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Derivative of cyclen with three methylene(phenyl)phosphinic acid pendant arms. Synthesis and crystal structures of its lanthanide complexes

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A new macrocyclic ligand 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraylmethyltrimethylenetris(phenylphosphinic acid) H_3L^1 was synthesised and its complexes with lanthanides were prepared. X-Ray analysis of seven Ln complexes (Ln = La, Ce, Nd, Eu, Tb, Er, Yb) shows a formation of dimers $[LnL^1]_2$ with phosphinic acid bridges in the solid state. All complexes are isostructural and the coordination polyhedra are formed by four N atoms and four O atoms of phosphinic acid groups. A water molecule is placed near the O_4 base. The Ln–O_w distance is strongly dependent on Ln(III), it varies from 2.815(6) Å in the La complex to 4.448(10) Å in the Yb complex. The ^{31}P NMR studies show formation of a rather complex mixture of isomers in solution. The dimer stability in solution is verified by reaction with triphenylphosphine oxide (tppo) and with pyridine *N*-oxide and by cyclic voltammetry.

Lanthanide complexes with azacycles usually substituted on nitrogen atoms by four equal pendant groups are widely investigated because of their use, *e.g.*, as contrast agents in MRI,[1,2] for labelling antigenic antibodies using radioisotopes[2,3] for both diagnostic and therapeutic purposes, and also as catalysts in the splitting of nucleic acids.[4] Cyclen derivatives with acetate side chains H_4DOTA (H_4DOTA = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) and its complexes are the most thoroughly studied substances of this kind.[5] The ligands with acetate side chains form thermodynamically stable metal complexes, the most stable being generally formed from those with di- and tri-valent metals.[5]

In addition, a study of H_4DOTA[6,7] analogues with side chains containing a methylenephosphonic acid[8–10] (–CH_2–PO_3H_2) or methylenephosphinic acid[8,11–17] (–CH_2–$P(R)O_2H$) pendant arm was initiated, in a search for ligands with properties different from compounds containing acetic acid arms. We focused on a study of the influence of the methylenephosphinic acid substituents on complexing properties of the azacycles. We published results dealing with the synthesis and complexing properties of 1,4,7-triazacyclononane and 1,4,7,10-tetraazacyclododecane substituted with methylenephosphinic acid pendant groups (R = –CH_2–$P(H)O_2H$).[18] In addition, we reported the synthesis,[19] structure and solution properties of 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayltetrakis[methylene(phenyl)phoshinic acid] H_4L^2 and 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetrayltetrakis[methylene(phenyl)phoshinic acid] H_4L^3. Formulae of the ligands mentioned are shown in Chart 1 together with their abbreviations.

Lanthanide complexes of both tetraacetic and tetrakis(methylenephosphinic) acid derivatives have a salt like character resulting in relatively high osmolality under physiological conditions. Therefore, new ligands containing acetic acid pendant arms with charge 3− have been introduced, such as H_3pydo3a (3,6,9,15-tetraazabicyclo[9,3,1]pentadeca-1(15),11,13-triene-3,6,9-triacetic acid)[20] and H_3hp-do3a (1,4,7,10-tetraazacyclododecane-1-(2-hydroxypropyl)-4,7,10-triacetic acid).[21] The aim of this paper is to synthesise a new cyclen derivative containing three methylenephosphinic acid arms H_3L^1, to prepare its complexes with yttrium and lanthanides, and to determine their structure by X-ray analysis.

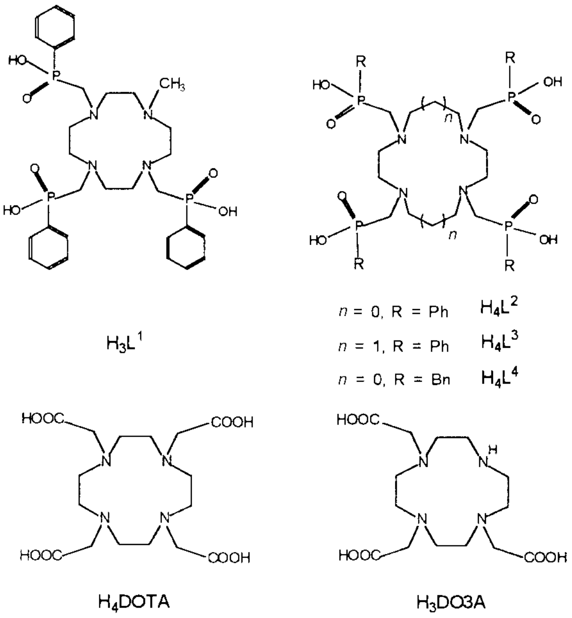
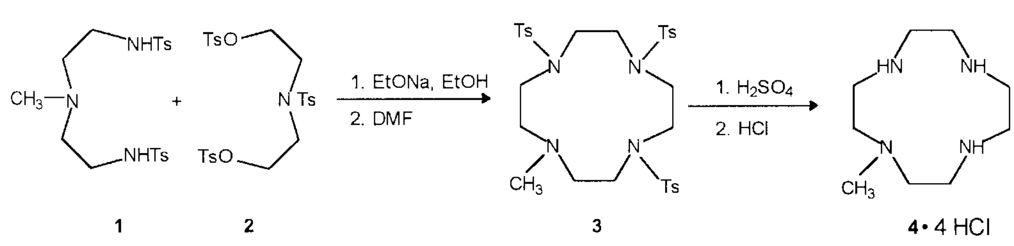


Chart 1

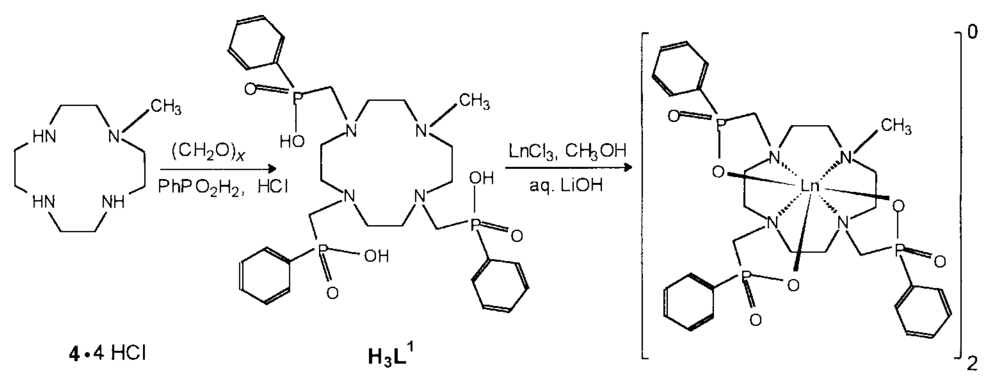
Results and discussion

Synthesis of H_3L^1

Synthesis of 1-methyl-1,4,7,10-tetraazacyclododecane followed Scheme 1. The syntheses of **1** and **2** are known from the literature.[22–25] A cyclisation procedure for formation of **3**, is also known; it was used, for example, for the synthesis of cyclene and 1,7-dimethylcyclene. However, we prefer the reaction of **1** with tosylated diethanolamine (**2**) which was found to be more convenient than using bis(2-chloroethyl)methylamine.[22–25] An alternative cyclisation procedure of *N*-methyldiethanolamine



Scheme 1



Scheme 2

ditosylate and diethylenetriamine tritosylate was not used due to difficulties in obtaining the former compound in a pure form.

The deprotection[26] of **3** gave 1-methyl-1,4,7,10-tetraazacyclododecane tetrahydrochloride **4** in high yield. Subsequently, H_3L^1 was synthesised by the Mannich reaction of **4** with paraformaldehyde and phenylphosphinic acid in aqueous HCl (Scheme 2). The optimised reaction conditions are described in the Experimental section. The ligand H_3L^1 was identified by ESI/MS spectrum, by both ^{1}H NMR and ^{31}P NMR spectra and correct organic analysis.

Preparation of the complexes

Direct reaction of an appropriate lanthanide oxide with H_3L^1 required heating under reflux overnight. Therefore, the reaction of H_3L^1 with lanthanide chlorides was found to be more convenient. An aqueous solution of LiOH was used for neutralisation of the reaction mixture because of solubility of LiCl in methanol. The complexes easily crystallise from the reaction mixture in pure form as hydrates, however they rapidly lose a part of the hydrated water. The stoichiometry of the compounds prepared was confirmed by elemental analysis and by electrospray ionisation mass spectroscopy ESI/MS. Predominant peaks in the spectra correspond to molecular ions associated with H^+, Li^+, Na^+ or K^+ ions.

Structures of the complexes

All compounds were found to crystallise in the space group $P2_1/c$ (no. 14) with similar values of lattice parameters (Table 1). The structures consist of centrosymmetrical electroneutral dimers. The structure of the dimer is shown in Fig. 1 and crystal packing is depicted in Fig. 2 and 3 for Ln = Yb. Table 2 lists selected bond distances and angles.

The $(L^1)^{3-}$ is co-ordinated to a lanthanide ion by four nitrogen atoms (N1–N4), two oxygen atoms from two monodentate phosphinate groups (O11, O21), and two oxygen atoms from two bidentate phosphinate groups (O31, O32^i). The nitrogen and oxygen atoms form bases N_4 and O_4 which are planar and parallel within experimental error. Twist angles of the bases around the local four-fold axis are in the range 28.0°– 33.1° the values being independent of ionic radii. Thus, the co-ordination polyhedra of Ln(III) seem to be "twisted square prismatic", therefore they are nearer to a square antiprism (ideal twist angle

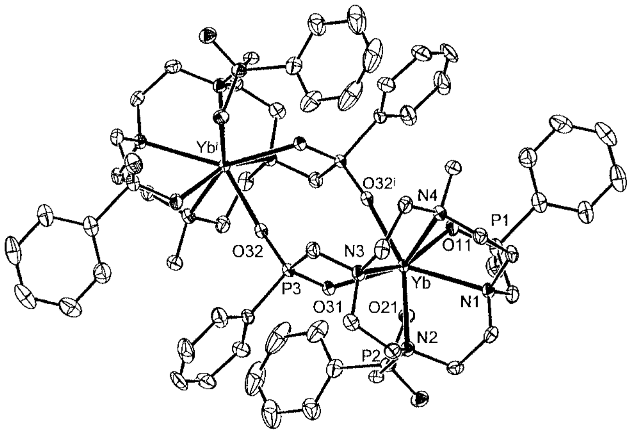


Fig. 1 View of $[YbL^1]_2 \cdot 6H_2O$ with the atom numbering scheme.

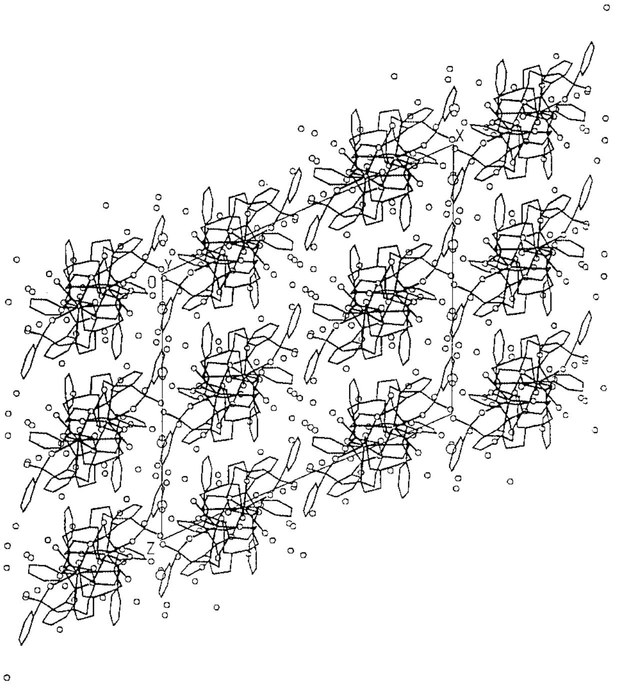


Fig. 2 Crystal packing of $[YbL^1]_2 \cdot 6H_2O$ (view along the *x* axis).

Table 1 Experimental data for the X-ray difraction studies of Ln(III) dimeric complexes $[LnL^1]_2 \cdot xH_2O \cdot yMeOH$

Ln	La	Ce	Nd	Eu	Tb	Er	Yb
x; y	6 ; 0	5 ; 1	7 ; 0	5 ; 2	6 ; 0	5 ; 0	6 ; 0
Formula	$C_{30}H_{52}N_4O_{13}P_3La$	$C_{32}H_{60}N_4O_{13}P_3Ce$	$C_{30}H_{52}N_4O_{13}P_3Nd$	$C_{32}H_{60}N_4O_{13}P_3Eu$	$C_{30}H_{52}N_4O_{12}P_3Tb$	$C_{30}H_{50}N_4O_{11}P_3Er$	$C_{30}H_{52}N_4O_{12}P_3Yb$
M	892.6	941.9	915.9	953.7	912.6	902.9	926.7
T/K	298(2)	170(1)	170(1)	170(1)	293(2)	293(2)	170(1)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	13.236(1)	13.194(3)	13.112(3)	13.2052(9)	13.047(3)	13.058(2)	12.970(1)
b/Å	20.229(4)	19.990(4)	19.758(5)	19.407(2)	20.238(6)	19.560(6)	19.961(2)
c/Å	15.659(2)	15.534(3)	15.928(5)	16.077(2)	15.841(4)	16.53(1)	15.784(2)
β/°	108.221(8)	107.21(3)	109.38(2)	110.617(9)	112.19(2)	111.32(9)	112.184(9)
U/Å^3	3982.4	3913.6	3892.5	3856.1	3873.0	3931.9	3783.8
Z	4	4	4	4	4	4	4
μ/mm^{-1}	1.25	1.35	1.52	1.82	2.01	2.31	2.66
Number of reflections measured	6270	28519	5670	4959	6233	4806	5547
Number of reflections observed [$I > 2\sigma(I)$]	5496	7669	4286	4087	4986	3698	4764
Number of independent reflections	6254	9815	5405	4724	5945	4806	5243
R_{int}	0.0522	0.0337	0.0767	0.0474	0.2310	—	0.0189

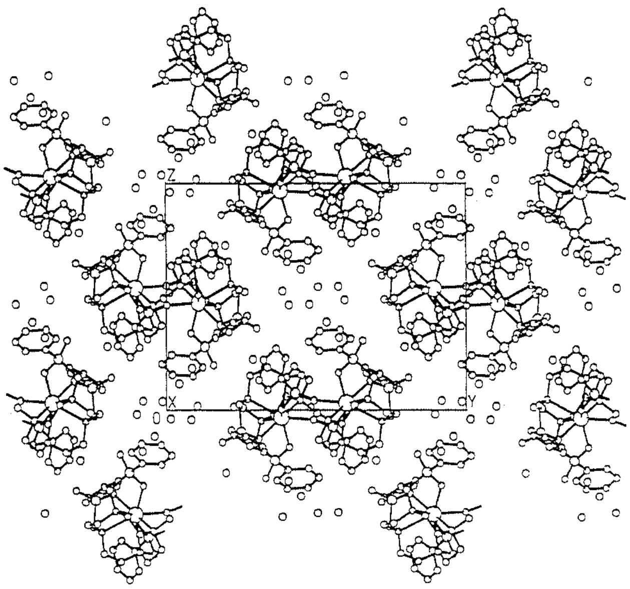


Fig. 3 Crystal packing of $[YbL^1]_2 \cdot 6H_2O$ (view along the y axis).

45°) than to a square prism (ideal twist angle 0°). The Ln(III) ion lies between coplanar O_4 and N_4 bases (Fig. 4) the distances between the bases being independent of Ln(III) radii (2.67(1) Å for La and 2.65(1) Å for Yb). However, with decreasing ionic radii, the lanthanide ion Ln(III) shifts from the O_4 base towards the N_4 base, as is shown in Table 2. Simultaneously with these shifts, distances of O atoms in the O_4 square base become smaller (O11–O31 = 4.631(6) Å and O21–O32^i = 4.480(6) Å for La; O11–O31 = 4.109(4) Å and O21–O32^i = 3.876(4) Å for Yb). The N_4 square base seems to be more rigid and differences in the N···N distances vary less (N1–N3 = 4.292(7) Å and N2–N4 = 4.223(7) Å for La, N1–N3 = 4.192(5) Å and N2–N4 = 4.126(5) Å for Yb).

In view of the potential utilisation of these complexes as contrast agents, an important feature of these structures is the position of the water molecule labelled O99. The vector Ln–O99 has the same direction in all the structures studied, and thus the molecule is situated approximately in the same direction toward the O_4 plane. However, the Ln–O99 distance is strongly dependent on Ln(III) and increases in the order: 2.815 Å La, 2.854 Å Ce, 3.171 Å Nd, 3.745 Å Eu, 4.278 Å Tb, 4.050 Å Er and 4.448 Å in the Yb complex. Thus, this water molecule (O99) can be considered as co-ordinated in La and Ce complexes and obviously unco-ordinated in the complexes of Eu, Tb, Er and Yb. The distance in $[NdL]_2$ is a little higher than that for the co-ordinated O atoms. Nevertheless, very weak Coulombic interaction is assumed even for Yb···O99. The O99 is also connected with O12 and O94 (3.02 Å and 3.11 Å in the Yb complex) through weak hydrogen bonds. From this point of view the position of the water molecule seems to be given rather by the room between phosphinic pendant arms above the O_4 base than by the interactions mentioned previously.

As was mentioned above, the size of the N_4 square bases in these structures are virtually the same as the common square {3333} conformation of the tetrazacyclododecane. This conformation corresponds to that of the lowest strain energy.[27] All chains are aligned in a *cis*-arrangement, *i.e.*, on one side of the ring. There are three types of torsion angles in the tetraazamacrocycles of these compounds, around C(n)–C(n + 1) bonds (average value −61°) and two conformationally non-equivalent angles around C–N bonds, N1–C1 (*gauche*) and around C2–N2 (*anti*). The angles around the C–N bonds give the average values of 76° (*gauche*) and 163° (*anti*).

The co-ordination of the phenylphosphinic acid group causes chirality of the phosphorus atoms. Configurations of the stereogenic phosphorus centres are the same in the seven

Table 2 Selected bond lengths (Å) and angles (°) in structures $[LnL^1]_2 \cdot xH_2O \cdot y MeOH$

Ln x ; y	La 6 ; 0	Ce (170 K) 5 ; 1	Nd (170 K) 7 ; 0	Eu (170 K) 5 ; 2	Tb 6 ; 0	Er 5 ; 0	Yb (170 K) 6 ; 0
Ln–O(99)	2.815(6)	2.854(6)	3.171(3)	3.745(12)	4.278(19)	4.050(30)	4.448(10)
Ln–O(11)	2.420(5)	2.392(4)	2.362(7)	2.333(5)	2.319(6)	2.254(16)	2.243(3)
Ln–O(21)	2.466(4)	2.476(4)	2.403(6)	2.341(4)	2.292(7)	2.260(14)	2.259(3)
Ln–O(31)	2.464(4)	2.434(4)	2.392(5)	2.364(4)	2.329(7)	2.281(14)	2.296(3)
Ln–O(32)^i	2.382(4)	2.380(4)	2.340(6)	2.285(4)	2.247(7)	2.219(15)	2.205(3)
Ln–Q(O)	0.8485(3)	0.9207(3)	0.948(3)	1.0139(3)	1.0357(4)	1.036(1)	1.0853(2)
Ln–N(1)	2.858(5)	2.851(5)	2.776(7)	2.716(5)	2.678(8)	2.652(17)	2.631(3)
Ln–N(2)	2.807(5)	2.789(5)	2.732(8)	2.652(5)	2.629(8)	2.584(19)	2.579(3)
Ln–N(3)	2.827(5)	2.802(5)	2.752(8)	2.675(5)	2.656(8)	2.616(19)	2.616(3)
Ln–N(4)	2.803(5)	2.769(4)	2.720(7)	2.664(5)	2.641(8)	2.634(19)	2.606(3)
Ln–Q(N)	1.8337(4)	1.8225(5)	1.734(3)	1.6589(4)	1.6241(5)	1.597(2)	1.5732(2)
Q(O)–Q(N)	2.6758(3)	2.7291(6)	2.6770(4)	2.6701(3)	2.6575(5)	2.631(2)	2.6529(3)
Q(O)–Ln–Q(N)	171.53(3)	167.71(3)	173.2(2)	173.66(2)	175.20(4)	175.12(9)	172.44(1)
O(99)–Ln–Q(N)	168.7(1)	168.5(1)	165.1(1)	159.1(2)	156.5(3)	157.2(5)	157.0(1)
O(99)–Ln–Q(O)	14.4(2)	18.2(1)	16.5(1)	21.2(2)	24.6(3)	22.6(5)	27.1(1)
Ln–(plane O_4)	0.838(2)	0.843(2)	0.942(3)	1.011(2)	1.030(3)	1.033(8)	1.003(1)
Ln–(plane N_4)	1.855(2)	1.822(2)	1.738(4)	1.658(3)	1.626(4)	1.596(10)	1.573(2)
N1 · · · N3	4.292(7)	4.310(7)	4.261(10)	4.244(7)	4.217(10)	4.184(26)	4.192(5)
N2 · · · N4	4.223(7)	4.210(6)	4.203(10)	4.159(7)	4.156(11)	4.135(28)	4.126(5)
O(11) · · · O(31)	4.631(6)	4.567(5)	4.414(9)	4.315(6)	4.234(9)	4.115(20)	4.109(4)
O(21) · · · O(32)^i	4.480(6)	4.486(5)	4.290(9)	4.068(6)	3.983(10)	3.881(23)	3.876(4)
twist angle of pen.1	−28.4(2)	−29.9(2)	−30(3)	−31(2)	−30.9(3)	−32.3(7)	−32.8(1)
pen.2	−28(2)	−30.2(1)	−29.2(3)	−29.7(2)	−29.4(3)	−29.7(7)	−32.8(1)
pen.3	−28(2)	−29.1(2)	−29.9(2)	−30.9(2)	−31.1(3)	−31.2(7)	−32.6(1)
pen.4	−32.3(2)	−30.9(2)	−33.1(3)	−32.5(2)	−32.0(3)	−32.0(6)	−31.3(1)
mean twist angle	−29.2(2)	−30(2)	−30.6(3)	−31(2)	−30.9(3)	−31.3(7)	−32.4(1)
Ln^i · · · Ln	6.208(1)	6.202(1)	6.132(1)	6.070(1)	6.024(1)	6.021(11)	5.968(1)
Ln^i–Ln–Q(N)	113.89(1)	114.65(2)	117.1(1)	119.86(1)	120.36(2)	121.25(7)	121.47(1)
Ln^i–Ln–Q(O)	64.60(2)	61.76(2)	62.3(2)	60.34(1)	59.09(2)	59.8(1)	56.63(1)
Ln^i–Ln–O(99)	77.2(1)	76.7(1)	77.7(1)	81.0(2)	83.1(3)	81.6(5)	81.3(1)

Q(O) is a centroid of the O_4 base, Q(A) is a centroid of the N_4 base.

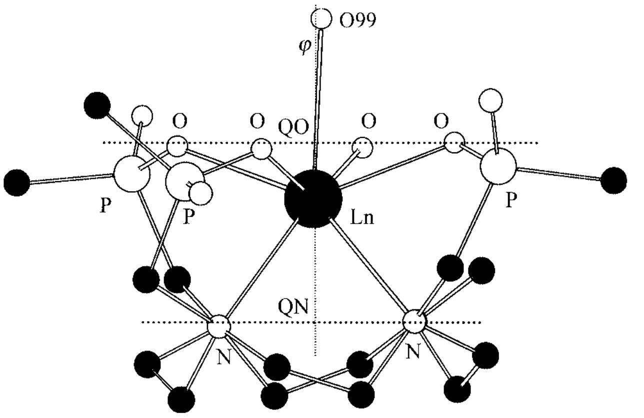


Fig. 4 Lanthanide co-ordination sphere, position of Ln between N_4 and O_4 planes.

structures studied. The usual *R*,*S* notation can be used for P1 and P2 atoms of non-bridging monodentate phenylphosphinic acid groups (Chart 2). To express the configuration of the P3 atom of the didentate bridging phenylphosphinic acid group using common rules is difficult. On the basis of a comparison of the torsion angles the configuration of the P3 atom is closer to the P1 atom and, therefore, it should be considered as *R*.

The pendant arms bearing the phenylphosphinic acid groups can be orientated clockwise (enantiomer Λ) or counterclockwise (enantiomer Δ) as is shown in Chart 3.

Both Λ and Δ isomers occur in each molecule of the dimeric complex in the ratio 1 : 1 because of the presence of the inverse centre. Thus, a molecule of the dimer can be regarded as the *meso* form, *i.e.*, a combination of two "monomeric" units with opposite configurations (Δ and Λ) of the pendant arms.

As was mentioned above, the coordination polyhedra are linked through an eight-membered ring, which is typical of phosphinates.[28] The presence of two P atoms and in particular two Ln(III) atoms with a flexible geometry leads to an irregular centrosymmetric conformation. The independent part of this ring can be described by the pattern $-g,+g,(-g),+g$, where $\pm g$ are ±*gauche* and $(-g)$ represents an intermediate position between *gauche* and *anti*.[29]

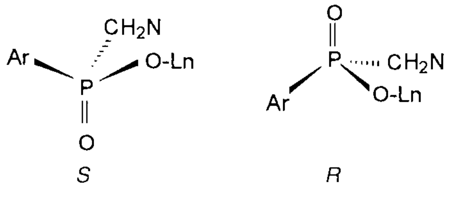


Chart 2

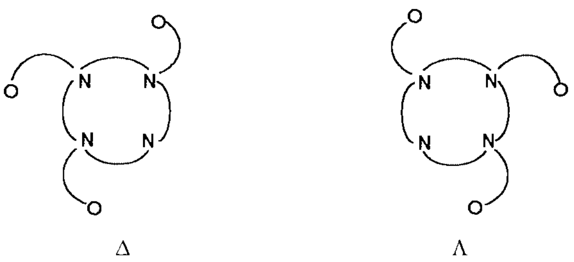


Chart 3

The packing of the dimeric complex molecules leaves infinite channels in the crystals which are parallel with the monoclinic axis. In all the seven structures studied, these channels are occupied by water and water and/or MeOH molecules of crystallisation, hydrogen-bonded to each other (distances O_w–O_w in the range 2.8–3.2 Å) and, some of them, to outward non-co-ordinated oxygen atoms from the phenylphosphinic acid groups (distances O_w–O_{n2} in the range 2.7–3.0 Å). The system of hydrogen bonds could be studied in detail only in the Yb complex, where all hydrogen atoms were determined. The non-co-ordinated oxygen atoms are linked to solvate molecules by a

Table 3 Cyclic voltammetric data for the electrooxidation of $[CeL^2]^-$ and $[CeL^1]_2$ in non-aqueous media. Concentration of substances 1–4 × 10^{-4} mol l^{-1}, 0.05 M $[Bu_4N]PF_6$ (E_{pa} = anodic peak potential, E_{pc} = cathodic peak potential, all data are in V *vs.* SCE)

Solvent	$[CeL^2]^-$ E_{pa}	E_{pc}	E_{pa}'	$[CeL^1]_2$ $E_{pa}(1)$	$E_{pc}(1)$	$E_{pa}(2)$	$E_{pc}(2)$
AN/EtOH[a]	0.71	0.62					
AN	0.64	0.55	0.76–0.80	0.83	0.72	1.04	0.95
DMF	0.58	0.36					

[a] Acetonitrile : EtOH, 9 : 1.

hydrogen bond network (O12–O99, O12–O96, O22–O88, O22–O96). Further hydrogen bonds connecting the molecules of solvent were also found. The diameters of channels (4.5–6.5 Å) are close to those observed in structures $Li[Ln(H_2O)L^2]\cdot 10H_2O$ (ref. 30) and smaller than in similar structures of benzylphosphinates.[31] Due to the size of the channels, it is not surprising that water (or MeOH) molecules have room enough to move along the channels and such a structure gives ample possibilities for disorder (both static and dynamic) of the channel contents. This feature really made the structure-solution difficult. In addition, the crystals outside in the mother liquid (even under an inert atmosphere) are highly unstable and thus, it is understandable, that solvation of single crystals varied, and precise determination was not possible by X-ray experiments. The cumulative effects of these factors, together with an extremely high mechanical brittleness of crystals, reduce substantially the accuracy and precision of the structure determinations of, *e.g.*, Er and Tb complexes. Similar problems are common with this type of compound.

A carboxylic analogue of H_3L^1, H_3DO3A forms a slightly different co-ordination sphere with a lanthanide under the same conditions, *i.e.*, in slightly basic solution.[32] The X-ray analysis showed that Gd(DO3A) crystallized as $[(GdDO3A)_3\cdot Na_2CO_3]\cdot 17H_2O$ in which each Gd atom is coordinated to four nitrogens of the macrocycle and the oxygen from each carboxylic arm. The coordination sphere is completed by co-ordination of two oxygens of the carbonate ion. Neither water molecule was co-ordinated to the Gd atom nor formation of the carboxylate bridges was observed. However, single carboxylic bridge formation was observed in the [La(HDOTA)-La(DOTA)] complex.[33] Nevertheless, a comparison of H_3L^1 and H_3DO3A complexes confirms the well-known better ability of the phosphinic acid group for didentate coordination and formation of the bridges connecting co-ordination polyhedra. Thus, the $N_4O_4(H_2O)$ co-ordination sphere observed for $[LnL^1]_2$ complexes is closer to that found for complexes with ligands containing three or four pendant arms such as H_4DOTA[33,34] or H_4L^4. In addition to the same conformation of the tetraazadodecane ring, a similar range of the twist angles between N_4 and O_4 bases around the four-fold axes is present. The distances between the N_4 and O_4 bases are close to those previously observed[33,34] and the trend of the lanthanide moving towards the N_4 base dependent on its size is also analogous to that in the structures with four pendant ligands.

In contrast to carboxylates, coordination of the phosphinic acid group leads to the formation of a centre of chirality. It seems to be understandable that the *RS* orientation of the phenylphosphinic acid group observed in $[LnL^1]_2$ complexes is analogous to the *RSRS* orientation in $Li[LnL^2]$ (ref. 30) and different from the *RRRR* orientation observed in $[LnL^4]^-$ complexes containing benzylphosphinic groups.[31]

Solution properties

The ^{31}P NMR studies of lanthanide complexes with phosphonic[10,35,36] and phosphinic acid derivatives[14,31] of cyclen showed the formation of isomeric mixtures in solution. This effect is also assumed to occur in $[LnL^1]_2$ solutions. Cyclic voltammetry (see below) confirmed the presence of the dimeric form even in solution. If we assume the centrosymmetric structure of the bridging phosphinate groups, then 16 isomers from (ΔRR–ΛSS) to (ΔSS–ΛRR) should occur in solution and in the ^{31}P NMR spectrum, 32 signals corresponding to the isomers and additional signals from bridging phosphorus atoms could be observed. If the isomerisation occurred on the bridging phosphorus atoms, the number of isomers and signals would be higher. Therefore, the ^{31}P NMR spectra of $[LnL^1]_2$, where Ln is La, Lu or Y, are complex and about 20 peaks are observed in a narrow region of 29–34 ppm. The number of peaks did not change even at 50 °C. The ^{13}C NMR spectra were also found to be complex, except for a sharp signal at 46 ppm corresponding to the methyl group.

Stability of the dimer and its ability to dissociate was tested by reactions with triphenylphosphine oxide (tppo) and with pyridine *N*-oxide, which are known to be good donors for lanthanide ions,[37] in a molar ratio of complex : oxide = 1 : 10. The ^{31}P NMR spectra showed no changes in the complex signal pattern in the range of 29–34 ppm after addition of tppo, only the intensity of the tppo signal increased with the increasing ratio of tppo/complex. The same results were obtained from the experiments with pyridine *N*-oxide. No changes of the spectra were observed after heating. Thus, the experiments confirmed the high stability of the dimer in methanolic solution.

The dimeric form, $[CeL^1]_2$, was also investigated by cyclic voltammetry. Electrochemical properties of the dimer were also compared with the monomeric complex $[CeL^2]^-$. Electrochemical oxidation of the $[CeL^1]_2$ in acetonitrile proceeds in two one-electron diffusion-controlled reversible steps at potentials $E_{pa}(1)$ 0.830 V and $E_{pa}(2)$ 1.040 V. This potential range is typical of a Ce(III)/Ce(IV) redox pair at a platinum electrode.[38] Thus, the $[CeL^1]_2$ is considered a molecule with two equivalent redox active centers (two Ce(III)-ions).[39] The fact that the oxidation proceeds in two steps proves that both Ce atoms are oxidised independently. There is no consecutive reaction, *i.e.*, mixed valence complexes Ce(III)–Ce(IV) are sufficiently stable due to electronic delocalisation over the whole $[CeL^1]_2$ molecule, where the oxidised part of the molecule acts as a substituent decreasing the electron density on the rest of the molecule. Therefore, the oxidation of the second Ce(III) is more difficult. The experiment verified an existence of the dimeric form in solution. In contrast to the $[CeL^1]_2$, electrochemical oxidation of the anionic compound $[CeL^2]^-$ proceeds generally in a single one-electron diffusion controlled reversible process at potentials (E_{pa}) between 0.550 V–0.700 V (see Table 3) depending on the solvent used. With increasing basicity of the solvent, the oxidation potential is shifted to less positive potentials and the cathodic counter-peak becomes broader. In acetonitrile, the anodic process involves two steps indicating a consecutive reaction after the primary electron transfer. The first step corresponds to the one-electron oxidation Ce(III)/Ce(IV) of the $[CeL^2]^-$ anion. The oxidized molecule undergoes most probably an intramolecular electron transfer resulting in oxidative splitting of one $PPh(O)O^-$ group under regeneration of the oxidation state +III at the central Ce ion. The second, more positive oxidation step (E_{pa}') then corresponds to the Ce(III)/Ce(IV) oxidation of the uncharged molecule bearing only three $PPh(O)O^-$ groups. This reaction pathway is supported by the results of the above reported oxidation experiments of $[CeL^1]_2$, where the potential of the first oxidation step of $[CeL^1]_2$ (with three $PPh(O)O^-$ groups around each Ce(III) ion) is very close to the E_{pa}' (Table 3). As for the reduction of $[CeL^2]^-$ or $[CeL^1]_2$, no cathodic process has been observed in the studied solvents at the platinum electrode up to −1.6 V.

Luminescence spectra of $[EuL^1]_2$ and $[TbL^1]_2$ in methanolic solution were also studied. The phenyl groups on 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.[11,40] The bands observed consist of $^5D_0$–^7F_J transitions and $^5D_4$–^7F_J transitions. The electric–dipole-allowed $^5D_0$–$^7F_2$ transition is known to be hypersensitive its intensity being strongly affected by polarisibility of the ligand.[31b,41] It is absent if the Eu^{3+} ion is in an inversion centre. In the spectrum of $[EuL^1]_2$ the $^5D_0$–$^7F_2$ signal is about twice as intensive as the $^5D_0$–$^7F_1$, which indicates the strong polarisibility of $(L^1)^{3-}$. For phosphinate complexes of the $[Eu(DOTA)(H_2O)]^-$ type, this transition produces one of the most intensive bands in the spectrum.[42] In the $^5D_0$–$^7F_2$ region of the luminescent spectrum of $[EuL^1]_2$, two well separated singlets are found whose intensities are comparable with that for the $^5D_0$–$^7F_1$ transition. This is consistent with the absence of an inversion centre in the emitting species and polarisibility of the ligand, enhanced by the presence of phenyl rings on phosphorus atoms. The $^5D_0$–$^7F_3$ transition is of low intensity in the spectrum, similarly to other $[Eu(DOTA)(H_2O)]^-$ type complexes.[43] The intensity of the $^5D_0$–$^7F_4$ multiplet in $[EuL^1]_2$ is smaller in comparison with that of $^5D_0$–$^7F_{1,2}$, in contrast to the complexes $Li[Eu(L^2)]$.[30]

In the spectrum of $[TbL^1]_2$, all the $^5D_4$–^7F_J transitions, where $J = 3,4,5,6$, were observed. The spectrum is the same as spectra of analogous $Li[TbL^2]$ (ref. 30) or $[TbL^4]$ (ref. 31, 44), which corresponds to the fact that luminescent spectra of Tb^{3+} are not as sensitive to the changes outside the first co-ordination sphere.

Conclusion

A new macrocyclic ligand derived from cyclene substituted with three methylene(phenyl)phosphinic acid pendant arms was synthesised and its complexes with lanthanides were prepared. X-Ray analysis of seven Ln(III) complexes (Ln = La, Ce, Nd, Eu, Tb, Er, Yb) showed the formation of dimers $[LnL^1]_2$ in the solid state. All complexes are isostructural and a coordination polyhedron is formed by four N atoms and four O atoms of the phosphinic acid groups. A water molecule is placed near the O_4 base; however, only in La and Ce structures can it be considered a part of the co-ordination sphere. The compounds are insoluble in H_2O, but soluble in methanol, forming complex mixtures of isomers in this solvent.

The ^{31}P NMR studies showed isomerisation of chiral phosphorus atoms and formation of rather complex isomeric mixtures in solution. The dimer stability was verified by reactions with triphenylphosphine oxide (tppo) and with pyridine *N*-oxide, which are good donors for lanthanide ions. The experiments confirmed high stability of the dimers in methanolic solution.

The cyclic voltammetry confirmed that the oxidation proceeds in two steps, proving that both Ce atoms are oxidised independently. There is no consecutive reaction, *i.e.*, the mixed-valence complexes Ce(III)–Ce(IV) are sufficiently stable.

Experimental

Instrumentation

The melting points were determined with a Boethius apparatus and are uncorrected. ^1H and ^{31}P NMR spectra were taken on a Varian Inova 400 MHz spectrometer, using *ca.* 0.1 M solutions in D_2O or $CDCl_3$, with chemical shifts reported in ppm from DSS or TMS (internal) and 85% H_3PO_4 (external) standards. The eluent for TLC of complexes on silica plates is $(CH_3)_3COH$, H_2O and CH_3CN in a 2:9:2 volume ratio.

Synthesis of precursors

Compounds $(TsNHCH_2CH_2)_2NMe$, $(TsOCH_2CH)_2NTs$, were synthesised by the previously described procedures.[21–25] The purity of products was checked by conventional methods (^1H NMR and ^{31}P NMR, if appropriate, spectra and elemental analysis). Solvents were purified and dried using established procedures.[45]

Synthesis of 1-methyl-4,7,10-tritosyl-1,4,7,10-tetraazacyclododecane (3). The disodium salt of **1** was prepared by addition of a solution of 2.65 g Na in 50 ml absolute ethanol to 24 g *N″*-methyl-*N′*,*N‴*-ditosyldiethylenetriamine in 42 mL of absolute ethanol at 40 °C. The reaction was completed by refluxing the solution for 20 min. The solvent was stripped off on a rotary evaporator at 80 °C and the white disodium salt was dissolved in 565 mL of dry DMF. To the solution formed, a solution of 92 g *N*-tosyldiethanolamine ditosylate in 300 mL of dry DMF was added during 3 h at 100–105 °C while stirring. This temperature was maintained for 1 h. To the cooled solution, 4 L of H_2O was added. The precipitated product was filtered off after standing overnight, washed with water and dried at 80 °C. The product was then purified by refluxing in ethanol, leaving the suspension to cool to room temperature and filtering off the white 1-methyl-4,7,10-tritosyl-1,4,7,10-tetraazacyclododecane from the slightly brownish solution. Yield 48 g, 65%, mp 201 °C. ^1H NMR: s 2.17 CH_3N (3H), s 2.43 CH_3Ar (6H), s 2.46 CH_3Ar (3H), bt 2.61 CH_2N (4H), t 3.06 CH_2N (4H), t 3.27 CH_2N (4H), t 3.51 CH_2N (4H), m AA′BB′ 7.29–7.64 CH aromatic (8H), m AA′BB′ 7.34–7.83 CH aromatic (4H). 1-Methyl-1,4,7,10-tetraazacyclododecane tetrahydrochloride **4** (*N*-methylcyclene) was released from **3** by modification of the Lázár procedure,[26] starting from 0.5 g of **3** and 4 mL of conc. H_2SO_4 and giving 85% yield, mp 237–239 °C (dec), ^1H NMR: s 2.54 CH_3N (3H), br m 2.8–3.4 NCH_2 ring (16H).

Synthesis of H_3L^1. Phenylphosphinic acid (0.55 g, 3.8 mmol) and *N*-methylcyclene tetrahydrochloride (0.2 g, 0.6 mmol) were dissolved in a mixture of 36% HCl (2 mL) and H_2O (2 mL). The mixture was heated in an oil bath at 95–100 °C and paraformaldehyde (0.17 g, 5.6 mmol) was added while stirring in 30 min intervals during 7 h. After the addition was completed, the mixture was heated for 2 h. The solution obtained was evaporated to dryness using a rotary evaporator and co-distilled with H_2O three times to remove excess of formaldehyde. The colourless oil was dissolved in H_2O, loaded on Dowex 50W-X8 in H^+ cycle and eluted with H_2O to remove excess of phenylphosphinic acid. Ligand H_3L^1 was eluted using dilute HCl. Ligand H_3L^1 was obtained in 57% yield. Analysis found (calculated): $C_{30}H_{43}N_4O_6P_3 \cdot 5H_2O \cdot HCl$: C 46.81 (46.49), H 7.41 (7.02), N 7.55 (7.23)%. ^1H NMR: s 1.68 CH_3 (3H), br m 2.3–2.7 NCH_2 ring (16H), d 2.95 NCH_2P (2H) $^2J_{PH} = 8.9$ Hz, d 2.98 NCH_2P (4H) $^2J_{PH} = 9.1$ Hz, m 6.9–7.2 aromatic CH (15 H). $^{31}P\{^1H\}$ NMR: s 29.79, (2P), s 29.60 (1P).

Preparation of the complexes $[LnL^1]_2 \cdot 6H_2O$. These complexes were prepared starting from an appropriate lanthanide oxide, which was dissolved in conc. hydrochloric acid upon warming in an oil bath. The solution formed was evaporated to dryness using a rotary evaporator. The residue obtained was dissolved in a methanol–water (80/20 v/v) mixture. A stoichiometric amount of H_3L^1 in a 40% solution of the same solvent was added and the mixture was heated to 50 °C. Then, 1% aqueous LiOH was added very slowly to this solution while stirring vigorously (during *ca.* 5 min) until the pH reached 8–9. During this addition a white precipitate was formed at about pH 7, which redissolved at a higher pH. The slightly turbid solution obtained was heated for 30 min and then filtered through filter paper (blue strip) and allowed to crystallise in a desiccator over P_2O_5. The crystals of $[LnL^1]_2{\cdot}6H_2O$ formed were filtered off and air-dried. Analytical data of these compounds are in agreement with the formula given. Single crystals for X-ray diffraction studies were prepared from methanol–water mixtures in the manner given above, but their isolation was done by the technique described in the Crystallography section. The solvation of the latter complexes is higher than that of air-dried complexes (see Table 1). The purity of the prepared complexes (especially with respect to uncomplexed Ln^{3+}) was proved by TLC in the mixture acetonitrile–water–^tBuOH 2:9:2 (v/v) on silica plates, using detection with a Xylenol Orange solution. The R_f of the complexes is 0.4, while R_f of the uncomplexed Ln^{3+} is 0.

The compounds $[LnL^1]_2{\cdot}6H_2O$ are soluble in methanol, sparingly soluble in water and almost insoluble in higher alcohols and less polar organic solvents. They have the same colours as hydrated Ln^{3+} cations. The compounds lose water extremely easily in the laboratory atmosphere forming lower hydrates. The decomposition of a single crystal of the compound could be seen after *ca.* 2–3 min.

X-Ray analysis

The well-formed and highly unstable (due to loss of solvent molecules) crystals of the compounds studied were obtained by slow evaporation of the solvent mixture (MeOH–H_2O 80:20) at room temperature and under normal pressure for a couple of weeks. The suitable crystals were selected in the mother liquor, picked up in a cool room (at 4 °C) and mounted at random orientations on glass fibres using a hydrophilic acrylate glue. The crystals were coated with a thin paraffin film and scanned at room temperature or at 170 K (Table 1). All attempts to protect the crystals in Lindenmann capillares (with and without mother liquor) failed due to their brittleness. Similar attempts using low-temperature methods and protecting the crystals with different silicone oils or other hydrophobic materials were also unsuccessful probably due to cracking of single crystals caused by inner temperature and pressure gradients. The stability of the crystals outside the mother liquor, without protecting paraffin films, is about 1 min at room temperature, about 10 min at 4 °C, and from 6–11 h with the films (depending on the crystal size and quality of the paraffin coating) at room temperature.

An Enraf-Nonius CAD4 diffractometer was used for measurements at 293(2) or 170(1) K in a dry nitrogen stream with Mo-Kα radiation ($\lambda = 0.71073$ Å), with the exception of Ce(III). Selected crystallographic and other relevant data for all compounds are listed in Table 1. The Ce(III) complex was measured at 170 K using a KUMA-diffractometer with imaging plate. The data were corrected for Lorenz polarisation, but not for absorption.

The extinction correction was applied using the standard procedure included in SHELXL97.[46] The structures were solved and refined by standard procedures (SHELXS86, SHELXL97).[47,46] Hydrogen atoms in CH_3, CH_2 and CH fragments were included in the calculated positions (SHELXL97), but hydrogen atoms from water molecules could not be found due to the bad quality of the data, with the exception of the Yb structure, where H atoms were found in the Fourier map and refined isotropically. We tried to refine the ocupancy of all uncoordinated water molecules.

CCDC reference number 186/1747.

See http://www.rsc.org/suppdata/dt/a9/a907018d/ for crystallographic files in .cif format.

Electrochemical measurements

Cyclic voltammetry was carried out at room temperature under an argon atmosphere using non-aqueous solvents and their mixtures: acetonitrile (Merck, for UV spectroscopy), dimethylformamide (purified[45] by azeotropic distillation followed by vacuum fractionation), methanol (Fluka, for HPLC) and ethanol (Lachema, freshly destilled). The supporting electrolyte $[Bu_4N]PF_6$ (Fluka, p.a. for polarographic use) was used in concentration 0.05 mol dm^{-3}. The standard three-electrode system consisted of a stationary platinum disk electrode 1 mm in diameter (working electrode), a platinum-wire auxiliary electrode and a saturated calomel electrode (to which all potentials are referenced) separated from the solution by a salt bridge. The concentration of the studied substances varied between (1–5) × 10^{-4} mol l^{-1}, the scan rates were 10–1000 mV s^{-1}. The stock solution of $Li[CeL^2]$ was 0.025 M in MeOH, the stock solution of $[CeL^1]_2$ was 0.025 M in acetonitrile–MeOH 1:1. A computer-controlled electrochemical system ETP Polarosensors (Prague) was used with the POLARO 2.0 software.

Luminescence spectra

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

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