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FULL PAPER

A Schiff-base bibracchial lariat ether selective receptor for lanthanide(III) ions †

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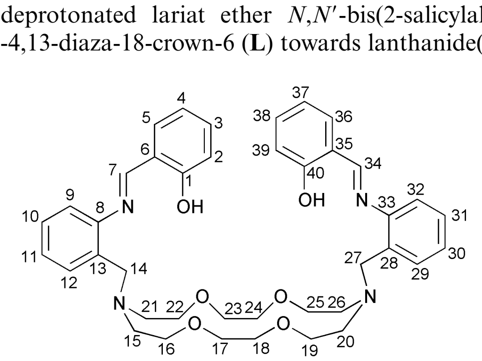
The bibracchial lariat ether *N*,*N*′-bis(2-salicylaldiminobenzyl)-4,13-diaza-18-crown-6 (**L**), in its di-deprotonated form, behaves as a selective receptor for lanthanide(III) ions. It only forms stable complexes with the three lightest members of the lanthanide series, lanthanum(III), cerium(III) and praseodymium(III). The X-ray crystal structures of these three complexes show the metal ion ten-coordinated and deeply buried in the cavity of the dianionic receptor. In all three structures the lariat ether presents a *syn* arrangement. However, the different size of the encapsulated metal ion modifies the conformation of the receptor, particularly in the fold of the crown, resulting in a very different coordination polyhedron for La(III) (distorted tetracapped trigonal prism) with respect to that of Ce(III) and Pr(III) (bicapped square antiprism). Spectrophotometric titration of the dianionic lariat ether with anhydrous $La(ClO_4)_3$ in acetonitrile allowed us to calculate log *K*[La(**L** − 2H)] = 4.65(4).

Introduction

The numerous and diverse possibilities that the macrocycles offer in many different fields (as models for biological systems, synthetic ionophores or therapeutic reagents, to study magnetic exchange phenomena or guest–host interactions, or even as selective extractive agents) continues to attract the attention of chemists. Nowadays, the literature reports a great variety of macrocyclic molecules which have been tailor-made for specific uses. Thus, lariat ethers, containing additional donor atom(s) in the side arm(s), have been designed to enhance the cation binding ability and the selectivity of the parent crown ether by means of further bonds of the side arm donor(s) to a cation lodged within the crown cavity.[1]

In the present paper we describe the coordinative ability of the di-deprotonated lariat ether *N*,*N*′-bis(2-salicylaldiminobenzyl)-4,13-diaza-18-crown-6 (**L**) towards lanthanide(III) ions.



L

Although the coordinative properties that the lariat ethers display towards alkaline and alkaline-earth ions have been the subject of numerous papers in recent decades, the coordination chemistry of the lanthanide ions with this type of macrocyclic receptor remains relatively unexplored. The studies available in the literature concerning lanthanide complexes with lariat ethers have been mainly focused on kinetic and thermodynamic aspects and they have overlooked the structural characterisation, particularly in the solid state. Moreover, to our knowledge, the papers reported to date in this field only relate to lariat ethers containing non-ionisable[2] or carboxylate[3] side arms. There is no example in the literature of lanthanide complexes with lariat ethers bearing ionisable pendant arms containing imine functional groups. The closest example to these types of ligand may be the hexaazamacrocycle reported by Kanesato and Itabaski.[4]

Results and discussion

Reaction of **L** [prepared *in situ* by the condensation of *N*,*N*′-bis(2-aminobenzyl)-4,13-diaza-18-crown-6 and salicylaldehyde] with triethylamine and the corresponding hydrated lanthanide perchlorate in 2-propanol led to complexes with the formula [Ln(**L** − 2H)](ClO_4) (Ln = La, **1**; Ce, **2**; and Pr, **3**). Attempts to obtain the expected complexes with the other lanthanide ions (Nd to Lu) under the same experimental conditions failed, precipitating the corresponding lanthanide hydroxide instead. In all these cases (Nd ⟶ Lu) hydrolysis of the Schiff-base and protonation of the *N*,*N*′-bis(2-aminobenzyl)-4,13-diaza-18-crown-6 precursor was also observed.

The IR and FAB-mass spectra of compounds **1**, **2** and **3** confirmed the formation of the Schiff-base lariat ether and its presence in the complexes. The IR spectra (KBr discs) feature a band attributable to the $\nu(C{=}N)_{imine}$ stretching mode at 1608 cm^{-1} for **1**, 1607 for **2** and 1609 cm^{-1} for **3**. This band appears at 1618 cm^{-1} in the spectrum of the uncoordinated lariat ether **L**,[5] and it is clearly shifted to lower wavenumbers by deprotonation and complexation. The presence of this band together with the absence of bands due to carbonyl and/or amine vibration modes confirms the formation of the imine. Bands corresponding to the $\nu_{as}(ClO)$ stretching and $\delta_{as}(O–Cl–O)$ bending modes

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† Electronic supplementary information (ESI) available: a Table of selected bond angles for complexes **1–3**, and a Table of θ_i and ω_i angles for **2** and **3**. See http://www.rsc.org/suppdata/dt/b1/b100872m/

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Table 1 Selected bond lengths (Å) for complexes **1**, **2** and **3**

	1	**2**	**3**
M–O(1)	2.310(3)	2.293(3)	2.279(3)
M–O(2)	2.313(3)	2.320(3)	2.291(4)
M–O(3)	2.805(3)	2.686(4)	2.679(4)
M–O(4)	2.806(3)	2.697(4)	2.687(4)
M–O(5)	2.713(4)	2.661(4)	2.648(4)
M–O(6)	2.810(3)	2.730(4)	2.723(5)
M–N(1)	2.757(3)	2.673(4)	2.654(4)
M–N(2)	3.029(3)	3.004(5)	3.001(5)
M–N(3)	3.016(4)	3.032(5)	3.026(6)
M–N(4)	2.779(3)	2.725(4)	2.711(5)

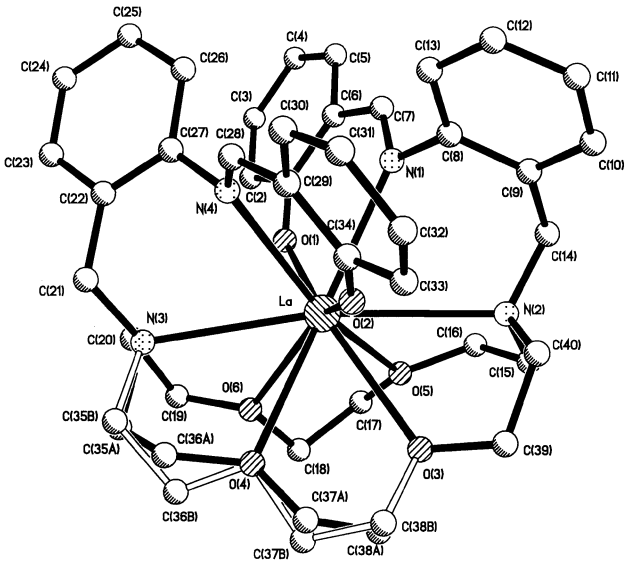


Fig. 1 Molecular structure of [La(**L** − 2H)]$^+$ (*Λ* isomer). Hydrogen atoms are omitted for simplicity.

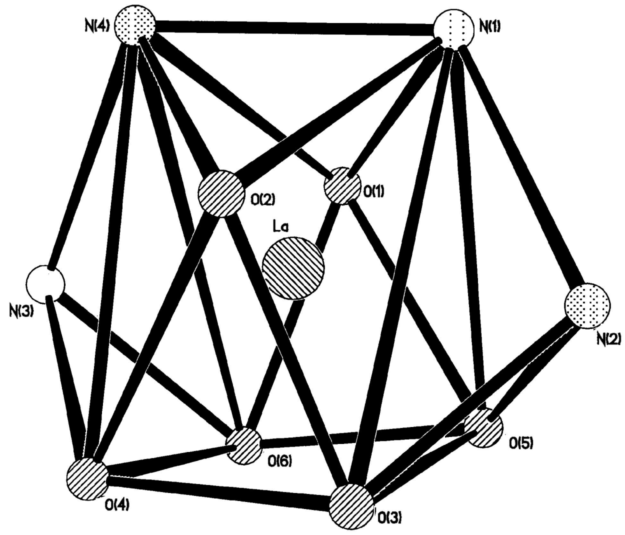


Fig. 2 View of the coordination polyhedron in [La(**L** − 2H)]$^+$.

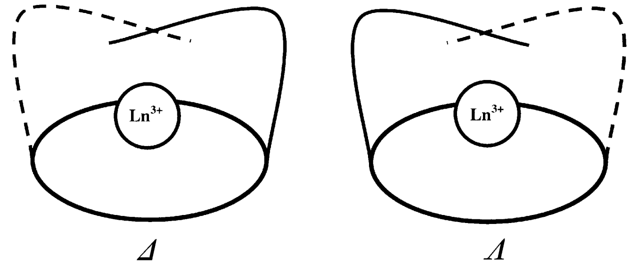
of the perchlorate groups appear at *ca.* 1090 and 622 cm^{-1}. The former appears as a very broad band and it is very uninformative with respect to the coordination mode of the perchlorate group. However, the absorption at 622 cm^{-1} appears clearly without splitting, as befits an uncoordinated anion. The FAB-mass spectra of the complexes display a very intense peak (100% BPI) at *m*/*z* 817 for **1**, 818 for **2** and 819 for **3** due to [Ln(**L** − 2H)]$^+$.

The ^{1}H NMR spectrum of the La(III) diamagnetic complex **1** was recorded in d$_3$-acetonitrile solution and assigned on the basis of two-dimensional COSY and NOESY experiments, showing the following signals: δ 8.02 (s, H7, H34), 7.16 (d, H9, H32), 7.12 (d, H2, H39), 7.04 (t, H11, H30), 6.72 (m, H3–H5, H36–H38), 6.48 (t, H10, H31), 6.09 (d, H12, H29) and 4.2–2.1 (m, H14–H27). The anionic nature of the receptor is confirmed by the absence of the signal due to the phenol protons that the spectrum of **L** exhibits at δ 13.21. Coordination to the metal shifts the signals corresponding to aromatic and imine protons to high field. As expected, the signals corresponding to the ethylenic protons of the crown moiety appear at high field as complicated multiplets due to the coordination of the metal by the oxygen atoms of the crown. The ^{1}H NMR spectra of the paramagnetic complexes, **2** and **3**, recorded in d$_3$-acetonitrile solution display 23 proton signals for the 46 protons of the ligand, thereby confirming the effective C_2 symmetry of the complexes in this solvent. This is also consistent with the ^{1}H NMR spectrum of **1**, for which only nine aromatic peaks are observed for the 18 aromatic protons of (**L** − 2H)$^{2-}$. The effect of the paramagnetic centre on the longitudinal (T_1) NMR relaxation processes is accounted for by the Solomon–Bloembergen–Morgan equation,[6] which is reduced to dipolar and Curie spin contributions for lanthanide complexes because contact contributions are negligible. Both remaining contributions depend on ($1/r_i^6$), and therefore T_1 measurements can provide structural information on lanthanide complexes in solution.[7] Although the assignment of the ^{1}H NMR spectra of **2** and **3** was not possible due to the short relaxation times of the proton nuclei preventing us performing 2D NOESY NMR experiments, the T_1 values measured for the 23 proton signals of **2** are very short, ranging from 2.72 to 115.83 ms. These values point to all the proton nuclei lying relatively close to the paramagnetic centre, suggesting that the whole set of the macrocyclic ligand donor atoms are bonded to the metal ion in acetonitrile solution.

X-Ray crystal structure of 1

Crystals of **1** contain the cation [La(**L** − 2H)]$^+$ and a well-separated perchlorate anion. Fig. 1 displays a view of the structure of the cation, where it is also possible to appreciate how the carbon atoms from one chain of the crown moiety, C(35), C(36), C(37) and C(38), are disordered into two positions with occupancy factors of 0.43 for C(35A) and C(36A) and 0.52 for C(37A) and C(38A). Selected bond lengths are given in Table 1 and angles in Table S1 (ESI),† respectively. The lanthanum ion is coordinated to the ten available donor atoms of the Schiff-base bibracchial lariat ether (**L** − 2H)$^{2-}$ and almost symmetrically positioned with respect to the ligand cavity. Bond lengths from both phenolate oxygen atoms to the lanthanum ion are almost equal [La–O(1) 2.310 Å, La–O(2) 2.313 Å] as well as those found from both pivotal nitrogen atoms [La–N(2) 3.029 Å, La–N(3) 3.016 Å] and those from both imine nitrogen atoms [La–N(1) 2.757 Å, La–N(4) 2.779 Å]. The distances between La and both pivotal nitrogen atoms and between La and the oxygen atoms of the crown moiety (2.7–2.8 Å) are longer than those found for lanthanum complexes with macrocycles containing pendant arms or crown ethers.[8,9] However, the distances between La and both phenolate oxygen atoms and between La and both imine nitrogen atoms are 0.1–0.2 Å shorter than those reported in the literature.[10,11] The four oxygen atoms of the crown moiety, O(3), O(4), O(5) and O(6), are essentially coplanar, with a mean deviation from planarity of just 0.0915 Å, and the lanthanum ion is located 1.8749 Å above this plane. The coordination environment of the metal may be best described as a distorted tetracapped trigonal prism (2 : 2 : 2 : 4). As shown in Fig. 2, the four oxygen atoms of the crown moiety, O(3), O(4), O(5) and O(6), together with both imine nitrogen atoms, N(1) and N(4), form the trigonal prism. Each phenolate oxygen atom, O(1) and O(2), is capping one rectangular face of the prism and each pivotal nitrogen atom, N(2) and N(3), is capping a triangular face.

Fig. 1 allows an appreciation of the conformation adopted by the bibracchial lariat ether in **1**. Both side arms are orientated on the same side of the crown moiety, resulting in a *syn* conformation. Likewise, the lone pairs of both pivotal nitrogen atoms are forced to point towards the receptor cavity in an *endo–endo* arrangement. It must be remarked that the *syn* conformation adopted by the lariat ether confers to the complex a chiral structure with two possible optical isomers, generally labelled as *Λ* or *Δ*, indicating either left-handed (*Λ*) or right-handed (*Δ*) structural chirality about the two-fold symmetry axis of the complex (Scheme 1). It could be surprising that in spite of its chirality the complex crystallises in the $P2_1/n$ space group, which is not chiral. This is because the crystal contains a racemic mixture of both enantiomers ($Z = 4$, two of them *Λ* and the other two *Δ*) centrosymmetrically related.



Scheme 1 Schematic representation of the two possible optical isomers (*Δ* and *Λ*) for [Ln(**L** − 2H)]$^+$.

The angles N(3)–C(21)–C(22) and N(2)–C(14)–C(9), which are related with the fold of the pendant arms in the receptor, are 114.5° and 113.5°. The planes defined by the benzene rings intersect at 64.1°, while the planes formed by the phenol rings intersect at 61.4°. The benzene and phenol rings of the same pendant arm are in different planes, which form angles of 64.5° and 73.7°. Distances between donor atoms give an idea about the shape and size of the receptor cavity. Both pivotal nitrogen atoms are far apart, 6.023 Å, as are both imine nitrogen atoms, 3.076 Å, and the distance between the phenolate oxygen atoms is 4.368 Å.

X-Ray crystal structures of 2 and 3

Crystals of **2** and **3** are isomorphous and consist of the cations, [Ce(**L** − 2H)]$^+$ and [Pr(**L** − 2H)]$^+$, respectively, and one well-separated perchlorate anion. As shown in Fig. 3 both complex cations contain the corresponding lanthanide ion ten-coordinated bound to all the donor atoms of the bibracchial lariat ether, similar to the lanthanum complex **1**. Tables 1 and S1 (ESI)† summarise the selected bond lengths and angles, respectively, for **2** and **3**. Distances between the corresponding metal ion and both phenolate oxygen atoms or both imine nitrogen atoms are in the range found in the literature.[12,13] However, the distances between the lanthanide ion (Ce or Pr) and both pivotal nitrogen atoms are considerably longer than those reported previously.[14] In fact, the distances Ce–N(3) and Pr–N(3), found for **2** and **3** respectively, are even longer than the distance La–N(3), found for complex **1**. Distances between Ln and the crown ether oxygen atoms are 0.1–0.2 Å longer than those previously reported for related compounds.[15]

The conformation of the bibracchial lariat ether in both complexes, **2** and **3**, is again *syn endo–endo* similar to that present in **1**, also resulting in structural chirality. However its fold around the trapped lanthanide ion is clearly different to that found in **1**. This fact is evident because the four oxygen atoms of the crown moiety are not coplanar in **2** and **3**. Now, the coordination polyhedron at the lanthanide (Ce, Pr) may be described as a distorted bicapped square antiprism which is considered to be comprised of two parallel planes: O(1), O(4), O(6) and N(4) define the upper pseudo-plane and O(3), O(5), O(2) and N(1) define the lower pseudo-plane, N(3) and N(2) capping the upper and lower planes, respectively (Fig. 4). The degree of distortion of the bicapped square antiprisms has been investigated quantitatively using a geometric analysis based on the determination of three angles, ϕ, θ_i and ω_i (Fig. 5).[16] The average bending of the upper [vs(j)] and lower [vi(j)] pseudo-planes is measured by the angle ϕ between the sum vectors $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ [$\boldsymbol{R}_1 = \Sigma_{j=1}^{j=4}\text{Ln} - \text{vs}(j)$, $\boldsymbol{R}_2 = \Sigma_{j=1}^{j=4}\text{Ln} - \text{vi}(j)$, and $\phi = 180°$ for an ideal square antiprism], while the angles θ_i reflect the flattening of the coordination polyhedron along the pseudo-C_3 axis. Finally, the angles ω_i show the deformation of the coordination polyhedron from a square antiprism (ideal value

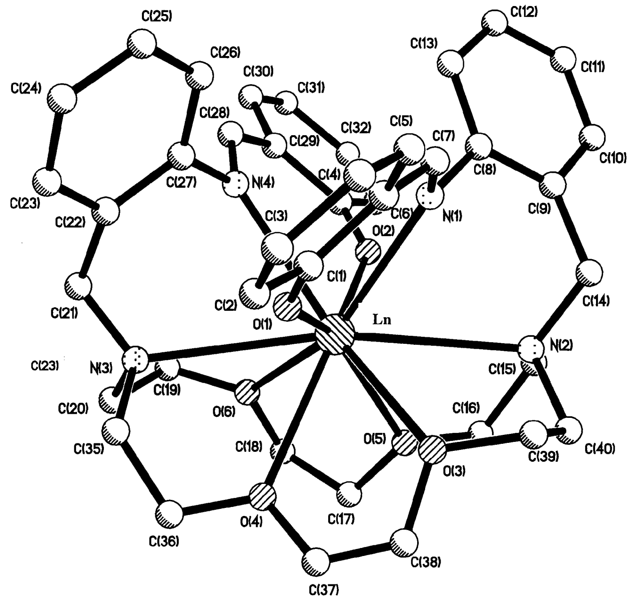


Fig. 3 Molecular structure of [Ln(**L** − 2H)]$^+$ (*Δ* optical isomers); Ln = Ce, Pr. Hydrogen atoms are omitted for simplicity.

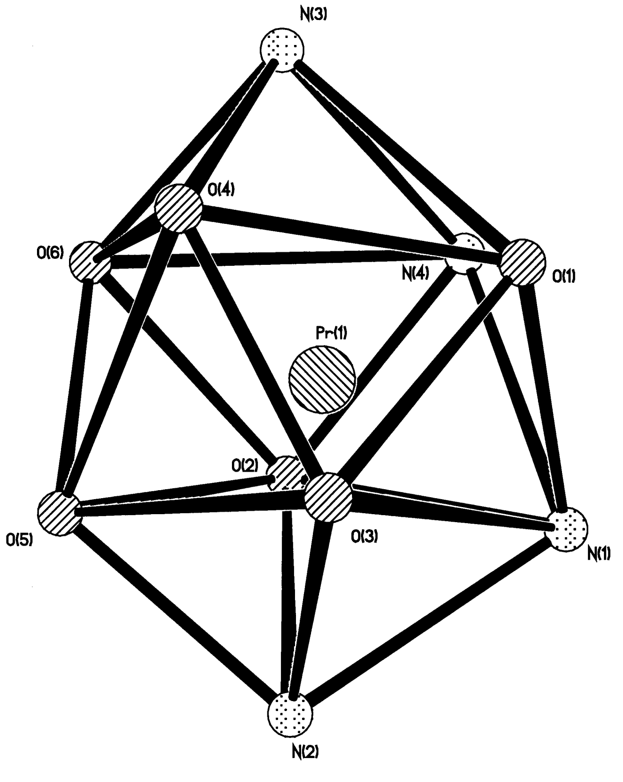


Fig. 4 View of the coordination polyhedron in [Ce(**L** − 2H)]$^+$ and [Pr(**L** − 2H)]$^+$.

Table 2 Geometric analysis of the coordination polyhedron in **2** and **3**

	2	**3**
$\alpha^1/°$ [a]	0.4	0.7
$\alpha^2/°$ [b]	167.08	166.80
d^1/Å [c]	0.1422	0.1373
d^2/Å [d]	0.1673	0.1616
d^3/Å [e]	2.3021	2.2951
d^4/Å [f]	1.8491	1.8504
d^4/Å [g]	1.8069	1.8054
$\phi/°$	171.43	170.71
Mean θ $vs_i - \boldsymbol{R}_1/°$	63.1	63.0
Mean θ $vs_i - \boldsymbol{R}_2/°$	64.3	64.2

[a] Angle between the upper and lower facial planes. [b] Angle N(2)–Ln–N(3). [c] Mean deviation from planarity of the upper facial plane. [d] Mean deviation from planarity of the lower facial plane. [e] Distance between the upper and lower facial planes. [f] Distance between N(2) and the upper plane. [g] Distance between N(3) and the lower plane.

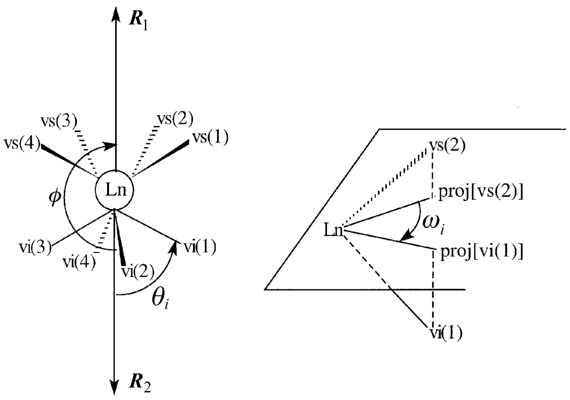


Fig. 5 Definition of the angles and vectors used in the analysis of a square antiprism coordination polyhedron.

45°) toward a square prism (ideal value 0°). In both cerium and praseodymium complexes the angle ϕ does not deviate much from the expected value for a perfect square antiprism (Table 2) if one takes into account the different nature of the donor atoms of the ligand. This indicates a small bending of the upper and lower facial planes, which is also confirmed by their almost parallel arrangement (Table 2). Analysis of the θ_i angles reported in Table 2 (see also Table S2, ESI)† shows that individual values range from 57.42° to 68.03° for **2** and from 57.28° to 68.54° for **3**, and do not deviate much from their mean values. The angles ω_i between projection vectors of the same plane are close to the ideal values of 90°, while the angles ω_i between projection vectors of different planes point to a somewhat distorted polyhedron for both Ce and Pr complexes, with values ranging from 29.48° to 55.75° for **2** and from 30.14° to 54.98° for **3**.

The angles N(3)–Ln–N(2), which should have an ideal value of 180° for a symmetrically bicapped square antiprism, amount to 167.08° for **2** and 166.80° for **3**. Moreover, the angles between the pseudo-C_4 axis of the coordination polyhedron, which can be defined as $\boldsymbol{R}_1 - \boldsymbol{R}_2$ (see Fig. 5), and the Ln–N(2) vector (ideal value 180°) take values of 171.7° for **2** and 171.8° for **3**, while the angles between the $\boldsymbol{R}_1 - \boldsymbol{R}_2$ and Ln–N(3) vectors (ideal value 0°) amount to 8.9° and 8.3°, respectively. These values reflect a certain degree of bending of the upper and lower capping N atoms with respect to the pseudo-C_4 axis of the coordination polyhedron, as is evident in Fig. 4.

The fold of the arms around the crown moiety in complexes **2** and **3** is very similar in both cases as suggested by the angles between the planes of the aromatic rings. The angle between planes containing the benzene rings is 123.5° for **2** and 122.2° for **3**, whilst the angle between planes defined by the phenol rings is 92.2° for **2** and 92.3° for **3**. Angles between the planes defined by the benzene and phenol rings of the same pendant arm amount to 79.9° and 100.9° for **2** and 79.7° and 101.8° for **3**. The angles N(3)–C(21)–C(22) and N(2)–C(14)–C(9) are 116.6° and 114.7° for **2** and 120.3° and 115.2° for **3**. Likewise, all these values are quite different to those found for the lanthanum complex **1**, discussed earlier, as a consequence of the different fold of the whole macrocyclic receptor to fit the metal ion.

The distances between both imine nitrogen atoms (3.181 Å for **2** and 3.168 Å for **3**) are slightly longer than those found in **1**. However, the distances between both pivotal nitrogen atoms (5.997 Å for **2** and 5.986 Å for **3**) and between both phenolate oxygen atoms (4.280 Å for **2** and 4.256 Å for **3**) are shorter. These data show how the ligand slightly modifies its cavity to fit the metal ion.

All these structural data show how the combination of rigidity and flexibility may be used to design a selective receptor able to discriminate between Ln(III) ions on the basis of small differences in ionic radii. **L** comprises two parts: the relatively flexible azacrown moiety and two unsaturated pendant arms. The conformation of **L** in these complexes is imposed by two factors: firstly, both bridgehead nitrogen atoms must adopt an *endo–endo* conformation to allow their coordination to the Ln(III) ion; the flexibility of the crown moiety allows these nitrogen atoms to approach the metal ion while maintaining the interactions between the cation and the oxygen atoms of the crown moiety. Secondly, in order to stabilise the complex it is also necessary to maintain the strong interaction between the phenolate oxygen atoms and the imine nitrogen atoms of the side arm with the metal ion. In order to place the donor atoms as close to the metal ion as possible, these arms are bent, although the degree of bending is limited by the rigidity of the unsaturated groups present. Particularly, the presence of an azomethine group limits their disposition because the lone pair of the imine nitrogen atom must point inwards to coordinate the Ln(III) ion.

To accommodate a particular metal ion (La to Pr) **L** experiences increased strain in the side chains, as shown by the angles N(3)C(21)C(22) and N(2)C(14)C(9), with values of 114.5(4)° and 113.5(4)° for **1**, 116.6(8)° and 114.7(5)° for **2**, and 120.3(11)° and 115.2(6)° for **3**, respectively. It is possible to see how the sp^3 carbon C(21) is forced to adopt an angle of 120°, typical of sp^2 hybridisation, when the encapsulated metal ion changes from La(III) to Pr(III). At the same time, when the encapsulated metal ion is smaller the rings also twist in order to place the phenolate oxygen atoms nearer to the smaller metal ion, with a consequent loss of conjugation.

It follows, therefore, that there is a limit to the size of metal ions which may be encapsulated within the cavity of **L**. The imposition of an *endo–endo* conformation for the crown moiety and the strain imposed by the distortion at carbons C(14) and C(21) of the arms renders all complexes with lanthanide(III) ions smaller than praseodymium unstable.

Spectrophotometric titrations

The electronic absorption spectrum of **L** in acetonitrile solution displays a maximum at 334 nm ($\varepsilon = 16798$ dm^3 mol^{-1} cm^{-1}) attributable to the imine chromophoric group and two more intense bands at 262.5 ($\varepsilon = 21068$ dm^3 mol^{-1} cm^{-1}) and 229.5 nm ($\varepsilon = 35230$ dm^3 mol^{-1} cm^{-1}). Deprotonation with triethylamine does not modify the spectrum, except for the intensity of the high-energy band, which drastically increases after addition of two equivalents of Et_3N. Upon complexation, the three $\pi \longrightarrow \pi^*$ transitions undergo a red shift, appearing at 379, 277 and 236 nm. The former undergoes an important shift (*ca.* 45 nm), thus enabling the formation of the complexes in solution to be monitored. The spectrophotometric titration of $(\mathbf{L} - 2H)^{2-}$ (1.557×10^{-5} M) with $La(ClO_4)_3$ was performed in dry acetonitrile over M : (**L** − 2H) molar ratios in the range 0–5.24. The data displayed a single inflection point when the La : **L** − 2H molar ratio was close to 1, indicating the existence of only one complex species in solution. The spectrophotometric titrations were satisfactorily fitted with the equilibrium (1), allowing the estimation of the stability constant of the

$$\mathrm{Ln}^{3+} + [\mathbf{L} - 2\mathrm{H}]^{2-} \rightleftharpoons [\mathrm{Ln}(\mathbf{L} - 2\mathrm{H})]^{+} \qquad (1)$$

lanthanum complex in acetonitrile solution, which amounts to $\log K[\mathrm{La}(\mathbf{L} - 2\mathrm{H})] = 4.65(4)$. The absolute value of the stability constant with the parent crown ether [2,2] (4,13-diaza-18-crown-6) as determined in acetonitrile is $\log K(\mathrm{La}[2,2]) = 9.7$.[17]

Analogous spectrophotometric titrations carried out with anhydrous $\mathrm{Eu(ClO_4)_3}$ did not show any change in the UV-Vis spectrum of $(\mathbf{L} - 2\mathrm{H})^{2-}$ upon addition of metal salt, suggesting that the Eu complex is not formed under these conditions, which also supports the selectivity of the ligand.

All these data show how the N-substitution of [2,2] with highly rigid pendant arms drastically decreases its coordination ability towards lanthanide ions, but on the other hand enhances its selectivity towards the lighter lanthanide ions.

Conclusions

In its di-deprotonated form, the Schiff-base bibracchial lariat ether *N*,*N*′-bis(2-salicylaldiminobenzyl)-4,13-diaza-18-crown-6 (**L**) behaves as a highly selective receptor towards lanthanide(III) ions. In fact, it only forms stable complexes with the three lightest ions of the series: lanthanum, cerium and praseodymium, which remain strongly bound and encapsulated within its cavity. In order to design selective receptors for lanthanide(III) ions some key features must be taken into account: the lanthanide contraction, the hard character of these metal ions, and their preference for high coordination numbers, which tends to decrease along the lanthanide series. A selective receptor must be comprised of an adequate number of suitably disposed donor atoms and overall it should be rigid enough and have a cavity size adapted to the metal ion. The lariat ether **L** possesses these features: it contains ten donor atoms arranged along a macrocycle and two side arms and, structurally, it presents the desirable characteristics. Thus, the presence of unsaturated pendant arms attached to a flexible azacrown provides more rigidity to this receptor increasing its selectivity. Even so, **L** is still flexible enough to adjust to fit a particular encapsulated lanthanide ion as shown by the different coordination environments found for the lanthanum complex (**1**) with respect to the cerium (**2**) and/or praseodymium (**3**) complexes. Structurally, **L** has a limit to the size of the particular lanthanide(III) ion which may be fitted within its cavity, overall stated by the imposition of an *endo–endo* conformation for the crown moiety, and the strain imposed by the distortion on the C(14) and C(21) carbons of the arms, rendering the complexes with lanthanide(III) ions smaller than praseodymium unstable.

Experimental

Materials

N,*N*′-Bis(2-salicylaldiminobenzyl)-4,13-diaza-18-crown-6 (**L**) was prepared as previously described. Lanthanide(III) perchlorate hydrates were purchased from Alfa laboratories and used as received. $\mathrm{La(ClO_4)_3}\cdot n\mathrm{H_2O}$ ($n \approx 2$) for UV-visible titrations was prepared from the oxide (Rhône-Poulenc, 99.99%) according to the literature method.[18] $\mathrm{La(ClO_4)_3}$ was prepared from the latter by slowly increasing the temperature from 30 to 80 °C under vacuum.[19] Salicylaldehyde (98%) and triethylamine (99%) were commercial reagents from Aldrich. Triethylamine and acetonitrile for spectrophotometric titrations were distilled over $\mathrm{CaH_2}$. Acetonitrile-d_3 for NMR measurements (ACROS, 99% D) was used as received.

CAUTION! Perchlorate salts combined with organic ligands are potentially explosive and should be handled in small quantity and with the necessary precautions.[20]

Preparation of the complexes

N,*N*′-Bis(2-aminobenzyl)-4,13-diaza-18-crown-6 (0.212 mmol) and salicylaldehyde (0.423 mmol) were dissolved in 2-propanol (25 cm^3) and heated to reflux. After 1 hour a solution of triethylamine (0.423 mmol) in 10 cm^3 of 2-propanol was added, and the resultant solution was heated to reflux for 2 hours. A solution of the corresponding hydrated lanthanide(III) perchlorate (0.212 mmol) in 10 cm^3 of the same solvent was then added and the reflux was maintained for 3 hours. The resultant solution was filtered while hot and the filtrate was left to evaporate slowly at room temperature to yield yellow crystals that were collected by filtration and dried under vacuum over $\mathrm{CaCl_2}$.

[La(L − 2H)](ClO$_4$) (1). Yield 0.165 g, 85%. Found: C, 52.6; H, 4.9; N, 6.1%. $\mathrm{C_{40}H_{46}ClN_4O_{10}La}$ requires: C, 52.4; H, 5.1; N, 6.1%. $\nu_{\max}$/cm^{-1} 1608 (C=N), 1537 (C=C), 1088 and 622 ($\mathrm{ClO_4^-}$). MS (FAB+): $m/z = 817$ (100%) $[\mathrm{La}(\mathbf{L} - 2\mathrm{H})^+]$. δ_H (500 MHz; solvent $\mathrm{CD_3CN}$, 295 K) 8.02 (s), 7.16 (d), 7.12 (d), 7.04 (t), 6.72 (m), 6.48 (t), 6.09 (d) and 2.1–4.2 (m). Λ_M (acetonitrile): 140.9 Ω^{-1} cm^2 mol^{-1} (1 : 1 electrolyte). Yellow crystals of **1**, suitable for single-crystal X-ray diffraction analysis, were grown by allowing diethyl ether to diffuse into an acetonitrile solution of the complex.

[Ce(L − 2H)](ClO$_4$) (2). Yield 0.171 g, 88%. Found: C, 52.9; H, 5.0; N, 6.2%. $\mathrm{C_{40}H_{46}ClN_4O_{10}Ce}$ requires: C, 52.3; H, 5.1; N, 6.1%. $\nu_{\max}$/cm^{-1} 1607 (C=N), 1537 (C=C), 1092 and 621 ($\mathrm{ClO_4^-}$). δ_H (500 MHz; solvent $\mathrm{CD_3CN}$, 295 K) 36.20, 30.35, 20.33, 18.79, 17.10, 15.72, 10.92, 8.52, 6.79, 5.09, 4.43, 1.19, 0.70, −1.49, −2.51, −4.11, −5.13, −6.90, −8.59, −11.59, −14.34, −20.05, −21.45. MS (FAB+): $m/z = 818$ (100%) $[\mathrm{Ce}(\mathbf{L} - 2\mathrm{H})^+]$. Yellow single-crystals of **2** suitable for X-ray diffraction were obtained by slow evaporation of 2-propanol solutions of the complex.

[Pr(L − 2H)](ClO$_4$) (3). Yield 0.175 g, 90%. Found: C, 51.9; H, 5.0; N, 6.0%. $\mathrm{C_{40}H_{46}ClN_4O_{10}Pr}$ requires: C, 52.3; H, 5.0; N, 6.1%. $\nu_{\max}$/cm^{-1} 1609 (C=N), 1535 (C=C), 1082 and 621 ($\mathrm{ClO_4^-}$). δ_H (500 MHz; solvent $\mathrm{CD_3CN}$, 295 K) 87.44, 71.72, 44.81, 44.04, 38.05, 34.71, 18.93, 11.06, 7.55, 3.72, 3.59, −10.26, −11.06, −11.13, −12.28, −18.25, −19.19, −21.83, −30.76, −32.01, −45.24, −60.38, −61.84. MS (FAB+): $m/z = 819$ (100%) $[\mathrm{Pr}(\mathbf{L} - 2\mathrm{H})^+]$. Yellow single-crystals of **3** suitable for X-ray diffraction were obtained by slow evaporation of 2-propanol solutions of the complex.

Measurements

Elemental analyses, proton and carbon NMR and mass spectra were carried out by Servicios Generales de Apoyo a la Investigación (Universidade da Coruña): elemental analyses were carried out on a Carlo Erba 1108 elemental analyser; FAB mass spectra were recorded using a FISONS QUATRO mass spectrometer with a Cs ion-gun and thioglycerol matrix; proton and carbon NMR spectra were run at 20 °C with a Bruker AC 200 F spectrometer or with a Bruker WM-500. Chemical shifts are reported in parts per million with respect to TMS. Longitudinal ^{1}H relaxation times (T_1) were measured by the inversion–recovery pulse sequence with a Bruker WM-500 spectrometer. The IR spectra were recorded as KBr discs using a Perkin-Elmer 1330 spectrophotometer and electronic absorption spectra were recorded at 25 °C using a Uvikon 941 Plus spectrophotometer. Conductivity measurements were carried out in *ca.* 10^{-3} M acetonitrile solutions at 20 °C using a Crison GLP 32 conductivimeter.

The spectrophotometric titration of **L** with $\mathrm{La(ClO_4)_3}$ was performed on a Lambda 7 spectrometer connected to an external computer. A solution of **L** (1.557×10^{-5} M) and $\mathrm{Et_3N}$ (10^{-3} M) in 25 cm^3 of dry acetonitrile was prepared, and then 100 µL aliquots of a 1.36×10^{-3} M solution of anhydrous

Table 3 Crystal data and structure refinement for **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{40}H_{46}ClLaN_4O_{10}$	$C_{40}H_{46}CeClN_4O_{10}$	$C_{40}H_{46}ClN_4O_{10}Pr$
M	917.17	918.38	919.17
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
T/K	293(2)	298(2)	298(2)
a/Å	8.96640(10)	19.3199(13)	19.3099(11)
b/Å	11.3821(2)	10.7801(7)	10.7631(6)
c/Å	38.61130(10)	21.0815(14)	21.0674(12)
β/°	91.525(1)	114.843(1)	114.910(1)
V/Å^3	3939.14(8)	3984.4(5)	3971.2(4)
F_{000}	1872	1876	1880
Z	4	4	4
D_{calc}/g cm^{-3}	1.547	1.531	1.537
μ/mm^{-1}	1.216	1.272	1.357
R_{int}	0.0244	0.0922	0.0671
No. measured reflections	23163	25652	20200
No. observed reflections	7820	5555	5855
Goodness-of-fit on F^2	1.237	0.905	0.947
R_1[a]	0.0496	0.0518	0.0559
wR_2 (all data)[b]	0.1235	0.1548	0.1850

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(||F_o|^2 - |F_c|^2)^2]/\Sigma[w(F_o^4)]\}^{1/2}$.

$La(ClO_4)_3$ (as determined by EDTA titration using xylenol orange as an indicator) in the same solvent were successively added. Plots of molar absorption coefficient as a function of the metal : ligand ratio gave a first indication of the number and stoichiometry of the complexes formed in solution; factor analysis[21] was then applied to the data to confirm the number of absorbing species. Eventually, a model for the distribution of species was fitted with a non-linear least-squares algorithm to give stability constants using the computer program SPECFIT.[22]

X-Ray crystallography

The crystal structure experimental specifications and refinement data are given in Table 3. Three-dimensional, room temperature X-ray data were collected in the θ range 1.06 to 28.29° for **1**, 1.20 to 28.30° for **2** and 1.20 to 28.31° for **3** on a Siemens Smart 1000 CCD instrument for **1** and on a Bruker Smart instrument for **2** and **3**. Reflections were measured from a hemisphere of data collected from frames each of them covering 0.3° in Ω. Of the 23163, 25652 and 20200 reflections measured, respectively, all of which were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections, 7820 for **1**, 5555 for **2** and 5855 for **3** independent reflections exceeded the significance level $(|F|/\sigma|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and refined in the riding mode. Refinement was performed with allowance for thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density of −1.119 and 0.686 e Å^{-3} for **1**, −0.895 and 1.475 e Å^{-3} for **2**, and −0.775 and 2.242 e Å^{-3} for **3** were found. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 3.99P]$ for **1**, $w = 1/[\sigma^2(F_o^2) + (0.0904P)^2 + 0.00P]$ for **2**, and $w = 1/[\sigma^2(F_o^2) + (0.1202P)^2 + 0.00P]$ for **3**, where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of the refinement. Some residual electronic density was found for **2** and **3** (corresponding to two molecules of water ≈ 20%) but not modelled in the refinement: 1.234 Å from H20A and 1.268 Å from H23 for **2**, and 1.297 Å from H40B and 1.390 Å from H12 for **3**. Complex scattering factors were taken from the program package SHELXTL[23] as implemented on the Pentium® computer.

CCDC reference numbers 157455–157457.

See http://www.rsc.org/suppdata/dt/b1/b100872m/ for crystallographic data in CIF or other electronic format.

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