Synthesis, crystal structures and NMR and luminescence spectra of lanthanide complexes of 1,4,7,10-tetraazacyclododecane with *N*-methylene(phenyl)phosphinic acid pendant arms †

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Complexes of 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayltetramethylenetetrakis(phenylphosphinic acid) H_4L^1 with yttrium and a number of lanthanides were synthesized and the crystal structures of $Li[LaL^1(H_2O)]\cdot 10H_2O$ and $Li[CeL^1(H_2O)]\cdot 10H_2O$ determined. The complexes are isostructural with *RSRS* configurations at the phosphorus atoms. The ligand is co-ordinated by four nitrogen atoms in a plane and by four phosphinate oxygen atoms in a parallel plane. The planes form a twisted square prismatic co-ordination sphere. A molecule of water capping the O_4 plane completes the co-ordination sphere of both ions. Solution properties of the complexes were investigated by ^1H and ^{31}P NMR. In solution six possible isomers with different configurations on phosphorus atoms are in equilibrium. The most abundant shows the *RRRS* configuration. A dynamic behavior similar to lanthanide complexes of 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid is not observed. The NMR as well as luminescence measurements show that no water molecule is co-ordinated directly to the lanthanide ions in solution. The ions Li^+ and Na^+ form stable ion pairs with the complexes in methanol-d_4 solution as confirmed by the lanthanide induced shift of ^7Li and ^{23}Na resonances in the presence of paramagnetic lanthanide ions. The ion pairs are not stable in aqueous solution. The alkali metal ion is located close to fourfold magnetic axes of the complexes above the oxygen atoms and between the phenyl rings. Luminescence spectra of $[LnL^1]^-$, Ln = Eu or Tb, indicate low symmetry of the species and co-ordination number 8.

Co-ordination chemistry of yttrium and lanthanide ions with macrocyclic ligands is widely investigated because of the importance of their medicinal and biochemical use, such as gadolinium complexes as contrast agents in magnetic resonance imaging,[1–4] ^{90}Y complexes in radioimmunotherapy[2,5] and luminescent europium and terbium complexes as probes.[2,6–9] To produce complexes for utilisation requires chelates with enhanced stability, selectivity and kinetic inertness. A number of aminopolycarboxylic acids, both acyclic and macrocyclic, were tested and the results reviewed.[1–4,6,10–12] Today, several contrast agents are in routine clinical use both as anionic complexes ($[Gd(dtpa)(H_2O)]^{2-}$ and $[Gd(dota)(H_2O)]^-$, where H_5dtpa = (carboxymethylimino)bis(ethylenenitrilo)tetraacetic acid and H_4dota = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) or as neutral species ($[Gd(bm-dtpa)(H_2O)]$ and $[Gd-(hp-do3a)(H_2O)]$, where the ligands are bis(methylamide) derivative of H_5dtpa and the hydroxypropyl derivative of H_4dota, respectively). In addition, many derivatives of the ligands were designed, synthesized and studied to improve properties of the contrast agents. The derivatives show different tissue specificity, *e.g.* those with benzyloxy substituents,[13] or polymer[14]- or dendrimer[15]-based contrast agents being useful in MRI angiography.

Some years ago a study of azacyclic derivatives of H_4dota with side chains containing a phosphonic acid ($CH_2PO_3H_2$) or phosphinic acid ($CH_2P(R)O_2H$) group was started, in a search for ligands with properties different from those of the compounds containing acetic acid groups. The investigations of tetrasubstituted phosphorus derivatives of H_4dota have shown[16–20] that the lanthanide ion in the complexes does not co-ordinate a water molecule in the inner co-ordination sphere, which is essential for the use as a MRI contrast agent, but the complexes show a larger outer-sphere contribution[20] to the relaxivity than their acetic analogues. Variation of the substituent on phosphorus has led to complexes with changed organ specificity[21] or makes it possible to attach the complexes to monoclonal antibodies.[22] On the other hand, highly charged lanthanide complexes of the above phosphonic acid derivatives form stable ion pairs with alkali metal ions even in aqueous solution[23,24] and $[TmL^6]^{5-}$ is used clinically as a shift reagent for ^{23}Na.[25] A gadolinium(III) complex of a tris(phosphonate) derivative of a pyridine-containing tetraazacycle[26] shows a short half-time for water exchange in the inner sphere, which is promising for design of new MRI contrast agents.

The R group in phosphinic acid derivatives contributes to a change in the ion selectivity and properties of the macrocyclic compound. Therefore, we studied its influence in a series of simple aminomethylphosphinic acids $H_2NCH_2P(R')O_2H$, where R' = H, methyl, phenyl, or *tert*-butyl.[27] Changes in complexing properties of the simple acids were surprisingly large, the formation constant values increasing in the order phenyl < methyl < *t*-butyl < hydrogen as substituent. Except for R' = H, the order follows that of increasing basicity of the acids. Thus, we focused on studying the influence of the methylene(phenyl)-phosphinic acid substituent on the complexing properties of azacycles, and published results dealing with the synthesis and complexing properties of 1,4,7-triazacyclononane and 1,4,7,10-tetraazacyclododecane derivatives with methylenephosphinic acid moieties (R = $CH_2P(H)O_2H$; H_4L^3).[28] Recently, we

reported[29] the synthesis, crystal structure and solution properties of 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayltetramethylenetetrakis(phenylphosphinic acid) H_4L^1 and 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetrayltetramethylenetetrakis(phenylphosphinic acid). Formulae of the ligands studied in this paper and those of analogous ligands are shown below.

The aim of this paper is to describe new complexes of H_4L^1 with yttrium and lanthanides and, on the basis of the solid structure determined by X-ray analysis, to discuss their NMR properties in solution.

R = Ph	H_4L^1
R = CH_2Ph	H_4L^2
R = H	H_4L^3
R = Et	H_4L^4
R = Me	H_4L^5
R = OH	H_8L^6
R = OCH_2CF_3	H_4L^7
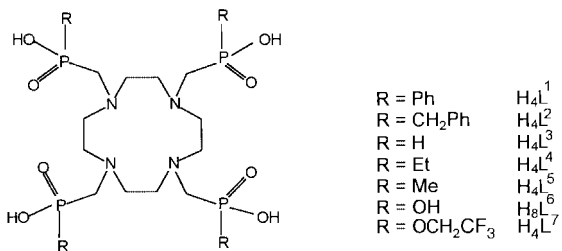
Results and discussion

Synthesis

Synthesis of H_4L^1 followed our procedure.[29] Lanthanide complexes with H_4dota and their analogues could be prepared by direct reaction of the appropriate lanthanide oxide with a ligand, e.g. ref. 30. The reaction usually requires prolonged heating in aqueous solution under reflux. We have tested this route and, in addition to the desired product, found some by-products.[31] Thus, the reaction of H_4L^1 with chlorides of lanthanides was found to be more convenient, faster and the formation of by-products was considerably reduced. The reaction between the ligand and lanthanide ion probably follows the mechanism proposed for complexes of H_4dota.[32] The complexation starts in slightly acidic solution accompanied by slow precipitation of an intermediate in which an interaction of phosphinic acid groups with the lanthanide is assumed. The intermediate is amorphous and probably polymeric in nature containing ligand and lanthanide in an approximately 1:1 stoichiometric ratio as confirmed by inductively couple plasma (ICP)-MS. Upon addition of base, the precipitate quickly dissolves to give a final product with lanthanide ion inside the macrocyclic cavity. In contrast to sodium or potassium salts, lithium salts of the complexes, Li[LnL]·nH_2O (n = 10 or 11), crystallised from the reaction mixture and hence aqueous LiOH was used for neutralisation of the reaction mixture. In addition, the solubility of LiCl in a methanol–water mixture is much better than that of the other chlorides. The complexes crystallised are hydrates which are stable only under mother-liquor and their dehydration in the air occurs at RT within a few minutes. The purity of the complexes prepared was checked by TLC which proved to be very sensitive to by-products.

The complexes are soluble in methanol and water or in their mixtures. They are stable in solutions in the range pH 5–11 for weeks, as expected for the kind of ligands.[33] Easy formation of the crystalline product is probably caused by the presence of a hydrogen bond network.

Structures of Li[La(L¹)(H₂O)]·10H₂O and Li[Ce(L¹)(H₂O)]·10H₂O

The compounds were found to be isostructural with two independent molecules in the unit cell. Owing to the instability of the hydrate mentioned in the Experimental section, and consequently the poor quality of the crystals, the R factors obtained are rather high. Nevertheless, the results obtained are sufficient for the description of geometry for both compounds. The Li[LaL¹(H₂O)]·10H₂O structure is shown in Fig. 1 and Table 1 lists selected bond distances and angles. The ligand
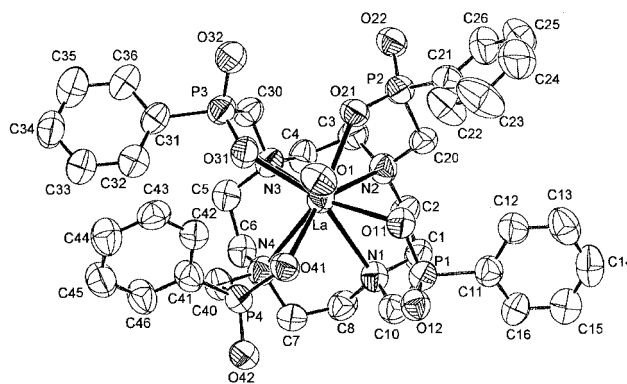

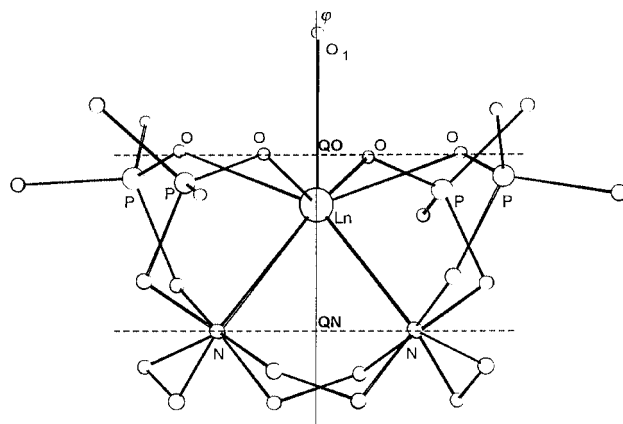**Fig. 1** View of Li[LaL¹(H₂O)]·10H₂O with the atom numbering scheme.

Fig. 2 Lanthanide co-ordination sphere, showing the lanthanide(III) atom between the N₄ and O₄ planes. QN is a centroid of N1, N2, N3 and N4 atoms. QO is a centroid of O11, O21, O31 and O41 atoms.
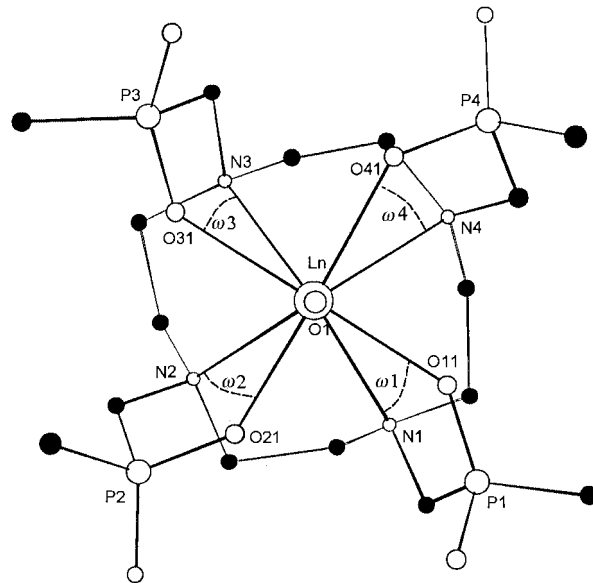

Fig. 3 Orientation of the methylenephosphinic acid pendant arms. Twist angles ω are listed in Table 2.

anion $(L^1)^{4-}$ is co-ordinated to the lanthanide ion by four nitrogen atoms and four phosphinate oxygen atoms. The nitrogen atoms as well as oxygen atoms form bases N_4 and O_4 that are planar and parallel (less than 0.9(0.3)°) within experimental error. The lanthanide lies between these planes, closer to the O_4 base as is shown in Fig. 2. The twist angle of the bases around the local fourfold axis is about 25° (see Fig. 3 and Table 2), i.e. lying between those in the ideal prism, 0°, and antiprism 45°, a little closer to the latter. Thus, the arrangement should be

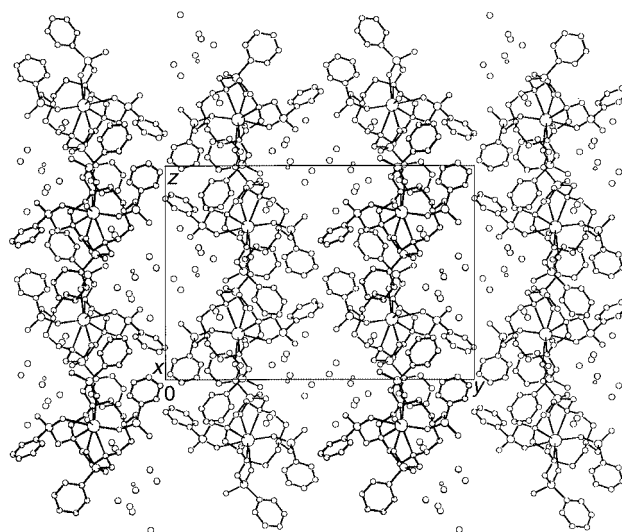**Table 1** Selected bond lengths (Å) in Li[LaL¹(H₂O)]·10H₂O and Li[CeL¹(H₂O)]·10H₂O

	La		Ce	
	molecule A	molecule B	molecule A	molecule B
Ln–O(1)	2.650(6)	2.625(6)	2.652(7)	2.583(7)
Ln–O(11)	2.460(6)	2.449(6)	2.435(6)	2.404(6)
Ln–O(21)	2.473(5)	2.476(6)	2.445(5)	2.458(6)
Ln–O(31)	2.436(6)	2.437(6)	2.413(6)	2.415(6)
Ln–O(41)	2.439(5)	2.426(7)	2.414(6)	2.400(6)
Ln–N(1)	2.859(6)	2.855(6)	2.847(6)	2.847(7)
Ln–N(2)	2.890(6)	2.876(7)	2.874(6)	2.883(6)
Ln–N(3)	2.869(6)	2.850(7)	2.833(7)	2.838(8)
Ln–N(4)	2.889(7)	2.869(7)	2.876(7)	2.863(7)

Table 2 Parameters of the co-ordination polyhedrons and conformation of macrocyclic rings

	La		Ce	
	molecule A	molecule B	molecule A	molecule B
Ln–Q(O)	0.802(1)	0.789(1)	0.804(1)	0.793(1)
Ln–Q(N)	1.931(1)	1.920(1)	1.911(1)	1.840(1)
Q(O)–Q(N)	2.730(1)	2.708(1)	2.713(1)	2.639(1)
Q(O)–Ln–Q(N)	174.0(1)	178.4(1)	176.8(1)	173.2(1)
O(1)–Ln–Q(N)	174.7(2)	178.1(2)	175.1(2)	176.5(2)
O(1)–Ln–Q(O)	10.9(2)	3.4(2)	7.8(2)	3.3(2)
Twist angle of				
pendant 1	23.7(2)	−23.6(3)	25.2(2)	−24.9(3)
pendant 2	26.4(2)	−26.2(2)	26.6(2)	−21.4(2)
pendant 3	23.2(3)	−25.4(2)	23.8(3)	−25.1(2)
pendant 4	24.6(2)	−27.2(2)	25.3(2)	−31.8(2)

Fig. 4 Crystal packing of Li[LaL¹(H₂O)]·10H₂O.

actions of phenyl rings. The interactions probably reflect the value of the twist angle of the bases found, which is rather lower than those observed for [Ln(L²)(H₂O)]⁻ structures.[18,30]

In both the structures studied the co-ordination polyhedrons are connected through hydrophobic interaction of phenyl groups as is shown in Fig. 4. Non-co-ordinated phosphinate oxygen atoms make hydrophilic infinite channels which are parallel to the monoclinic axis. The channels are occupied by molecules of crystal water, hydrogen bonded to each other (O$_w$···O$_w$ in the range 2.7–3.2 Å) and, some of them, to the non-co-ordinated oxygens (O$_{P\text{-}O}$···O$_w$ 2.6–3.0 Å). The Li⁺ ions should be located in these channels; however, their positions could not be determined in the X-ray experiment at $R > 0.1$. This structure motif is the same as in [LnL²]⁻,[18,30] but the diameter of the channels is smaller (5–6 Å). The size of the channels is probably associated with the fact that the crystalline product was only obtained with Li⁺ ions as outer-sphere cations. Water molecules have enough space to move along the channels and this probably causes the mentioned instability of the hydrates. The channel content gives ample possibilities for disorder (both static and dynamic) and makes structure solutions difficult. For this reason, a precise determination of the hydrate stoichiometry in both compounds is beyond the X-ray experiment. We can only estimate the stoichiometry as being close to Li[Ln(L¹)(H₂O)]·10H₂O.

NMR spectra

From the structures Li[La(L¹)(H₂O)]·10H₂O and Li[Ce(L¹)(H₂O)]·10H₂O, it is known that the orientation of the phosphinic groups in the solid state is *RSRS*, thus two signals in the ³¹P-{¹H} CP-MAS NMR spectrum are expected. If Li⁺ is bonded to one phosphinate then three phosphorus atoms are non-equivalent and thus three signals should be observed. Three peaks (δ 33.05, 31.85 and 29.16) were observed in the spectrum of Li[La(L¹)(H₂O)]·nH₂O and also in that spectrum of Li[Lu(L¹)]·nH₂O (δ 28.08, 22.49 and 20.51). This points to a similar structural motif in the solid state for all the lanthanide complexes. In addition, in the spectrum of Li[Y(L¹)]·nH₂O, four peaks at δ 32.15, 31.35, 26.11 and 24.02 were found. A comparison with the spectra of La^{III} and Lu^{III} indicates that the peak above δ 30 is split, probably due to an additional interaction of the phosphinate, *e.g.* Li⁺ or with water molecules.

Co-ordination of each phosphinate group of the ligand to Ln^{III} produces an asymmetric center at each phosphorus. If the *R* or *S* orientation of each group is independent of the orientation of the other phosphinates then six diastereoisomers are possible, *RRRR*, *RRRS*, *RRSS*, *RSRS*, *RSSS* and *SSSS*. In solution, a reorientation of the *RSRS* configuration, which was

termed the square antiprism. A molecule of water capping the O₄ base of the twisted prism completes the co-ordination sphere of the lanthanide. The average bond distances of the lanthanum ions and the donor atoms of the ligands in the unit cell are a little longer than for cerium (La–O 2.45, Ce–O 2.42, La–N 2.87, Ce–N 2.86 Å).

A comparison of the co-ordination polyhedron of [La(L¹)(H₂O)]⁻ with those of [La(L²)(H₂O)]⁻ (ref. 30) and of complexes of H₄L² with other lanthanides[18,30] shows that the N₄ square remains virtually the same with the common square (3,3,3,3) conformation of the [12ane]N₄ ring. The conformations of the tetraaza rings of both the co-ordination polyhedra in the elemental unit cell are different. One co-ordination polyhedron corresponds to the Δ conformation, the other to the Λ conformation. The average La–N distance in [La(L¹)(H₂O)]⁻ (2.87 Å) is a little higher than in [La(L²)(H₂O)]⁻ (2.80 Å)[30] and the average La–O$_{(P\text{-}O)}$ distances are virtually the same. The La–O$_w$ distances in [La(L¹)(H₂O)]⁻, 2.65 and 2.62 Å, are also very close to that in [La(L²)(H₂O)]⁻, 2.66 Å,[30] however, they are longer than in Na[La(Hdota)La(dota)]·10H₂O.[34] A comparison of the Ln–O$_w$ distances indicates that the co-ordination spheres of small lanthanides such as Tm or Lu in [LnL¹]⁻, as in [LnL²]⁻, would not contain a molecule of water. The conformations of the pendant arms are the same; however, the orientation of the phosphinate groups in [La(L¹)(H₂O)]⁻ corresponds to the formation of the *RSRS* diastereoisomer, different from the *RRRR* or *SSSS* diastereoisomers described[18,30] for [Ln(L²)(H₂O)]⁻ structures. This dissimilarity probably follows from hydrophobic interactions of phenyl groups and ionic interactions through oxygen atoms of phosphinic acid groups, Li⁺ and crystal water mentioned hereinafter. The benzyl substituent in H₄L² is more flexible due to the methylene bridge, and thus has more possibilities for non-covalent hydrophobic inter-

Table 3 Relation between the R/S, Λ/Δ isomers and the number of signals in the ^{31}P NMR spectrum

Isomer	Conformation of pendant arms	Number of non-equivalent ^{31}P nuclei
RRRR	Δ	1
RRRS	Δ	4
RSRS	Δ	2
RRSS	Δ	4
SSSR	Δ	4
SSSS	Δ	1
		Total: 16

found in the solid state, occurs and formation of a mixture of diastereoisomers at the phosphorus atoms is observed. The NMR results indicate that equilibrium is usually reached in 30 min at room temperature. The solution would contain the six isomers. In addition to the R or S orientation of the phosphorus atoms, two possible orientations, clockwise (Δ) and counterclockwise (Λ), of the methylene groups in the pendant arms are possible. If the Λ and Δ isomerisation is included in the consideration, then the Δ-(RRRR) is an enantiomer to the Λ-(SSSS) and analogously for the other combinations. The enantiomers are not distinguishable by NMR, however the enantiometric pair Δ-(RRRR)/Λ-(SSSS) is distinguishable from Δ-(SSSS)/Λ-(RRRR). For this reason, only one isomeric form (Δ) is considered in the following text and thus RRRR refers to the Δ-(RRRR)/Λ-(SSSS) enantiomeric pair.

Thus, in the ^{31}P NMR spectrum of the six isomers, one signal would be observed for RRRR and for SSSS isomers, four signals for RRRS, RRSS and RSSS isomers and two for the RSRS isomer, the total number of peaks being[35] 16, as shown in Table 3. The intensities of the signals for each isomer should be the same; however, the abundance of the isomers in solution would not be the same. In the literature[18,30] only RRRR isomers of lanthanide complexes with analogous ligands were observed in the solid state and were also predominant in solution. We assume that in solutions of H_4L^1 lanthanide complexes, where no interactions of phenyls are likely, the RRRR is also the dominant species and the abundance of the other isomers roughly decreases with the number of S-oriented phosphinates. The isomerisation at the phosphorus atom together with the Δ or Λ conformation of the cyclodecane ring is discussed in detail on the basis of ^{19}F NMR spectra of lanthanide(III) complexes with H_4L^7 by Kim et al.[35] They confirmed that the abundance of complexes with the RRRR configuration is the highest but can be altered in the presence of other molecules, such as cationic surfactants (e.g. cetylpyridium chloride).

We studied ^{31}P NMR spectra of methanolic and aqueous solutions of the lanthanide complexes with H_4L^1. All the sixteen ^{31}P NMR peaks were observed in a methanolic solution of $Li[Lu(L^1)]$. The spectrum is shown in Fig. 5 together with a tentative assignment of the signals to the isomers. It is apparent that no species is dominant in solution as in spectra[18] of $[Lu(L^2)(H_2O)]^-$. According to the intensities observed (Fig. 5) and assumptions mentioned above, the abundance of the isomers decreases in the order RRRS > RRRR > RRSS > RSRS > RSSS > SSSS. The character of the spectrum in aqueous solution is similar, but the intensities and positions of the peaks are shifted. Thus, the RRRS (4 peaks) seems to be dominant followed by the RSRS isomer (2 peaks). The abundance of the RRRR isomer decreased and a peak corresponding to the SSSS isomer almost disappeared. With increasing temperature, broadening and coalescence of some peaks occur, and thus only eight broad peaks were observed at 75 °C.

In spectra of $Li[Y(L^1)]$ in both methanolic and aqueous solution, a coupling $^2J_{YP} \approx 5$ Hz was observed for all peaks. This points to the fact that all phosphinic groups are co-ordinated in solution. The spectrum of a methanolic solution of the com-
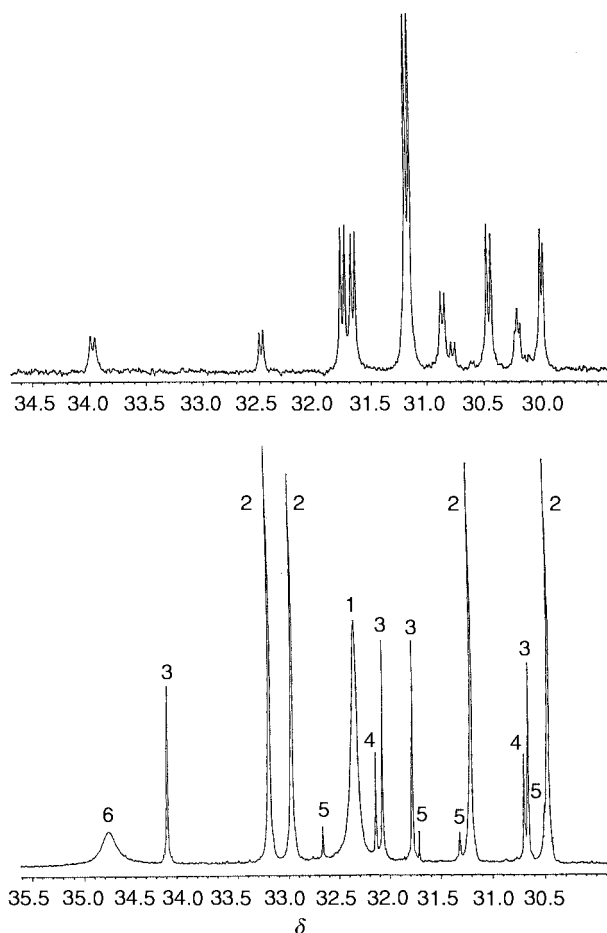

Fig. 5 The ^{31}P NMR spectra of $Li[YL^1]$ (upper) and $Li[LuL^1]$ (lower) in methanolic solutions. In the lower spectrum 1 corresponds to RRRR, 2 to RRRS, 3 to RRSS, 4 to RSRS, 5 to RSSS and 6 to the SSSS isomer.

plex is also shown in Fig. 5. In it the RRRS (four doublets) and RRRR (one doublet) isomers are dominant. The abundance of the other isomers is lower than in $Li[Lu(L^1)]$ solutions. In the NMR spectrum of a methanolic solution of $Li[La(L^1)(H_2O)]$ four broad peaks only were found.

The ^{31}P NMR spectra were also investigated for complexes of paramagnetic lanthanides in both methanolic and aqueous solutions. A mixture of the isomers was observed in all samples as is shown in Fig. 6 for $Li[Eu(L^1)]$. The abundance of the isomers roughly corresponds to those found for complexes Lu and Y. Changes in the ^{31}P NMR chemical shift of the major RRRS isomer for a lanthanide is shown in Fig. 7. It is apparent that the maximum or minimum values of the ^{31}P NMR chemical shift were found for Tb^{3+} and Dy^{3+}, or Tm^{3+}, respectively. According to the literature,[36] the observed chemical shift δ_{obs} may be quantified by eqn. (1) where δ_{dia} corresponds to the

$$\delta_{obs} = \delta_{dia} + \delta_{dip} + \delta_{con} \qquad (1)$$

shift of an analogous diamagnetic ion (La^{3+}), δ_{dip} is the pseudo-contact term and δ_{con} the contact term. Generally, the observed paramagnetic shift (LIS = lanthanide induced shift) is given by the sum of pseudo-contact and contact contributions, eqn. (2). Eqn. (2) may be transformed, as shown in Bleaney et al.,[37]

$$LIS_{obs} = LIS_{pc} + LIS_c \qquad (2)$$

into eqn. (3) where G is the geometrical term, F is a term

$$LIS_{obs} = GC_j + F\langle S \rangle_{av} \qquad (3)$$

containing the hyperfine coupling constant, C_j is a numerical

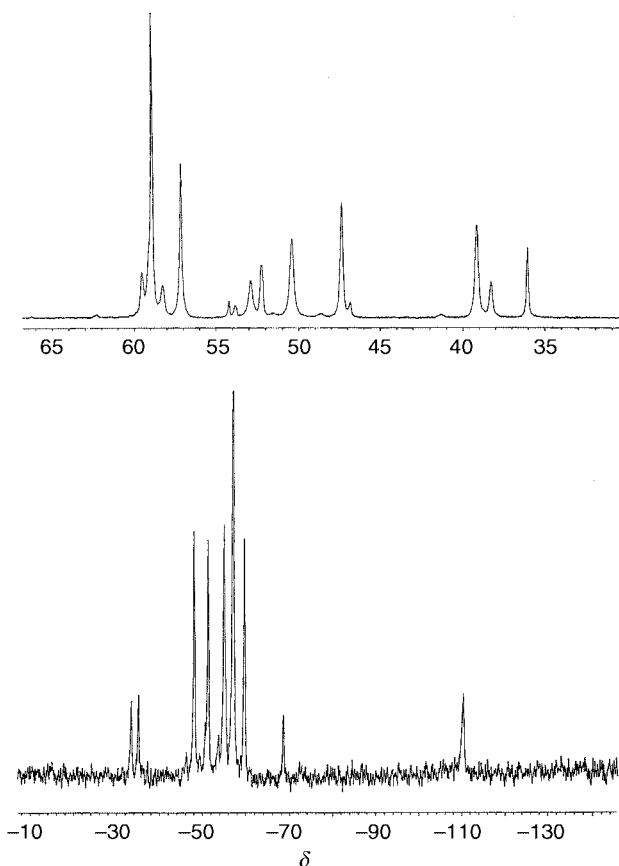**Fig. 8** Analysis of the ³¹P NMR data for aqueous solutions of [LnL¹]⁻ complexes using the equation $\delta(^{31}\text{P})/\langle S \rangle_{av} = GC_j/\langle S \rangle_{av} + F$.

Fig. 6 The ³¹P NMR spectra of Li[EuL¹] (upper) and Li[YbL¹] (lower) in methanolic solutions.

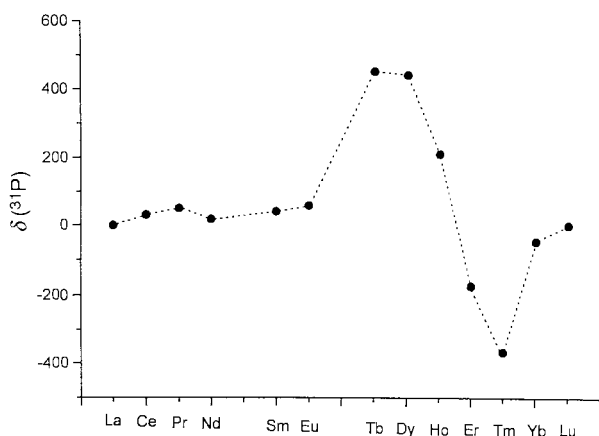**Fig. 7** Dependence of ³¹P NMR shift of Li[LnL¹] on lanthanide in aqueous solutions (*RRRR* isomer).

coefficient derived from matrix elements of *J* and $F\langle S \rangle_{av}$ is the thermal average spin moment. Both C_j and $\langle S \rangle_{av}$ are known for each lanthanide ion.[36] Eqn. (3) may be transformed into (4) and (5).

$$\text{LIS}_{obs}/\langle S \rangle_{av} = (GC_j/\langle S \rangle_{av}) + F \tag{4}$$

$$\text{LIS}_{obs}/C_j = G + F(\langle S \rangle_{av}/C_j) \tag{5}$$

An analysis of the ³¹P NMR data for aqueous solutions of [LnL¹]⁻ complexes using eqn. 4 is plotted in Fig. 8. The results found for methanolic solution are very close to those for aqueous solutions. The plot using eqn. (4) suggests that lanthanides fall on one straight line with a slope (*G* term) about 4 and an intercept about zero. The single straight line indicates the same co-ordination sphere for all lanthanide ions. This is different
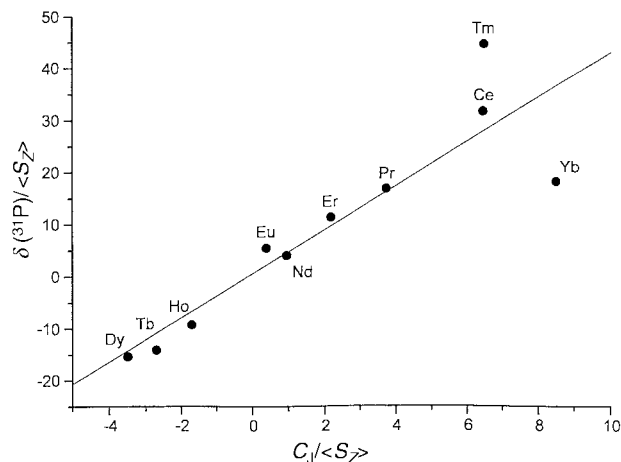
from the results observed for [LnL²]⁻ complexes.[18,30] The plot of that series fell into two straight lines, one line connecting Ce, Pr and Nd, ions with co-ordination number 9, the other connecting ions with co-ordination number 8, from Dy to Yb. A comparison with the literature[30] results for [LnL²]⁻ complexes indicates a similar value of the slopes for both our and Aime's series for ions from Dy to Yb. Thus, the co-ordination number in complexes [LnL¹]⁻ in solution would be 8 even for Ce, Pr and Nd. From this point of view, water is not co-ordinated to cerium in aqueous solution as was found in the solid state. An explanation follows from the hydrophobic interaction of phenyls in an isolated molecule and the interaction results in hindrance of the O₄ base in solution. A similar behaviour of the phenyls was observed in ³¹P NMR spectra for conformation changes of H₄L¹.[29] In contrast to [TmL²]⁻,[30] the ³¹P NMR shift of [TmL¹]⁻ does not fit the straight line observed. This is probably due to the high sensitivity of its signals to temperature.[38]

The plot according to eqn. (5) shows that it is not possible to find any correlation between δ_P/C_j and $\langle S \rangle/C_j$. This corresponds to the small value of the *F* term estimated from eqn. (4). As expected, the contact term is very small in comparison with the pseudo-contact term.

In addition, ⁷Li NMR spectra of all the compounds in methanolic solution were investigated; the dependence of ⁷Li NMR chemical shifts on the lanthanide ion is similar to those found for ³¹P NMR spectra, but the sign of ⁷Li LIS_obs is opposite. As expected, a maximum value of δ_{Li} was found for Li[DyL¹] and Li[TmL¹]. The opposite sign in comparison with δ_P can be explained by the different position of ⁷Li and ³¹P nuclei in space determined by the McConnel cone.[36] In addition, Li⁺ is located close to the negatively charged phosphinic acid groups in methanolic solution. When a methanolic solution of NaClO₄ was added to a solution of Li[LnL¹] the value of δ_{Li} decreased to zero due to substitution of Li⁺ with Na⁺ ions. In aqueous solutions, the δ_{Li} signals lie in a narrow region close to zero. This indicates dissociation of the ionic pair and formation of Li(H₂O)ₙ⁺ species which does not interact with the complex.

The ¹H NMR spectra of Li[Ln(L¹)], Ln = La, Y or Lu, were also measured; however, they are very complicated due to a number of diastereoisomers in solution. Overlapping of the signals was observed in the spectra of Y and Lu and even after an H,H-COSY experiment the signals could not be assigned. In ¹H NMR spectra of Li[Ln(L¹)] complexes where Ln is a paramagnetic lanthanide ion the paramagnetic shifts depend on the position of the hydrogen atoms relative to the magnetic axis of the complex. Thus, for the selected hydrogen atoms, the same dependence of the shifts (according to eqn. (4)) on the lanthanide as found for ³¹P NMR shifts was observed. In contrast to ³¹P NMR spectra, a number of isomers were not determined

because of the mentioned number of peaks. The paramagnetic broadening of the peaks increases with increasing temperature for most lanthanides. On the other hand, the character of the spectra is virtually the same in the temperature range 25–50 °C, the positions of the peaks being very temperature sensitive.[38]

The spectrum of Li[Eu(L^1)] in methanol-d_4 solution was investigated in detail due to the convenient relaxation time and a very low paramagnetic broadening of the signals. The number of signals is high, but the scale is very broad and thus the peaks are well distinguished. It is possible to determine separate groups of the signals corresponding to the atoms from H$_c$ to H$_f$. Their assignment is also confirmed by an H,H-COSY experiment at 25 °C, corresponding to the literature results.[18] In the spectrum, 12 cross-peaks were found from the H$_a$–H$_b$ correlation and this points to 12 different types of the pendant arms. The number of cross-peaks in this region corresponds to the number of non-equivalent phosphinic acid groups found in the ^{31}P NMR spectrum and confirms the R/S isomerisation at the phosphorus atoms and the Λ and Δ isomerism at the arms. Correlation between hydrogen atoms of the ring was also studied using the cross-peaks corresponding to H$_{a-f}$ in the H,H-COSY spectrum. There were found 24 correlations from H$_c$ to H$_d$ and to H$_f$. No interaction with the H$_e$ of the macrocycle was observed, probably due to the H$_b$CCH$_e$ torsion angle and Karplus–Conroy curve.[39] Integral intensities of the peaks indicate that the abundance of the isomers decreases from the $RRRS$ (4 peaks) to the $RRRR$ isomer (1 peak), *etc.*, as was observed in ^{31}P NMR spectra.
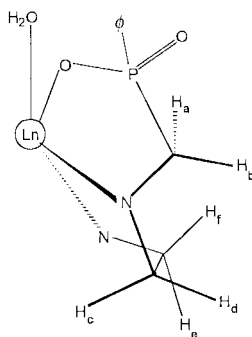
The ^{1}H NMR spectra of Li[Eu(L^1)] in D$_2$O solution are similar to those measured in methanol-d_4. The peaks are shifted, the scale (+30 to –17 ppm) being not as large as in methanol; however, the abundance of the isomers is the same. As in spectra of other lanthanides, the spectrum is temperature-sensitive for both $\delta(\tau)$ and $\Delta\nu_{1/2}$. Coalescence of the peaks in the separated groups is observed at 95 °C; however, the peaks are broad ($\delta\nu > 150$ Hz).

Luminescence spectra

The phenyl groups bonded to the phosphorus atoms show a characteristic absorption at 254 nm and hence the absorption band could be used as an antenna for excitation of a proximate lanthanide ion.[6] The emission spectra of Li[Eu(L^1)]·nH$_2$O and Li[Tb(L^1)]·nH$_2$O in water are depicted in Fig. 9. The bands observed consist of ^{5}D$_0$–^{7}F$_J$ transitions and ^{5}D$_4$–^{7}F$_J$ transitions.

At 579 nm the ^{5}D$_0$–^{7}F$_0$ transition is found as a single, quite intense peak without shoulder or splitting. This transition is electric dipole allowed and can only be observed in low-symmetry environments (less than D_3), particularly when the molecule in question has no inversion centre, and its intensity increases with decreasing symmetry of the complex.[40] The relatively high intensity of the peak in comparison with that of the next transition (^{5}D$_0$–^{7}F$_1$) also indicates the low symmetry of the complex species in solution. This is different from the symmetric complex anion [Eu(L^2)]$^-$ where no peak for ^{5}D$_0$–^{7}F$_0$ was found.[18]
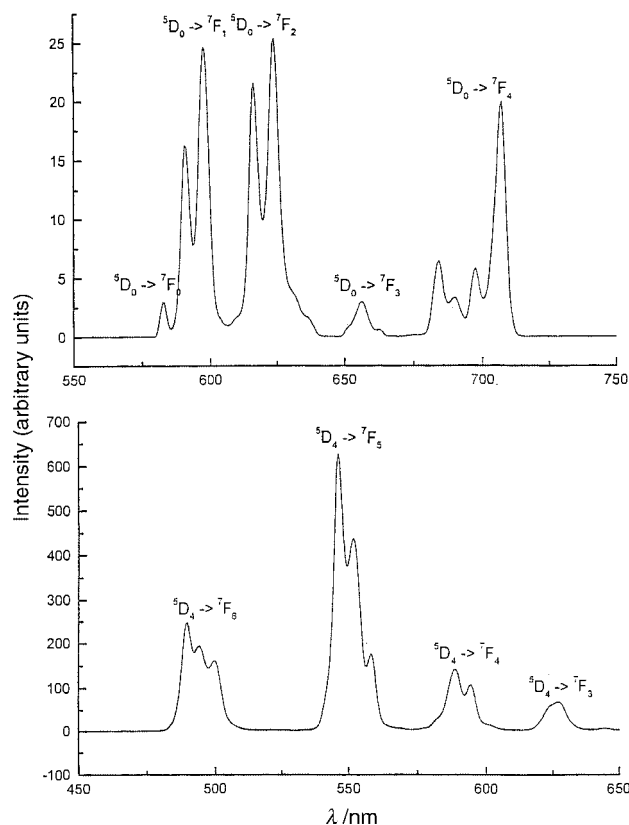

Fig. 9 Luminescence spectra of Li[EuL^1] (upper) and Li[TbL^1] (lower) in aqueous solutions.

In the ^{5}D$_0$–^{7}F$_1$ region two well separated singlets of non-equal intensity were found. The presence of two signals leads to the conclusion that the symmetry of the emitting species is C_3 or higher.[18,40] The ^{5}D$_0$–^{7}F$_1$ transition is not environmentally sensitive. In contrast to [Eu(dota)(H$_2$O)]$^-$,[40b] we did not observe small signals in the ^{5}D$_0$–^{7}F$_1$ part of the spectrum, which were attributable to the presence of isomers with different torsion angles θ of pendant arms. The separation of the two singlets in the ^{7}F$_1$ multiplet is proportional to the crystal field coefficient A_2^0,[41] similarly to the dipolar contribution to the paramagnetic NMR shift.[37] The separation of the components in the ^{7}F$_1$ multiplet of Li[Eu(L^1)] is 197 cm^{-1}, close to the 190 cm^{-1} found for [Eu(dota)(H$_2$O)]$^-$ and different from [Eu(H$_2$O)$_n$]$^{3+}$, for which the separation is only 40 cm^{-1}. This separation corresponds to the predominant contribution of the dipolar shift to the LIS, as was also observed in the NMR spectra.

The electric dipole allowed ^{5}D$_0$–^{7}F$_2$ transition is known to be hypersensitive, its intensity being strongly affected by the polarisability of the ligand.[18,40] It is absent if the Eu^{3+} ion is in an inversion centre. For phosphinate complexes of the [Eu(dota)-(H$_2$O)]$^-$ type this transition produces one of the most intense bands in the spectrum.[20] In the ^{5}D$_0$–^{7}F$_2$ region of the luminescence spectrum of [EuL^1]$^-$ two well separated singlets are found whose intensities are comparable with that for the ^{5}D$_0$–^{7}F$_1$ transition. This is consistent with the absence of an inversion centre in the emitting species and polarisability of the ligand, enhanced by the presence of phenyl rings on phosphorus atoms.

The ^{5}D$_0$–^{7}F$_3$ transition is of low intensity in the spectrum, similarly to other [Eu(dota)(H$_2$O)]$^-$ type complexes.[40b] The intensity of the ^{5}D$_0$–^{7}F$_4$ multiplet in Li[Eu(L^1)] is smaller in comparison with that of ^{5}D$_0$–^{7}F$_{1,2}$, in contrast to similar complexes.[40b]

In the spectrum of Li[TbL^1], all the ^{5}D$_4$–^{7}F$_J$ transitions, where $J = 3,4,5$, or 6, were observed. The spectrum is the same as that of analogous [TbL^5]$^-$,[18,30,42] which corresponds to the

fact that the luminescent spectra of Tb^{3+} are not as sensitive to changes outside the first co-ordination sphere.

Luminescence spectroscopy was used for estimation of the number of water molecules co-ordinated to the lanthanide in aqueous solutions. The lifetimes of the excited state in H_2O/D_2O are 1.18/2.01 ms (transition $^5D_0$–$^7F_1$, 598 nm, pH 7) for $[EuL^1]^-$ and 4.10/4.31 ms ($^5D_4$–$^7F_5$, 546 nm, pH 7) for $[TbL^1]^-$. According to Horrocks's equation,[43] the numbers of the co-ordinated water molecules determined are 0.4 for $[EuL^1]^-$ and 0.1 for $[TbL^1]^-$ with an accuracy ±0.5. If the number of water molecules was estimated according to the recent equation,[44a] then 0.12 was found for $[EuL^1]^-$ and 0 for $[TbL^1]^-$. Thus, using Horrock's equation the co-ordination of water cannot be excluded; using the equation from Parker's group indicates that no molecule of water is co-ordinated to the lanthanide.

From the literature,[44] it is well known that luminescence spectra of some Eu^{3+} and Tb^{3+} complexes with 1,4,7,10-tetra-azacyclododecane derivatives depend on pH, concentration of O_2 in solution, and possibly on other factors. We have tested the sensitivity to pH and O_2; however, no influence of O_2 concentration or pH in the range of 2–11 was observed.

Conclusion

The X-ray analysis of $Li[Ln(L^1)(H_2O)]\cdot10H_2O$ complexes, where Ln = La or Ce, showed analogous ligand co-ordination, that found in similar complexes. The co-ordination sphere is completed by a water molecule. In contrast to previously studied lanthanide complexes with macrocyclic ligands bearing phosphinic acid pendant arms, the conformation at the phosphorus atoms is *RSRS*.

In solution, the *RSRS* form isomerises. Probably due to hydrophobic interaction of phenyl groups, a full set of the possible isomers is formed. The LIS_{obs} contributions obtained from the ^{31}P NMR measurements indicate co-ordination number 8 for all lanthanides in aqueous solution. The result points to a loss of the co-ordinated water in solution. This effect is explained by hydrophobic interaction among the phenyls above the O_4 plane and repulsion of the water molecule. The complex anion $[LnL^1]^-$ forms stable ion pairs with both Li^+ and Na^+ in methanolic solutions.

In luminescence spectra of $[LnL]^-$, Ln = Eu or Tb, all transitions expected were found confirming a relatively low symmetry of the Eu^{3+} species. The estimated co-ordination number determined from the luminescence lifetime of the $^5D_0$ and $^5D_4$ excited states is 8, verifying that no water molecule is co-ordinated to the Ln^{3+} in solution.

Experimental

The ligand $H_4L^1\cdot4H_2O$ was synthesized using our procedure.[29]

Preparation of complexes $Li[LnL^1]\cdot nH_2O$

These complexes were prepared starting from the appropriate lanthanide oxide (Ln_2O_3 for Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb or Lu, Pr_6O_{11} or Tb_4O_7) or chloride ($CeCl_3\cdot7H_2O$) which was dissolved in concentrated hydrochloric acid by warming on an oil-bath. The solution formed was evaporated to dryness using a rotary evaporator. The residue was dissolved in 80% (v/v) aqueous methanol. A stoichiometric amount of H_4L^1 dissolved in 40% aqueous MeOH was added and the mixture heated to 50 °C. Then, 1% aqueous LiOH was added very slowly while stirring (approximately during 20 min) until the pH reached 8–9. During this addition a white precipitate was formed at pH 7, which was redissolved at higher pH. The slightly turbid solution obtained was filtered through a filter-paper (blue strip) and allowed to crystallise at laboratory temperature. The first crop of crystals (well formed prisms) was separated and the mother liquor afforded pure $Li[LnL^1]\cdot nH_2O$ ($n \approx 11$) in the form of long thin needles, which were filtered off.

During drying in air a loss of crystal water occurred and $Li[LnL^1]\cdot 6.5H_2O$ was formed. Analytical data (C,H,N) of these compounds are in accord with the formulae given.

Their purity (especially with respect to non-co-ordinated Ln^{3+} and by-products) was verified by TLC in water–CH_3CN–t-BuOH 4:1:1 (v/v), using detection with xylenol orange and UV. The R_f of non-bound Ln^{3+}, a by-product and $Li[LnL^1]$ are 0, 0.4 and 0.6 respectively. The complexes are almost insoluble in higher alcohols and less polar organic solvents. They have the same colours as hydrated Ln^{3+} ions. After formation, these compounds extremely easily lose water of crystallisation. Single crystals for X-ray diffraction studies were prepared in the same manner.

NMR measurements

The ^1H and ^{31}P NMR spectra were recorded on a Varian Unity Inova 400 spectrometer in CD_3OD or D_2O solutions at 25 °C (operating frequencies 399.96 and 161.907 MHz), with t-BuOH as internal standard for ^1H measurements and 85% H_3PO_4 as external standard for ^{31}P. The 5 mm broad band probe was used. The spectral window used was 100 kHz and temperature controlled by a VT regulator, containing a thermocouple calibrated using MeOH and $HOCH_2CH_2OH$ according to a literature procedure.[45] The ^7Li and ^{23}Na NMR spectra (operating frequencies 155.44 and 105.75 MHz) were measured using the full substitution method, delay time 1 s and LiCl in D_2O and NaCl in D_2O (1 mol dm^{-3}), as external references on a Varian Inova 400 spectrometer at 25 °C. The spectral width was ±10 ppm. The ^{31}P CP/MAS NMR spectra of solid samples were measured at room temperature using a standard procedure (161.9 MHz, spinning 4 kHz, contact time 0.5 s and repetition time 8 s with $CaHPO_4$ as an external standard). The 1-D NMR spectra of paramagnetic complexes were measured at a 100 kHz spectral window and TOF parameter ±50 kHz first to find all of the signals. Then these parameters were optimised. The 2-D experiment (H,H-COSY) on $[EuL^1]^-$ was recorded at 399.961 MHz and at 25 °C. Data were collected with 1024 increments in F2, 2048 points in both F1 and F2. The delay time between pulses was 0.75 s. The data obtained were processed using exponential weighting and a sine bell function in F2, while in F1 a line broadening function and shifted sine bell function were used. Variable-temperature experiments were carried out on a 5 mm broad band VT probe, the thermocouple being calibrated with methanol and ethylene glycol using published procedure.

Luminescence spectra

Luminescence experiments were carried out on a Perkin-Elmer LS 50B luminescence spectrometer in a 1 cm cell. The excitation wavelength was 250 nm for complexes of Eu and 265 nm for Tb. Europium(III) emission spectra were recorded in the range 550–900 nm, terbium spectra in the range 450–760 nm, using a 10 nm excitation slit, 2.5 nm emission slit, 0.1 ms delay time and 430 nm filter in both cases. The luminescence decay was observed up to 7.7 ms for Eu and 19 ms for Tb.

Crystallography

The well formed but highly unstable (due to the loss of solvent molecules) crystals of $Li[La(L^1)(H_2O)]\cdot10H_2O$ and $Li[Ce(L^1)-(H_2O)]\cdot10H_2O$ were obtained by slow evaporation of the solvent mixture (MeOH–water 1/1). Data were collected on a "KUMA kappa axis" (Poland) four circle diffractometer equipped with a CCD area detector (resolution 16.7 pixels (mm)). Selected crystallographic data for both compounds are listed in Table 4.

Hydrogen atoms in CH_2 and CH fragments were included in calculated positions (SHELXL 97);[46] however, hydrogen atoms from the solvate water molecules, similarly to Li^+ ions, could not be found due to the poor quality of the data and a number of possible disorders. We tried to refine the occupancy of all

Table 4 Experimental data for the X-ray diffraction studies of Li[LaL^1(H$_2$O)]·10H$_2$O and Li[CeL^1(H$_2$O)]·10H$_2$O

Formula	C$_{36}$H$_{66}$LaLiN$_4$O$_{19}$P$_4$	C$_{36}$H$_{66}$CeLiN$_4$O$_{19}$P$_4$
M	1128.7	1129.9
T/K	170(1)	170(1)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	24.145(2)	24.188(5)
b/Å	24.458(1)	24.412(5)
c/Å	20.160(2)	20.087(4)
β/°	113.86(1)	113.81(3)
U/Å³	10888(1)	10851(4)
Z	8	8
μ/mm^{-1}	0.97	1.02
Number of reflections measured	86193	85745
Number of reflections observed [$I > 2\sigma(I)$]	17475	17356
Number of independent reflections	25133	25206
R_{final}	0.1239	0.1395

unco-ordinated water molecules. Site occupancy factor (s.o.f.) values of unity were obtained for 9 and 8 molecules, values close to unity (0.80–0.99) for 8 and 9 molecules and lower values for 6 and 7 molecules for the La and Ce.

After overcoming all difficulties mentioned above, we were able to obtain R values close to 0.12–0.14. This is a poor result from the crystallographic point of view, but a very important and useful result from the chemical point of view for this type of compounds.[47] Similar R factors were reached for complexes [LnL^2]$^-$.[30]

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See http://www.rsc.org/suppdata/dt/1999/3585/ for crystallographic files in .cif format.

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