono- and bidentate chelating nitrates, but the separation ($\Delta\nu$) of the nitrate stretching fundamentals has been used as a criterion to distinguish between the degree of covalence of the nitrate co-ordination.[20] The magnitude of this separation of *ca.* 160 cm^{-1} may be indicative of an interaction of the oxygen atoms of the nitrates with the lanthanide ions, suggesting a bidentate bonding.[21] The presence of spectral bands at *ca.* 1380 and *ca.* 850 cm^{-1} also indicates the presence of ionic nitrate groups.[22,23] In the structure of the complex $[LaL'(NO_3)_3]$ it was found that all three nitrates chelate to the metal.[24] It may be that the presence of the aromatic rings enhanced the rigidity of our ligand, preventing the macrocycle from folding to allow one nitrate to chelate on one side and two nitrates on the other side of the ring plane. Then one could envisage a ring with one nitrate on each side and a free anion.

The FAB mass spectral results (Table 2) serve an important role in confirming the monomeric [1 + 1] (dicarbonyl and diamine) nature of the complexes. The most intense peaks correspond to $[LnL(NO_3)_2]^+$; the spectra also commonly show peaks corresponding to $[LnL(NO_3)]^+$.

The ^1H NMR spectrum of the lanthanum complex was run immediately after dissolution in $(CD_3)_2SO$, but unfortunately it was not very informative. 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.

The cerium complex was examined by cyclic voltammetry and differential pulse voltammetry at 10^{-3} mol dm^{-3} in 0.1 mol dm^{-3} NBu_4ClO_4 in Me_2SO at scan rates of 200 and 10 mV s^{-1} respectively. An irreversible oxidation peak is observed at a potential of +0.42 V with respect to ferrocene–ferrocenium which suggests that the oxidation of Ce^{3+} to Ce^{4+} promotes other reactions with cleavage of the macrocycle.

Perchlorate Complexes.—The Schiff-base condensation of 1,5-bis(2-aminophenoxy)-3-oxapentane and 2,6-diformylpyridine, in the presence of hydrated lanthanide perchlorates in absolute ethanol, produces complexes of general formula $[LnL][ClO_4]_3{\cdot}xH_2O{\cdot}yEtOH$ (Ln = La, Ce, Pr, Nd, Eu, Gd, Tb, Ho or Er). The microanalytical data and yields are in Table 3. The ease as well as the yield of the metal-template macrocyclic synthesis appear to depend on the ionic radius of



L′

Table 1 Analytical, yield and molar conductance (in MeCN) data for the complexes $[LnL(NO_3)][NO_3]_2$

	Analysis (%)[a]				
Ln	C	N	H	Yield (%)	Λ/Ω^{-1} cm^2 mol^{-1}
La[b]	39.00 (38.70)	12.00 (11.30)	3.00 (3.40)	85.4	176.9
Ce	39.15 (38.70)	12.40 (11.75)	2.90 (2.95)	71.2	155.3
Pr	38.75 (38.65)	11.55 (11.75)	3.00 (2.95)	85.9	155.6
Nd	40.40 (38.50)	12.35 (11.70)	3.05 (2.95)	85.1	170.3
Gd	38.50 (37.80)	10.95 (11.50)	3.00 (2.90)	48.7	145.0

[a] Calculated values in parentheses. [b] The compound crystallizes with 0.5 methanol.

Table 2 Infrared, FAB mass spectral data and magnetic moments for the complexes $[LnL(NO_3)][NO_3]_2$

	IR (cm^{-1})			Mass spectrometry (FAB)		
Ln	$\nu(C{=}N)_{imine}$	ν_{py}	$\nu(NO_3)$	Peak	Assignment	μ/μ_B
La	1615	1590, 1460, 659	1450, 1380, 1330, 1295, 850, 760, 745	650	$[LaL(NO_3)_2]^+$	—
Ce	1610	1590, 1460	1450, 1380, 1330, 1290, 850, 760, 740	651	$[CeL(NO_3)_2]^+$	1.88
Pr	1615	1585, 1460	1450, 1380, 1330, 1290, 850, 750, 745	652	$[PrL(NO_3)_2]^+$	3.46
Nd	1610	1580, 1460	1440, 1380, 1325, 1290, 840, 750, 740	653	$[NdL(NO_3)_2]^+$	3.27
Gd	1615	1585, 1460, 659	1450, 1380, 1330, 1290, 850, 760, 745	669	$[GdL(NO_3)_2]^+$	7.60

the metal ion. Our results also show that the counter ion (NO_3^- or ClO_4^-) is important to the template process, because the balance between the size of the cation and anion will determine the extent of dissociation of the metal salt in the reaction media. This is reflected in the molar conductance values (Table 3) of the complexes measured in MeCN at 25 °C. Although these lie in the range reported for 2:1 electrolytes[13] in this solvent, the complexes of La, Ce, Nd and Ho have values intermediate between those for 2:1 and 3:1 electrolytes, indicating a weak co-ordination of the perchlorate anion.

Thermal analysis of the holmium complex shows that it initially loses water in the range 75–199 °C and an expected explosive decomposition occurs at about 349 °C due to the presence of the perchlorate group. Owing to the explosive behaviour of the lanthanide perchlorate complexes, no further attempts were made to obtain the thermograms for the other compounds.

The magnetic moments of the complexes (Table 4) are also close to the values found for the nitrate complexes and show little deviation from the theoretical values for tripositive lanthanide ions.[14–16] The FAB mass spectra (Table 4) of the complexes follow the trends observed in the nitrate complexes. The highest-molecular-weight peak is that of $[LnL(ClO_4)_2]^+$ for all the complexes.

All the complexes have similar IR spectra, indicating that they have similar structures. The data (Table 4) are consistent with the presence of imine linkages, each complex exhibiting the ν(C=N) mode at *ca.* 1620 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. The bands at *ca.* 1580, 1450 and 440 cm^{-1} of co-ordinated pyridine are also present.[18]

The perchlorate assignments were made by comparison to literature values.[25,26] Although regarded as a weakly co-ordinating anion, perchlorate is known to co-ordinate under special conditions. Such interactions normally manifest themselves by a splitting of the antisymmetric Cl–O stretching mode due to a reduced symmetry of the co-ordinated species. In the IR spectra of all complexes bands attributable to the asymmetric Cl–O stretching mode at *ca.* 1080 cm^{-1} (ν_3) and the asymmetric Cl–O bending mode (ν_4) at *ca.* 620 cm^{-1} are present. The higher-energy band shows considerable splitting, and is actually three maxima at *ca.* 1040, 1080 and 1120 cm^{-1}. The broadening or splitting of the ν_3 and ν_4 bands suggests some interaction of at least one of the ClO_4^- anions with the metal. The greater intensity of the peak at 1080 cm^{-1} compared to those of the side peaks at 1120 and 1040 cm^{-1} suggests the coexistence of ionic perchlorate.[4] However the C–O–C stretching mode for the polyether chain in the ligand also falls in this region, and in the absence of crystal structure determinations our information is insufficient to allow the assignment of definitive molecular geometries. It is however possible to suggest that a similar structure to that proposed for the nitrate complexes will be found.

The ^1H NMR spectrum of the diamagnetic lanthanum complex was run in $(CD_3)_2SO$ and CD_3CN. The spectrum in $(CD_3)_2SO$ is complicated and indicates different types of products are present, suggesting an equilibrium in solution at least between the complex and the free macrocycle, again due to solvent *vs.* ligand competition as shown earlier. Signals at δ 9.22 and 8.91 can be assigned to the –CH=N– protons in the complex and in the ligand respectively. Furthermore the pyridine and phenyl regions show a great number of signals and there are additional multiplets in the region for the ethoxy bridge protons. However a spectrum run immediately after dissolution in CD_3CN gave the expected simple spectrum: δ 9.08 (s, 2 H, CHN), 8.52 (t, 1 H, C_5H_3N), 8.30 (d, 2 H, C_5H_3N), 7.64–7.28 (m, 8 H, C_6H_4), 4.63 (m, 4 H, $C_6H_4OCH_2$) and 4.35 (m, 4 H, OCH_2CH_2). The spectrum obtained after *ca.* 24 h was complicated, similar to that in $(CD_3)_2SO$, which indicates that the complex is liable to dissociate in solution.

Experimental

Elemental analyses were carried out on a Carlo Erba 1108 elemental analyser. The IR spectra were recorded, as Nujol

Table 3 Analytical, yield and molar conductance (in dmf) data for the complexes $[LnL(ClO_4)][ClO_4]_2 \cdot xH_2O \cdot yEtOH$

Ln	*x*	*y*	Analysis (%)*			Yield (%)	$\Lambda/\Omega^{-1}\ cm^2\ mol^{-1}$
			C	N	H		
La	1	—	32.40 (32.75)	2.55 (2.75)	4.95 (4.95)	53.1	338.4
Ce	2.5	—	31.60 (31.70)	2.45 (2.95)	4.55 (4.80)	49.2	339.6
Pr	0.25	—	34.15 (33.65)	2.65 (2.65)	5.35 (5.00)	39.8	283.5
Nd	—	0.75	34.45 (34.00)	2.20 (2.55)	5.10 (4.85)	60.6	307.8
Eu	—	—	33.05 (32.95)	2.50 (3.20)	5.00 (5.00)	31.6	266.8
Gd	0.25	—	32.10 (32.75)	5.10 (5.00)	1.95 (2.50)	27.8	287.5
Tb	2.75	—	29.40 (30.85)	2.80 (2.95)	4.30 (4.70)	17.0	278.4
Ho	0.5	—	33.55 (33.80)	1.90 (2.90)	5.15 (4.75)	18.7	316.4
Er	0.5	—	33.10 (33.70)	2.70 (2.90)	4.70 (4.70)	16.5	292.4

* Calculated values in parentheses.

Table 4 Infrared, FAB mass spectral data and magnetic moments for the complexes $[LnL(ClO_4)][ClO_4]_2 \cdot xH_2O \cdot yEtOH$

	IR (cm^{-1})			Mass spectrometry (FAB)		
Ln	$\nu(C=N)_{imine}$	ν_{py}	$\nu(ClO_4)$	Peak	Assignment	μ/μ_B
La	1620	430, 1450, 1580	620, 630, 1050, 1090, 1140, 1150	724	$[LaL(ClO_4)_2]^+$	—
Ce	1620	440, 1440, 1580	630, 640, 1040, 1080, 1100, 1140	725	$[CeL(ClO_4)_2]^+$	2.56
Pr	1620	430, 1440, 1580	620, 630, 1040, 1090, 1140	726	$[PrL(ClO_4)_2]^+$	3.05
Nd	1620	430, 1450, 1590	620, 630, 1040, 1080, 1140	729	$[NdL(ClO_4)_2]^+$	3.81
Eu	1620	430, 1450, 1580	630, 640, 1010, 1040, 1080, 1140	738	$[EuL(ClO_4)_2]^+$	2.00
Gd	1620	430, 1450, 1580	630, 640, 1040, 1080, 1160	743	$[GdL(ClO_4)_2]^+$	7.68
Tb	1620	430, 1450, 1580	630, 640, 1050, 1080, 1140, 1150	—		—
Ho	1620	430, 1450, 1580	620, 630, 1040, 1050, 1080, 1150	750	$[HoL(ClO_4)_2]^+$	9.82
Er	1620	440, 1450, 1580	620, 630, 1050, 1090, 1140, 1150	753	$[ErL(ClO_4)_2]^+$	9.01

mulls or KBr discs, using a Perkin Elmer 1330 spectrometer, proton NMR spectra on a Bruker WM 250 spectrometer and FAB mass spectra using a VG AUTOSPEC 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 or acetonitrile solutions at 20 °C using a WTW conductivimeter LF3. Thermograms were obtained with a Perkin Elmer ATG-7 thermogravimetric system (heating rate, 20 °C min^{-1}; atmosphere, nitrogen).

2,6-Diformylpyridine was prepared according to the literature method,[27,28] and 1,5-bis(2-aminophenoxy)-3-oxapentane was prepared by reduction of the corresponding dinitro precursor using a similar procedure to that described previously.[29,30] Lanthanide(III) nitrates and perchlorates were commercial products from Alfa and Aldrich laboratories used without further purification. Solvents were of reagent grade purified by the usual methods. **CAUTION:** perchlorates are potentially explosive.

Condensation between 2,6-*Diformylpyridine and* 1,5-*Bis*(2-*aminophenoxy*)-3-*oxapentane in the Absence of Metal Ions.*—2,6-Diformylpyridine (1 mmol) was mixed with the diamine (1 mmol) in hot methanol (25 cm^3). The solution was gently refluxed with magnetic stirring for *ca.* 2 h. The colour changed to yellow and a yellow powder precipitated. The product was filtered off, washed with ethanol and dried under vacuum. No identifiable product could be isolated.

Reaction of 2,6-*Diformylpyridine and* 1,5-*Bis*(2-*aminophenoxy*)-3-*oxapentane in the Presence of Lanthanide*(III) *Ions.*—*General procedure for* $[LnL][NO_3]_3$. To a refluxing solution of 2,6-diformylpyridine (1 mmol) in methanol (15 cm^3) was added a solution of the hydrated lanthanide nitrate (1 mmol) (Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Yb or Lu) in methanol (15 cm^3). The solution was stirred vigorously and heated while a methanolic solution of 1,5-bis(2-aminophenoxy)-3-oxapentane (1 mmol) was added slowly. Within 5–10 min a yellow precipitate began to deposit. Refluxing was continued for *ca.* 2 h. The product was filtered off, washed with methanol and dried under vacuum. Complexes of Tb, Dy, Yb and Lu prepared by this procedure did not give good analyses.

The complexes appear to be air stable, soluble in dimethylformamide and dimethyl sulfoxide and insoluble in all other common solvents.

General procedure for $[LnL][ClO_4]_3$. 2,6-Diformylpyridine (1 mmol) and $Ln(ClO_4)_3 \cdot xH_2O$ (Ln = La, Ce, Pr, Nd, Eu, Gd, Tb, Ho or Er) were dissolved in hot absolute ethanol (40 cm^3). 1,5-Bis(2-aminophenoxy)-3-oxapentane (1 mmol) dissolved in absolute ethanol (15 cm^3) was slowly added. Stirring and heating of the solution was maintained during the addition and the solution was then refluxed for 2 h. A yellow-green powder precipitated, was filtered off, stirred with diethyl ether, filtered off again and dried under vacuum. The terbium complex was black.

The complexes appear to be air stable, soluble in acetonitrile, dimethyl sulfoxide and dimethylformamide, moderately soluble in methanol and dichloromethane, and insoluble in chloroform, water and carbon tetrachloride.

Acknowledgements

We thank Professor M. Laguna, University of Zaragoza-C.S.I.C. (Spain) for the mass spectra and La Xunta de Galicia (XUGA20902A90) and Dirección General de Investigación Científica y Técnica (PS90-0194) for financial support.

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Received 4*th January* 1994; *Paper* 4/00009I