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Proton NMR, luminescence and electrochemical study of 18-membered Schiff-base macrocyclic lanthanum(III) complexes

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An NMR, electrochemical and photophysical study has been made of lanthanide(III) complexes with a 18-membered hexadentate Schiff-base N_4O_2 polyoxaazamacrocycle L^1 derived from the condensation of 2,6-bis(2-aminophenoxymethyl)pyridine and 2,6-diformylpyridine, as well as their interaction with the chelating agents 1,10-phenanthroline and 2,2′-bipyridine. Separation of the contact and pseudocontact contributions to the observed ^1H NMR lanthanide-induced shift values point to an isostructural series of $[Ln(L^1)][ClO_4]_3$ (Ln = La–Eu, except Pm) in acetonitrile. The interaction of the lanthanum(III) complex with 1,10-phenanthroline and 2,2′-bipyridine was demonstrated by the use of different spectroscopic techniques and the stability constant for the 1,10-phenanthroline adduct was calculated from ^1H NMR data. Upon excitation through the metal excited levels, the terbium(III) complex displays the typical luminescence originating from the excited $^5D_4$ level, while the adduct with 1,10-phenanthroline presents emission upon excitation through the ligand bands. The reaction of 2,6-bis(2-aminophenoxymethyl)pyridine and 2,6-diformylpyridine and the perchlorate of Gd^{III} or Tb^{III} in ethanol solution yielded a reduced macrocycle L^2 instead of the expected complexes of L^1. Electrochemical studies in acetonitrile solution showed that the reduction of the imine groups is favoured when the ionic radius of the lanthanide(III) ion decreases.

Introduction

Trivalent lanthanide complexes with macrocyclic ligands[1] have been the subject of numerous studies in view of their potential applications as contrast agents for magnetic resonance imaging,[2,3] catalysts in RNA hydrolysis,[4,5] and luminescent stains for fluoroimmunoassays and protein labelling.[6] The search for novel lanthanide compounds suitable for these applications requires a previous study of the co-ordination properties of these metal ions. Owing to the hard character of the lanthanide(III) ions, the investigation of their co-ordination properties has focused initially on the complexation with oxygen-donor ligands. Presently, however, a great variety of lanthanide(III) complexes with different kind of ligands, acyclic or cyclic, anionic or neutral, containing various types of donor atoms are described in the literature. Some examples include complexation of these cations with neutral bidentate chelating ligands such as 1,10-phenanthroline and 2,2′-bipyridine[7–12] on which stability studies in different solvents have been performed, leading to the conclusion that a sizable interaction occurs in non-aqueous solution only. Horrocks and co-workers[13] have recently reported ternary europium(III) complexes in aqueous solution with aromatic β-diketone ligands and 1,10-phenanthroline, finding that the presence of both ligands reinforces their co-ordination ability to the metal ion, what may be described as "synergistic co-ordination".

The usefulness of paramagnetic trivalent lanthanide ions for gaining structural information in solution by lanthanide induced NMR shifts (LIS) is also well established.[14,15] However, few data have been reported on the solution structure of macrocyclic complexes with Schiff bases, even though many of these complexes have been prepared and studied.[16,17] Moreover, the strong and long-lived luminescence emission of lanthanide(III) ions relevant to luminescent and laser materials has been widely investigated in many co-ordination compounds, in particular in β-diketonates, supermolecules or polymers, but again complexes with macrocyclic Schiff bases have attracted little attention.[18–20]

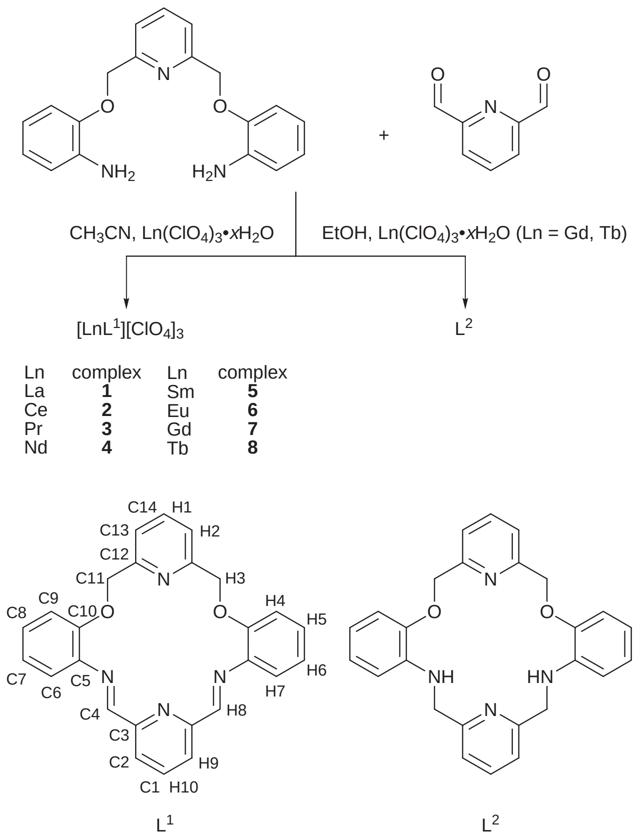
The redox activity of ligand systems co-ordinated to transition metals has also been the subject of numerous investigations.[21] In particular, it has recently been shown that the binding of Yb^{III} to a ketophenolate unit of the drug daunomycin has a profound effect on the reduction potential of the drug.[22] However, the effect of the co-ordination of lanthanide(III) ions to Schiff-base macrocycles on their redox properties remains unexplored.

In previous work we have reported the ability of the trivalent lanthanide ions to promote the formation of Schiff base macrocyclic ligands[23–28] and have recently presented the metal template synthesis of trivalent lanthanide complexes with macrocyclic ligand L^1 (see Scheme 1).[29] In this paper we report a ^1H NMR structural study of mononuclear trivalent lanthanide complexes $[Ln(L^1)][ClO_4]_3$ in acetonitrile. The electrochemical and photophysical properties of these complexes and their interaction with the bidentate chelating ligands 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) are also presented and discussed.

Results and discussion

Solution structure of the $[Ln(L^1)][ClO_4]_3$ complexes (Ln = La–Eu)

The proton NMR spectra of the complexes were recorded in CD_3CN solution and the data are summarized in Table 1. This points to all the complexes having an effective C_2 symmetry in solution. Moreover, solutions are stable and no decomposition was observed after one month. The assignment for the lanthanum diamagnetic complex **1** was made on the basis of COSY and NOESY two-dimensional experiments. In the



Ln	complex	Ln	complex
La	**1**	Sm	**5**
Ce	**2**	Eu	**6**
Pr	**3**	Gd	**7**
Nd	**4**	Tb	**8**

Scheme 1

case of the complexes of Ce (**2**) and Nd (**4**) the observed T_1 relaxation times were long enough for nuclear overhauser effect difference spectroscopy (NOEDIF) measurements to be recorded, allowing the unequivocal assignment of all the protons. The ^{1}H NMR spectrum and assignments of the neodymium complex **4** is shown on Fig. 1. Assignments for the complexes of Pr (**3**) and Eu (**6**) were made on the basis of signal integration, linewidth analyses and the results obtained for the complexes of Ce and Nd. For the samarium complex **5**, with its very small isotropic shifts and sharp signals, some assignments could be made by comparison with the diamagnetic complex of La.

A summary of the ^{1}H LIS values for the $[Ln(L^1)]^{3+}$ complexes **2–6**, measured relative to the diamagnetic lanthanum complex **1**, is given in Table 2. It is well established that the LIS values induced by a paramagnetic centre in the NMR signals of a nucleus located in its vicinity have two contributions: the Fermi contact (δ_c) and the dipolar or pseudocontact shift (δ_{pc}), eqn. (1)

$$\Delta_{i,j} = \delta_c + \delta_{pc} = F_i \langle S_z\rangle_j + G_i C_j \qquad (1)$$

where $\Delta_{i,j}$ is the LIS of the observed nucleus i induced by the lanthanide(III) ion j, F_i is the hyperfine coupling constant of nucleus i, which governs the contact interaction between that nucleus and the ion, $\langle S_z\rangle_j$ and C_j are respectively the spin expectation value and the magnetic constant (Bleaney factor) of the paramagnetic lanthanide,[30–32] and G_i is the geometric factor of nucleus i, which contains the structural information about the complex. Contact and pseudocontact contributions can be separated[33] by using a method based on the rearrangement of eqn. (1) into two linear forms (2) and (3). Plots of $\Delta_{i,j}/C_j$ *versus*

$$\Delta_{i,j}/C_j = (F_i \langle S_z\rangle_j/C_j) + G_i \qquad (2)$$

$$\Delta_{i,j}/\langle S_z\rangle_j = F_i + (G_i C_j/\langle S_z\rangle_j) \qquad (3)$$

$\langle S_z\rangle_j/C_j$ and $\Delta_{i,j}/\langle S_z\rangle_j$ *versus* $C_j/\langle S_z\rangle_j$ for a given nucleus should be linear for an isostructural series of compounds. However, it has been reported that variations from linearity may occur even when there is no drastic structural change along the lanthanide series.

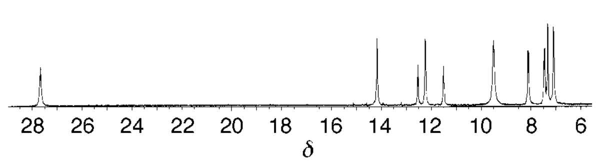


Fig. 1 The 200 MHz proton NMR spectrum of the neodymium complex **4**, 4 mmol dm^{-3} in CD_3CN, at 25 °C.

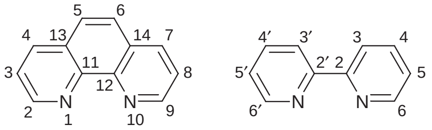
The pseudocontact and contact contributions to the observed LIS values separated by using eqns. (2) and (3) are displayed in Table 2. All plots are linear, indicating that the complexes are isostructural in acetonitrile solution. The data also show that nearly all the protons have both contact and pseudocontact contributions. The contact contribution is usually the most important, being larger for the imine protons, as a result of a strong interaction between the imine nitrogen atoms and the lanthanide ion. For the paramagnetic complexes, the ratios of $(T_{1\ dip})^{-1}$ for different positions should be proportional to the ratios of the inverse sixth power of the relevant metal–proton distances.[34] The T_1 values obtained by the inversion recovery method for the cerium complex **2** and corrected for the diamagnetic contribution using data from the lanthanum complex **1** yield the following Ce–H distances relative to the imine protons H8 : 1.36 : 1.25 : 0.92 : 1.51 : 1.14 : 1.00 : 1.21 : 1.41 for H1, H2, H3, H5, H7, H8, H9 and H10, respectively. The relative distances obtained by this method are consistent with all the protons lying relatively close to the lanthanide(III) ion, suggesting that the whole set of the macrocyclic ligand donor atoms is bonded to the metal ion in acetonitrile solution.

Synthesis and characterisation of $[La(L^1)(phen)][ClO_4]_3\cdot 2H_2O$ 9 and $[La(L^1)(bipy)][ClO_4]_3\cdot 2H_2O$ 10 adducts

Equimolar amounts of 2,6-diformylpyridine and 2,6-bis-(2-aminophenoxymethyl)pyridine in the presence of $La(ClO_4)_3\cdot 6H_2O$ and 1,10-phenanthroline or 2,2′-bipyridine in acetonitrile led to the isolation of the analytically pure products **9** and **10** in very good yield. The complexes are soluble and stable in acetone, methanol and acetonitrile. The presence of an absorption band at 1606 cm^{-1} due to $\nu(C{=}N)_{imine}$ in their IR spectra, as well as the absence of carbonyl and amine vibrational modes, confirms that condensation and cyclisation occurred. The absorption bands at 1120 and 627 cm^{-1} of both complexes are due to the ν_{asym}(Cl–O) and δ_{asym}(O–Cl–O) vibrational modes of perchlorate ions, respectively. The highest energy band shows considerable splitting, with three maxima at 1144, 1121 and 1088 cm^{-1}, suggesting some interaction of at least one of the ClO_4^- anions with the metal ion. The larger intensity of the peak at 1121 cm^{-1} compared with the side peaks suggests the coexistence of ionic perchlorate. Shifts in the frequency of IR absorption bands of the bidentate chelating ligands upon reaction with $[La(L^1)][ClO_4]_3$ confirm the co-ordination of these ligands to La^{III}.[35,36] Vibrational bands attributed to C–H out of plane bending modes, appearing at 740 and 855 cm^{-1} in the spectrum of free 1,10-phenanthroline, are shifted to lower wavenumbers for **9**, appearing at 732 and 847 cm^{-1} respectively. The lowering of the ring stretching vibration from 1427 cm^{-1} for free 1,10-phenanthroline to 1421 cm^{-1} for **9** is also noteworthy. The band assigned to the C–H out of plane bending mode at 750 cm^{-1} in the spectrum of the unco-ordinated 2,2′-bipyridine is shifted to 762 cm^{-1} for complex **10**.

Further evidence for co-ordination of both the macrocycle and the chelating ligand in the complexes comes from the FAB mass spectrum of **10** which presents a peak at *m*/*z* 913 due to $[La(L^1)(bipy)(ClO_4)_2]^+$, beside others corresponding to the sequential loss of 2,2′-bipyridine and counter ions at *m*/*z* 757, $[La(L^1)(ClO_4)_2]^+$; 658, $[La(L^1)(ClO_4)]^+$; and 558, $[La(L^1)]^+$. On the other hand, the spectrum of the 1,10-phenanthroline

Table 1 Proton NMR chemical shifts (ppm from TMS) for the complexes in CD_3CN solution. The ^1H NMR data of free 1,10-phenanthroline and 2,2′-bipyridine are also reported for comparison (see Scheme 1 for labelling of the macrocycle)



	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	H-2,9[a]	H-3,8[a]	H-4,7[a]	H-5,6[a]
1	8.19	7.80	5.84	7.63	7.70	7.47	7.70	9.20	8.36	8.57				
2	11.10	8.70	5.11	5.75	6.27	6.02	5.61	13.58	11.33	9.26				
3	12.61	13.03	8.04	5.75	5.22	5.20	4.86	23.55	16.45	14.89				
4	11.53	12.30	9.74	8.26	7.15	7.40	7.61	27.96	14.25	12.58				
5	8.71	8.40	6.38	7.34	7.55	7.23	7.68	8.81	9.12	9.25				
6	3.66	1.14	0.98	6.36	7.67	6.59	7.48	−24.87	0.75	1.11				
phen											9.08	7.65	8.30	7.80
9	8.13, t, 1 H	7.62, d, 2 H	5.57, s, 4 H	7.28, d, 2 H	7.41, t, 2 H	7.20, t, 2 H	7.47, d, 2 H	9.09, s, 2 H	8.32, t, 1 H	8.53, br, 2 H	8.76, d, 2 H	7.72, br, 2 H	8.57, br, 2 H	8.01, s, 2 H
											H-3,3′[b]	H-4,4′[b]	H-5,5′[b]	H-6,6′[b]
bipy											8.42	7.87	7.37	8.66
10	8.14, t, 1 H	7.65, d, 2 H	5.73, s, 4 H	7.47, d, 2 H	7.60, t, 2 H	7.37, t, 2 H	7.70, d, 2 H	9.13, s, 2 H	8.30, d, 2 H	8.50, t, 1 H	8.34, br, 2 H	8.02, t, 2 H	7.54, m, 2 H	8.65, br, 2 H

[a] Hydrogen atoms corresponding to 1,10-phenanthroline. [b] Hydrogen atoms corresponding to 2,2′-bipyridine.

Table 2 ^1H NMR LIS values[a] and separation of the contact and pseudocontact contributions for $[Ln(L^1)]^{3+}$ (Ln = Ce, Pr, Nd, Sm, Eu or Yb) paramagnetic complexes in CD_3CN solution (see Scheme 1 for labelling)

	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
2	−2.91	−0.90	0.73	1.88	1.43	1.45	2.09	−4.38	−2.97	−0.69
3	−4.42	−5.23	−2.20	1.88	2.48	2.27	2.84	−14.35	−8.09	−6.32
4	−3.34	−4.50	−3.90	−0.63	0.55	0.07	0.09	−18.76	−5.89	−4.01
5	−0.52	−0.60	−0.54	0.29	0.17	0.24	0.02	0.39	−0.76	−0.68
6	4.53	6.66	4.86	1.27	0.03	0.88	0.22	34.07	7.61	7.46
F	0.42 ± 0.04	0.83 ± 0.09	0.74 ± 0.15	0.33 ± 0.05	0.14 ± 0.01	0.29 ± 0.03	0.21 ± 0.05	4.44 ± 0.15	0.69 ± 0.12	0.89 ± 0.14
G	0.39 ± 0.05	0.03 ± 0.10	−0.23 ± 0.10	−0.32 ± 0.03	−0.29 ± 0.01	−0.27 ± 0.01	−0.36 ± 0.02	0.04 ± 0.06	−0.35 ± 0.08	0.01 ± 0.17

[a] Positive values are to high field.

adduct **9** displays peaks due to species without 1,10-phenanthroline only: *m*/*z* 757, $[La(L^1)(ClO_4)_2]^+$; 658, $[La(L^1)(ClO_4)]^+$; and 558, $[La(L^1)]^+$.

The molar conductivity of 10^{-3} mol dm^{-3} solutions of the adducts in acetonitrile amounts to $\Lambda_M = 295$ and 293 Ω^{-1} cm^2 mol^{-1} for **9** and **10**, respectively. These data reveal that the two complexes behave as 2 : 1 electrolytes in this solvent,[37] consistent with the co-ordination of one perchlorate ion.

Electronic absorption spectra display a broad band centred at 358 nm ($\varepsilon = 9400$ dm^3 mol^{-1} cm^{-1}) due to the C=N chromophore in the macrocyclic ligand in both complexes **9** and **10**. The absorption band of free phen (263 nm) remains unchanged in the spectrum of **9**, while two bands are seen in the spectrum of **10** at 273 and 280 nm (free bipyridine: 280 nm). These data point to weak interaction with the bidentate chelating ligands.

The proton NMR spectra of the adducts were measured in CD_3CN and assignments were made on the basis of ^{1}H COSY correlation spectra and by comparison with the data for **1** (Table 1). The signals of the macrocyclic protons are shifted to high field by *ca.* 0.04–0.35 ppm for complex **9** and 0.00–0.16 ppm for **10**, with respect to the chemical shifts of **1**. The proton signals of 1,10-phenanthroline or 2,2′-bipyridine in the adducts **9** and **10** are also shifted compared to their position in the ^{1}H NMR spectra of the unco-ordinated species in the same solvent. Resonances arising from the phenanthroline protons 2 and 9 are shifted upfield by 0.32 ppm for **9**, while the 3,8; 4,7 and 5,6 proton signals are shifted downfield by 0.07, 0.27 and 0.21 ppm, respectively. In the spectrum of the bipyridine adduct **10**, the signals due to the protons at the 3 and 3′ positions are shifted upfield by 0.08 ppm while the resonances of protons in the 4, 4′ and 5, 5′ positions are shifted downfield by 0.15 and 0.17 ppm, respectively. These data confirm that the interaction between 1,10-phenanthroline or 2,2′-bipyridine and La^{III} leads to co-ordination of the bidentate chelating ligands. When an excess of the lanthanum complex **1** or of a bidentate chelating ligand is added to solution of **9** or **10**, a single resonance is observed for each non-equivalent set of protons, indicating that both phen and bipy are in fast exchange on the NMR timescale. The proton NMR spectra of both adducts remain unchanged after one month, pointing to a good stability of these entities.

When increasing amounts of $[La(L^1)][ClO_4]_3$ are added to an acetonitrile solution of 1,10-phenanthroline monohydrate the signal of the water protons shifts downfield with respect to a solution of phenanthroline hydrate. The value of $\Delta\delta$ depends on the ratio $R = [La(L^1)][ClO_4]_3$: phen. It is small when $R < 1.1$, but it becomes sizeable for $R > 1.1$, reaching 0.17 ppm for $R = 1.31$ and indicating that water is expelled from the inner co-ordination sphere of the metal ion by phenanthroline.

Assignment of the ^{13}C NMR spectra (Table 3) was achieved with the help of heteronuclear correlation spectroscopy (^{1}H–^{13}C COSY) and distortionless enhancements by polarisation transfer (DEPT) spectroscopy. Very slight displacements are observed in the chemical shifts of the macrocycle carbon atoms, compared to those of complex **1**, but significant changes occur for the 1,10-phenanthroline and 2,2′-bipyridine carbon signals upon co-ordination: resonances due to the carbon atoms in the 2,9 phen positions in **9** are shifted upfield by 0.8 ppm and the peaks due to the carbon atoms in the 3,8, 4,7, 5,6, and 13,14 positions are shifted downfield by 1.1, 3.8, 0.4 and 0.7 ppm, respectively. Similar shifts are also observed for **10**: the signal of the 6,6′ carbon atoms is shifted upfield by 1 ppm and those arising from the 3,3′, 4,4′ and 5,5′ carbon atoms are shifted by 1.6, 3.1 and 1.6 ppm, respectively.

The interaction of 1,10-phenanthroline with complex **1** was quantitatively characterised by monitoring changes in the ^{1}H resonance of the 2,9 protons. Only one resonance was observed indicating rapid exchange on the NMR timescale. Under these conditions the observed chemical shift δ is the average of the chemical shifts of the nucleus in the free and co-ordinated forms, weighted by the fractional populations $\delta = f_c\delta_c + f_f\delta_f$ where f_c and f_f are the fractional populations of the co-ordinated and the "free" ligand, respectively ($f_c + f_f = 1$). Assuming the formation of a 1 : 1 adduct only and defining $\Delta = \delta - \delta_f$, both the apparent stability constant K and $\Delta_{max} = \delta_c - \delta_f$ may be deduced, eqn. (4).[38] Data for $[La(L^1)][ClO_4]_3$

$$\Delta = \Delta_{max}K[Ln]/(1 + K[Ln]) \qquad (4)$$

binding to 1,10-phenanthroline were fitted by equation (4) up to a ratio $R = 1.25$ ($\Delta = 0.411$ ppm) by a non-linear curve-fitting routine, which yielded log $K = 2.63 \pm 0.04$ and $\Delta_{max} = 0.58 \pm 0.02$ ppm. The value of the binding constant is slightly lower than the one found by ^{139}La NMR spectroscopy for the 1 : 1 adduct between lanthanum(III) nitrate and 1,10-phenanthroline: log $K_1 = 3.3 \pm 0.3$.[39] This demonstrates that L^1 strongly binds La^{III} and also points to some steric hindrance resulting in a more difficult coordination of phen.

Photophysical properties of $[Ln(L^1)][ClO_4]_3$ (Ln = Nd, Gd, or Tb)

Absorption spectra of solutions of the complexes **1**–**8** in acetonitrile present a broad band centred at *ca.* 27560 cm^{-1} ($\varepsilon = 13950$ dm^3 mol^{-1} cm^{-1}), assigned to the imine chromophoric groups, and a second band at *ca.* 37594 cm^{-1} (28125 dm^3 mol^{-1} cm^{-1}) arising from the benzene rings. In the solid state, these transitions are shifted to lower energy: the reflectance spectra of both the gadolinium(III) (**7**) and terbium(III) (**8**) complexes display a broad band with a maximum at 23310 and 23981 cm^{-1}, respectively, and a weak band at 35842 and 36496 cm^{-1}, respectively. In addition to such transitions (24038 and 36765 cm^{-1}), the reflectance spectrum of **4** displays the characteristic neodymium(III) absorptions split by crystal field effects: 17452, 17271 and 17153 ($^4I_{9/2} \longrightarrow {}^4G_{5/2}$); 13605, 13605 ($^4I_{9/2} \longrightarrow {}^4S_{3/2}$); 13316 ($^4I_{9/2} \longrightarrow {}^4F_{7/2}$); 12706, 12642, 12563 and 12500 cm^{-1} ($^4I_{9/2} \longrightarrow {}^4F_{5/2}$).

The luminescence spectra of 2×10^{-4} mol dm^3 solutions of the complexes of Gd (**7**) and Tb (**8**) in anhydrous acetonitrile at room temperature and under excitation through the imine band at 23419 cm^{-1} consist of a broad emission from the $^1\pi\pi^*$ state, with maximum at 19980 (Gd) and 19940 cm^{-1} (Tb). No emission from the $^3\pi\pi^*$ state was observed even upon freezing the solution at 77 K. However, the excitation spectrum of **8** recorded under the same conditions, but setting the analysing wavelength on the maximum of the $^5D_4 \longrightarrow {}^7F_5$ transition (18349 cm^{-1}), displays a sharp band at 36179 cm^{-1} attributed to excitation to the Tb($^5I_7$) level.[40] Upon excitation through the latter, the complex emits strong lines corresponding to transitions from the $^5D_4$ to the ^7F_J manifolds (Fig. 2): 15468 ($J = 2$), 16064 ($J = 3$), 17094 ($J = 4$), 18349 ($J = 5$), and 20387 cm^{-1} ($J = 6$). The integrated relative intensities of these transitions are 1.00, 1.62, 0.34 and 0.12 for $J = 6$, 5, 4 and 3, respectively. Lifetime measurements ($\lambda_{exc} = 18349$, $\lambda_{an} = 36179$ cm^{-1}) yield $\tau(^5D_4) = 1.47 \pm 0.01$ ms while the absolute quantum yield of the metal-centred luminescence amounts to 8.7×10^{-2} %. Neither the $^5D_4$ lifetime nor the quantum yield is enhanced when **8** is dissolved in deuteriated acetonitrile. However, a substantial and unusual decrease of both the emission intensity and the $\tau(^5D_4)$ lifetime (0.63 ± 0.03 ms) occurs upon freezing the solution at 77 K.

A strong concentration dependence of the integrated area of the $^5D_4 \longrightarrow {}^7F_J$ emission bands was observed for solutions of complex **8** in acetonitrile (Fig. 3). The emission is poor for concentrations higher than 2×10^{-4} mol dm^{-3} due to intermolecular collisional quenching processes. The maximum emission intensity corresponds to concentrations between 1.3×10^{-4} and 3.5×10^{-5} mol dm^{-3}. At lower concentrations a drastic decrease is observed due to the dissociation of the complex.

Information on the solvation state of luminescent lanthanide complexes in methanol may be gained by comparison of the luminescence lifetimes in protonated and deuteriated methanol

Table 3 Carbon NMR shifts (ppm) for the complexes in CD_3CN solution. Data for free 1,10-phenanthroline and 2,2′-bipyridine are also reported for comparison (see Scheme 1 for labelling)

	C1	C2	C3	C4	C5/C10	C6	C7/C8	C9	C11	C12	C13	C14	C-2,9[a]	C-3,8[a]	C-4,7[a]	C-5,6[a]	C-11,12[a]	C-13,14[a]
1	143.8	122.9	155.9	164.3	153.1 152.9	116.1	132.4 125.9	121.0	74.6	137.4	132.5	141.5						
phen													150.7	124.0	136.9	127.4	146.8	129.5
9	143.3	122.7	155.1	164.1	152.6 152.4	116.2	131.8 125.6	120.4	75.2	137.4	132.5	140.9	149.9	125.1	140.7	127.8	n.o.	130.2
													C-2.2′[b]	C-3,3′[b]	C-4,4′[b]	C-5,5′[b]	C-6,6′[b]	
bipy													156.7	121.4	137.9	124.8	150.0	
10	143.7	123.1	155.8	164.3	152.9 153.0	116.2	132.4 125.9	121.0	74.7	137.4	132.6	141.4	n.o.	123.0	141.0	126.4	149.0	

Labelling for phen and bipy according to literature numbering; n.o. = not observed. [a] Carbon atoms corresponding to 1,10-phenanthroline. [b] Carbon atoms corresponding to 2,2′-bipyridine.

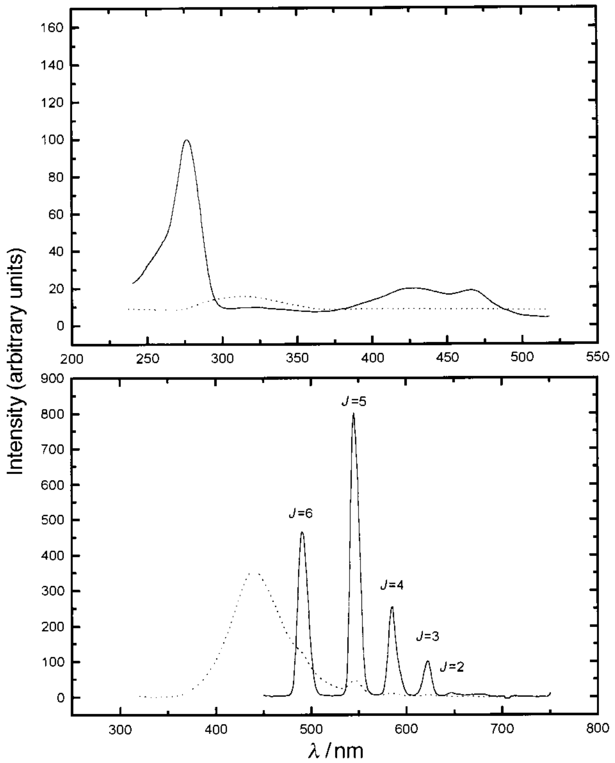


Fig. 2 Excitation (top) and emission spectra (bottom) of a solution of 2 × 10^{-4} mol dm^{-3} $[Tb(L^1)][ClO_4]_3$ in degassed acetonitrile (solid lines) and of the same solution after addition of one equivalent of 1,10-phenanthroline (dotted lines).

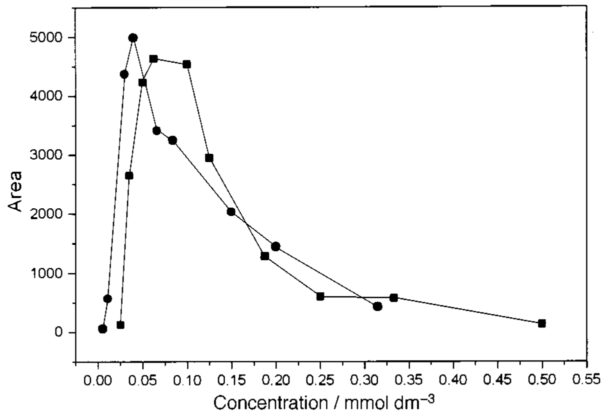


Fig. 3 Variation of the integrated area (arbitrary units) of the $^5D_4 \longrightarrow {}^7F_J$ transitions in the phosphorescence spectra of solutions of $[Tb(L^1)][ClO_4]_3$ **8** (■, $\lambda_{exc} = 276.4$ nm) and $[Tb(L^1)][ClO_4]_3$: phen (1 : 1) (●, $\lambda_{exc} = 303.2$ nm) in degassed acetonitrile. Vertical scales are not comparable.

and by use of the empirical relationship developed by Horrocks and co-workers[41] between the number of co-ordinated OH oscillators (q) and the differences in observed rate constants, eqn. (5). The luminescence decays of methanol solutions of

$$q = 8.4\,(\tau_H^{-1} - \tau_D^{-1}) \tag{5}$$

complex **8** are monoexponential corresponding to τ_H and τ_D values equal to 1.12 ± 0.01 and 3.61 ± 0.02 ms, respectively, which in turn yields $q = 5.1 \pm 0.5$. Assuming that ligand L^1 is co-ordinated to the Tb^{III} through all its donor atoms, a value $q = 2$–3 was expected. As no special care was taken to work under anhydrous conditions, the larger experimental q probably reflects the presence of two water and one methanol molecules bonded to the Tb^{III} in these solutions.

Addition of one equivalent phenanthroline to a 2 × 10^{-4} mol dm^{-3} solution of the terbium complex **8** in acetonitrile results in a blue shift of the absorption band due to the imine chromophoric group, from 27599 to 29155 cm^{-1}. In the excitation spectrum the band assigned to the Tb($^5I_7$) level vanishes while a new band appears at 32980 cm^{-1} (Fig. 2). The emission spectrum under excitation through the latter consists of a broad ligand-centred band at 22727 cm^{-1} ($^1\pi\pi^*$ state emission) together with weak emission bands arising from the Tb($^5D_4 \longrightarrow {}^7F_J$) transitions: 16076 ($J = 3$), 17078 and 16907 ($J = 4$), 18329 ($J = 5$) and 20366 cm^{-1} ($J = 6$). The integrated and relative intensities of the $^5D_0 \longrightarrow {}^7F_J$ transitions amount to 1.00, 1.65, 0.36 and 0.11 for $J = 6$, 5, 4 and 3, respectively and a concentration quenching similar to the one evidenced for **8** is observed (Fig. 3). The $^5D_4$ lifetime is short (0.335 ± 0.003 ms) probably because of the presence of a back transfer to the $^3\pi\pi^*$ level of the ligand. The quantum yield of the metal-centred luminescence (3 × 10^{-2}%) is three times smaller than that of **8**, pointing to a poorer energy transfer from the ligand to the Tb^{III}. No emission from the Tb^{III} was observed after addition of bipy to acetonitrile solutions of **8**.

Formation of the reduced macrocycle L^2 and electrochemical study

The reaction between 2,6-bis(2-aminophenoxymethyl)pyridine and 2,6-diformylpyridine in ethanol solution in the presence of the perchlorates of Gd and Tb yields a compound corresponding to the reduced macrocycle L^2. Evidence for the formation of this macrocycle arises from the absence of the stretching band at 1607 cm^{-1} due to the imine groups in the IR spectrum and from the presence of the band at 3390 cm^{-1} due to the amine groups. The ^{1}H NMR spectrum displays two single peaks attributable to the methylene protons while there is no peak due to the imine protons. Reduction of ligand L^1 is also observed when the gadolinium (**7**) or terbium (**8**) complex is dissolved in ethanol and heated to reflux. The reaction can easily be followed by monitoring the decreasing intensity of the electronic absorption band at 350 nm due to the imine groups. The spectrum of the free reduced macrocycle is obtained after heating at 50 °C during a few hours. The reduction occurs with the complexes of Eu and Sm as well, but the kinetics is substantially slower. Although examples of unexpected reduction of Schiff base macrocycles have been described,[42,43] no detailed investigation has been reported in order better to understand the reasons for this reaction. Infrared spectroscopy provides evidence that the reduction is promoted by ethanol: a 10^{-3} mol dm^{-3} solution of the gadolinium complex in 1 : 1 acetonitrile–ethanol was prepared and heated for 17 h at 50 °C in a closed cell. After this period of time the IR spectrum displays a new band at 1719 cm^{-1} attributable to acetaldehyde. No such reduction process was detected when the reaction was carried out in methanol, acetonitrile or 2-propanol. The following two mechanisms can be invoked to explain the reduction process.

Mechanism 1:

$$[Ln(L^1)][ClO_4]_3 + 2EtOH \longrightarrow [Ln(L^2)][ClO_4]_3 + 2\,CH_3COH \qquad \text{Step 1}$$

$$[Ln(L^2)][ClO_4]_3 \longrightarrow Ln^{3+}(solv) + 3ClO_4^-(solv) + L^2 \qquad \text{Step 2}$$

In the first step, the solvent reduces the ligand with formation of the lanthanide complex of macrocycle L^2 and of acetaldehyde. Step two involves a quick demetallation of this complex due to the smaller affinity of the lanthanide(III) ions for the reduced macrocycle.

Mechanism 2:

$$[Ln(L^1)][ClO_4]_3 \longrightarrow Ln^{3+}(solv) + 3ClO_4^-(solv) + L^1 \qquad \text{Step 1}$$

$$L^1 + 2\,EtOH \longrightarrow L^2 + 2\,CH_3COH \qquad \text{Step 2}$$

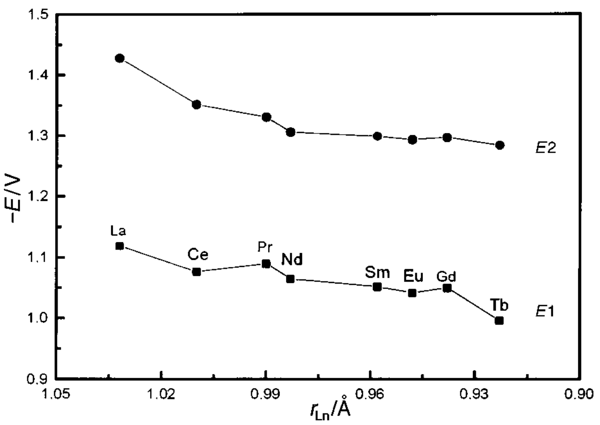


Fig. 4 Electrochemical data for the $[Ln(L^1)][ClO_4]_3$ complexes in 0.1 mol dm^{-3} tetrabutylammonium perchlorate acetonitrile solution. Potentials are given using Fc–Fc$^+$ as the reference.

In the second mechanism, the first step consists in the demetallation of the complex by the solvent followed by the reduction of the macrocyclic ligand by ethanol.

To distinguish between these two mechanisms we have investigated the redox behaviour of the complexes in dry acetonitrile by cyclic voltammetry. All the lanthanide complexes present a similar voltammogram comprised of two irreversible peaks ($E1$ and $E2$) due to the reduction of the imine groups. Progressive shifts of the reduction waves to less negative potentials were observed upon decreasing the ionic radius of the lanthanide(III) ion (Fig. 4), with a total potential difference of 100 and 140 mV between the complexes of La^{III} and Tb^{III} for $E1$ and $E2$, respectively. That is, less energy is needed for the reduction of the $[Ln(L^1)][ClO_4]_3$ complexes when the ionic radius of the metal ion is smaller.

In order to investigate the effect of the ionic radius and of the charge of the metal ion on the reduction potential of the imine groups we have synthesized the barium and sodium complexes of L^1. The cyclic voltammogram of the barium complex **11** is similar to those of the lanthanide(III) complexes, except for an important shift of the reduction potentials to less negative values ($E1$ −1.41 V and $E2$ −1.59 V *versus* Fc–Fc$^+$). The sodium complex **12** presents a single reduction wave also shifted to less negative potential with respect to the lanthanide complexes ($E = -1.75$ V). These data indicate that the reduction of the macrocycle L^1 is more favoured upon co-ordination to the lanthanide(III) ions than to Ba^{2+} and Na$^+$. The redox potentials obtained by cyclic voltammetry seem to be related to the energy of the ν(CH=N) stretching mode. This mode is located at *ca.* 1608 cm^{-1} for the lanthanide complexes, while it appears at higher wavenumbers for the barium and sodium complexes (1621 and 1626 cm^{-1}, respectively), which suggests that more energy is required to reduce the imine groups when the CH=N bond is stronger.

The data obtained by cyclic voltammetry show that the variation in the redox potentials from Ce to Gd is very small, and does not justify the fact that the reduction does not occur in the case of the cerium(III) complex but occurs for the gadolinium(III) complex if mechanism 1 were assumed. Therefore, we think that this behaviour may be related to differences in the formation constants of the complexes due to the size of the macrocycle cavity since the interaction between L^1 and lanthanide(III) ions decreases with decreasing ionic radii of the metal ions. As a consequence, the complexes of Gd and Tb will dissociate more in ethanol solution than those with the lighter lanthanide(III) ions. Therefore, mechanism 2 appears to be more realistic than mechanism 1.

Conclusion

The polyoxaaza Schiff-base macrocycle L^1 is a strongly binding versatile ligand for co-ordination to the lanthanide(III) ions. The proton LIS and lanthanide induced relaxations (LIR) effects observed in the paramagnetic $[Ln(L^1)][ClO_4]_3 \cdot xH_2O$ complexes indicate that L^1 acts as a hexadentate ligand in acetonitrile solution, displaying a strong interaction between the imine nitrogen atoms and the lanthanide ion. These complexes are co-ordinatively unsaturated, which allows the additional co-ordination of small chelating bidentate ligands such as phen and bipy; phen removes water from the inner co-ordination sphere upon co-ordination to lanthanum complex **1**. The terbium(III) complex **8** shows emission arising from the Tb^{III} upon excitation through its excited levels. Addition of phen to an acetonitrile solution of **8** allows one to observe emission from the Tb^{III} upon excitation through the ligand bands, but the low value obtained for the lifetime could indicate the presence of back transfer to the $^3\pi\pi^*$ state of the ligand.

The reaction of 2,6-(2-aminophenoxymethyl)pyridine, 2,6-diformylpyridine and gadolinium(III) or terbium(III) perchlorate in ethanol solution gives the reduced macrocycle L^2 instead of the expected complex of L^1, clearly revealing that the solvent acts as the reductant in this reaction. Reduction potentials obtained by cyclic voltammetry experiments indicate that the reduction of the imine groups is more favourable on decreasing the ionic radius of the lanthanide(III) ion.

Experimental

Chemicals and starting materials

2,6-Diformylpyridine was prepared according to literature methods,[44,45] 2,6-bis(2-aminophenoxymethyl)pyridine monohydrate by reduction of the corresponding dinitro precursor as described previously.[46] Lanthanum(III) perchlorate and 2,2′-bipyridine (99%) were commercial products from Alfa laboratories used as received, 1,10-phenanthroline monohydrate (99.5%) reagent from Merck. Solvents were of reagent grade purified by the usual methods.[47] Acetonitrile-d$_3$ (ACROS, 99% D) was used as received.

CAUTION: perchlorates are potentially explosive, especially when in contact with organic amines and they should be handled with all the necessary care!

Measurements

Elemental analyses (Carlo Erba 1108 analyzer), ^{1}H and ^{13}C NMR (Bruker AC 200 F spectrometer) and FAB mass spectra (Fisons Quatro spectrometer with Cs ion-gun and 3-nitrobenzyl alcohol or disulfur matrix) were obtained by Servicios Generales de Apoyo a la Investigación (Universidade da Coruña). Longitudinal ^{1}H relaxation times (T_1) were measured by the inversion-recovery pulse sequence. The paramagnetic contributions to the relaxation rates were corrected for diamagnetic effects using the T_1 values for the lanthanum complex under the same experimental conditions. The IR spectra were recorded as KBr discs and/or Fluorolube® mulls using a Perkin-Elmer 1330 spectrophotometer.

Conductivity measurements were carried out on *ca.* 10^{-3} mol dm^{-3} acetonitrile solutions at 25 °C using a Crison Micro CM 2201 conductivimeter. Cyclic voltammetry experiments were made using Autolab equipment with a PGSTAT 20 potentiostat at 25 °C. A platinum electrode was used as the working electrode and a platinum rod as the counter electrode. A silver wire was used as a pseudo reference electrode and calibrated with ferrocene as internal standard. All the potentials reported in this work are referenced to the classical Fc$^+$–Fc standard couple. All experiments were carried out in acetonitrile under dry argon and with 0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte.

Electronic spectra were recorded at room temperature with a Perkin-Elmer Lambda 7 spectrometer using 1.0 or 0.1 cm quartz cells, reflectance spectra from finely ground powders dispersed in MgO (5%) with MgO as reference on a Perkin-Elmer Lambda 900 spectrometer fitted with a PELA-1000 integration sphere from Labsphere. Low resolution excitation and emission spectra were recorded on Perkin Elmer LS-50B spectrometer equipped for low-temperature (77 K) measurements. The quantum yields of the complexes were determined[48] for 2×10^{-4} mol dm^{-3} solutions in acetonitrile using $[Tb(terpy)]^{3+}$ as reference. Lifetimes (τ) are averages of at least 3–5 independent determinations.

Syntheses of the complexes

The complexes $[Ln(L^1)][ClO_4]_3 \cdot xH_2O$ **1**–**8** (Ln = La–Tb, except Pm) were prepared as previously described (**1**, **2**, $x = 0$; **3**, **4**, **6**–**8**, $x = 1$; **5**, $x = 3$).[20]

$[La(L^1)(phen)][ClO_4]_3 \cdot 2H_2O$ 9. 2,6-Diformylpyridine (0.3 mmol) dissolved in acetonitrile (40 mL) was slowly added to a refluxing acetonitrile solution (30 mL) of 2,6-bis(2-aminophenoxymethyl)pyridine (0.3 mmol), $La(ClO_4)_3 \cdot 6H_2O$ (0.3 mmol) and 1,10-phenanthroline (0.3 mmol). The resultant mixture was refluxed during 3 h, filtered and evaporated to dryness. The brown microcrystalline precipitate was recrystallised from acetonitrile–toluene and the solid obtained was filtered off and dried under vacuum (yield 90%) (Found: C, 42.4; H, 3.3; N, 7.8. $C_{38}H_{28}Cl_3LaN_6O_{14} \cdot 2H_2O$ requires C, 42.5; H, 3.0; N, 7.8%).

$[La(L^1)(bipy)][ClO_4]_3 \cdot 2H_2O$ 10. The complex was synthesised by the procedure described for **9** but using 0.3 mmol of 2,2′-bipyridine instead of phen (yield 89%) (Found: C, 41.4; H, 3.4; N, 7.8. $C_{36}H_{28}Cl_3LaN_6O_{14} \cdot 2H_2O$ requires C, 41.2; H, 3.1; N, 8.0%).

$[Ba(L^1)][ClO_4]_2 \cdot H_2O$ 11. 2,6-Bis(2-aminophenoxymethyl)-pyridine monohydrate (0.3 mmol) and $Ba(ClO_4)_2 \cdot 3H_2O$ (0.3 mmol) were dissolved in hot absolute ethanol (35 mL). 2,6-Diformylpyridine (0.3 mmol) dissolved in absolute ethanol (20 mL) was slowly added. Stirring and heating was maintained during the addition and the solution then refluxed during 2 h. The yellow powdered precipitate was filtered off, washed with diethyl ether and dried under vacuum (yield 75%) (Found: C, 40.3; H, 2.7; N 7.2. $C_{26}H_{20}BaCl_2N_4O_{10} \cdot H_2O$ requires C, 40.3; H, 2.9; N, 7.2%). ν(CH=N) 1621, ν(py) 1580, $\nu(ClO_4^-)$ 1121 cm^{-1} (KBr disc). δ_H (200 MHz; solvent CD_3CN) 8.92 (s, 2 H, CHN), 8.31 (t, 1 H, py), 8.06 (d, 1 H, py), 7.20–7.80 (m, 11 H, aryl, py) and 5.49 (s, 4 H, CH_2O). FAB mass spectrum: *m*/*z* 657, $[Ba(L)(ClO_4)]^+$ (100%).

$[Na(L^1)][ClO_4] \cdot H_2O$ 12. 2,6-Bis(2-aminophenoxymethyl)-pyridine monohydrate (0.3 mmol) and $NaClO_4 \cdot H_2O$ (0.3 mmol) were dissolved in hot absolute ethanol (35 mL). 2,5-Diformylpyridine (0.3 mmol) dissolved in absolute ethanol (20 mL) was slowly added. Stirring and heating was maintained during the addition and the solution then refluxed for 1 h. It was concentrated to 20 mL and 20 mL of diethyl ether were added; a yellow precipitate separated and was filtered off, washed with diethyl ether and dried under vacuum (yield 75%) (Found: C, 55.8; H, 3.9; N 10.1. $C_{26}H_{20}ClN_4NaO_6 \cdot H_2O$ requires C, 55.7; H, 4.0; N, 10.0%). ν(CH=N) 1626, ν(py) 1582, $\nu(ClO_4^-)$ 1101, 1090, 623 cm^{-1} (KBr disc). δ_H (200 MHz; solvent CD_3CN) 8.82 (2 H, s, CHN), 8.19 (1 H, t, py), 7.86–7.96 (3 H, m, py), 7.12–7.52 (10 H, m, aryl, py) and 5.28 (4 H, s, CH_2O).

Reaction between 2,6-bis(2-aminophenoxymethyl)pyridine and 2,6-diformylpyridine in the presence of the perchlorates of Tb and Gd in ethanol solution

A solution of 2,6-diformylpyridine (0.3 mmol in 30 mL) was slowly added to 35 mL of a refluxing ethanol solution of 2,6-bis(2-aminophenoxymethyl)pyridine (0.3 mmol) and gadolinium or terbium perchlorate (0.45 mmol). After the addition was complete the resultant solution was refluxed during 16 h. It was filtered while hot and slowly evaporated at room temperature to yield the reduced macrocycle L^2 as white crystals (yield 45%) (Found: C, 72.2; H, 5.4; N 12.9. $C_{26}H_{24}N_4O_2 \cdot 0.5H_2O$ requires C, 72.0; H, 5.8; N, 12.9%). IR (KBr disc): ν(NH) 3390, ν(py) 1578 cm^{-1}; δ_H (200 MHz; solvent $CDCl_3$) 7.71, 7.59 (1 H, t, py), 7.33, 7.19 (2 H, d, py), 6.98–6.70 (8 H, m, aryl), 5.10 (4 H, s, CH_2O), 4.57 (2 H, br, NH) and 4.32 (4 H, s, CH_2N). FAB mass spectrum: *m*/*z* 425 (100%).

Determination of the stability constant of $[La(L^1)(phen)][ClO_4]_3$ was carried out at 23 °C in acetonitrile containing tetrabutylammonium perchlorate ($I = 0.1$ mol dm^{-3}) and 4.4 mmol dm^{-3} of 1,10–phenanthroline; $[La(L^1)][ClO_4]_3$ concentrations ranged between 1.1 and 6 mmol dm^{-3}.

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