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Lanthanide Complexes of 2,2′,2′′-(10-{[Hydroxy(phenyl)phosphoryl]methyl}-1,4,7,10-tetraazacyclododecan-1,4,7-triyl)triacetic Acid: Structural Characterisation of Intermediates from the Proposed Complexation Mechanism in the Systems of Ln^{III}-dota-Type Ligands

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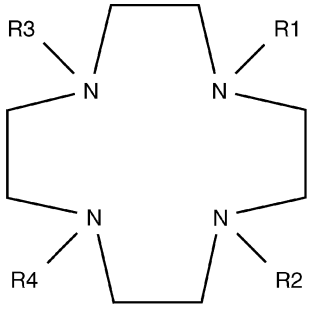
The crystal and molecular structures of ten lanthanide complexes of H_4do3aP^{Ph} [2,2′,2′′-(10-{[hydroxy(phenyl)phosphoryl]methyl}-1,4,7,10-tetraazacyclododecan-1,4,7-triyl)-triacetic acid] are presented here. These complexes constitute a new type of coordination compounds within the Ln-dota family. They represent an intermediate stage on the way from the ligand to the classical in-cavity complexes. The important role of intramolecular H-bonds for the process was observed. These intermediate complexes in the solid state form several isostructural groups with the different coordination polyhedra (square antiprisma or dodecahedron) of lanthanide ions.

Introduction

During the last decade, nuclear magnetic resonance imaging (MRI) has become a powerful and excellent clinical modality in diagnostic medicine. This noninvasive radiological technique provides anatomic images that arise from mapping of protons in various tissues with water molecules responsible for most of the signals. Introduction of a highly paramagnetic substance may significantly increase image contrast, which depends on the abundance of hydrogen atoms and their relaxation time. In particular, gadolinium(III) complexes are utilised as contrast agents (CA) in MRI,[1] because of the high magnetic moment of Gd^{III} and a relatively long electron relaxation time. The use of gadolinium salts as contrast agents is limited by their immense intrinsic toxicity; the Gd^{III} ion must be therefore encapsulated in a stable complex, usually with octadentate N,O ligands.[1] Similarly, stable complexes of analogous ligands were devised for applications of metal radionuclides for diagnosis and therapy in nuclear medicine.[2] The above-mentioned medical utilisations require intravenous application; the complexes have to be kinetically and thermodynamically stable, because several competing dissociation equilibria exist in vivo.[3] Macrocyclic ligands derived from [4,7,10-tris(carboxymethyl)-1,4,7,10-tetraazacyclododecan-1-yl]acetic acid (H_4dota; see Scheme 1) ensure the required stability of the Gd^{III} complexes. Prior to slow formation of the final thermodynamically stable polychelates, various intermediate species[4] are rapidly formed in a solution containing the ligand and the lanthanide salt. Some of these intermediates are sufficiently stable to be studied.



R1=R2=R3=R4 = CH_2COOH = **H_4dota**

R1= $CH_2P(Ph)OOH$, R2=R3=R4 = CH_2COOH = **H_4do3aP^{Ph}**

Scheme 1. Structures of the main ligands discussed in this paper (for structures of other ligands, see Schemes S1a and S1b in the Supporting Information).

From previously published experimental results, two reaction mechanisms can be proposed.[5] The first one consists of three phases.[3,6–11] Phase I involves formation of $[LnH_2L(H_2O)_x]^+$ complexes (for clarity, H_4L represents H_4dota), in which the Ln^{III} ion is located outside the cage formed by four nitrogen atoms and four oxygen atoms of the pendant groups. Two protons bound to two opposite nitrogen atoms of the tetraaza ring are oriented in towards

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the cage. The Ln^{III} ion is coordinated to the oxygen atoms of the pendant groups only and located above the plane formed by the four nitrogen atoms because of electrostatic repulsion between this cation and the protons on the tetraaza ring. The coordination number (CN) of the cation is usually nine, because the coordination sphere of the cation is completed by water molecules. During Phase II, the $[LnH_2L(H_2O)_x]^+$ complex loses a proton from one nitrogen atom to form a $[LnHL(H_2O)_x]$ complex without any change in bonding modes. Phase III consists of a concerted rearrangement of the intermediate complex; the Ln^{III} ion penetrates the cage formed by the four nitrogen atoms of the macrocycle ring and four oxygen atoms of the pendant groups. At the same time, the intermediate complex $[LnHL(H_2O)_x]$ loses the last proton from the tetraaza ring to form the $[LnL(H_2O)_x]^-$ complex, in which the four nitrogen atoms and the four oxygen atoms are coordinated to Ln^{III}. In dependence of the nature of the ligand and ionic radius of Ln^{III}, the CN of the Ln^{III} ion is either completed to nine by one water molecule or remains eight.

The second complexation mechanism consists of two phases only.[12–15] Phase I involves formation of a $[LnHL(H_2O)_x]$ species containing only one proton. This proton is located on a nitrogen atom of the tetraaza ring; the Ln^{III} cation is coordinated to the four oxygen atoms of the pendant groups and at least one nitrogen atom of the macrocycle. The Ln^{III} ion is located in the plane of the four oxygen atoms. In Phase II, the intermediate complex $[LnHL(H_2O)_x]$ loses the remaining proton and a rearrangement simultaneously occurs in the complex; the Ln^{III} cation enters the coordination cage during this process. The proton of the NH^+ group may transiently migrate to one pendant group during this phase. The previously suggested and observed intermediate complexes are listed in Table S1; some of their structural characteristics are listed in Table S2 in the Supporting Information.

In the recent work of Moreau and coworkers,[5,16] coordination mechanism of two derivatives of dota (the tetracarboxyethyl-dota[5] and tetra-2-glutaryl-dota[16]) with three lanthanide cations (Eu^{III}, Gd^{III} and Tb^{III}) was identified by complementary techniques in solution [potentiometry, luminescence spectroscopy and EXAFS (Extended X-ray Absorption Fine Structure)]. Potentiometry enabled determination of the number and stoichiometry of the various complexes present in solution and calculation of their relative stabilities as well as their acidity constants. Study of the Ln^{III} coordination environment by EXAFS provided the number of bonds in the coordination sphere of Ln^{III} along with their type and bond lengths. Luminescence spectroscopy provided the number of water molecules bound to the europium or terbium cations. Therefore, these techniques are convenient for the study of the complexation process in solution.

In our recent work,[17] we prepared and structurally characterised an intermediate complex of the type $[LnH_2L(H_2O)_x]^+$ [L = 2,2′,2′′-(10-{[hydroxy(phenyl)phosphoryl]methyl}-1,4,7,10-tetraazacyclododecan-1,4,7-triyl)-triacetic acid, H_4do3aP^{Ph}] in the solid state. Structures of two isomers of a dimeric compound $[Er\{H_2do3aP^{Ph}\}(H_2O)_2]_2Cl_2\cdot xH_2O$ represent the first example of the above-mentioned intermediates that were isolated and characterised by X-ray diffraction. Both of these structures contain exclusively an O-coordinated ligand. This is the most remarkable difference from the N_4O_4 coordination known from structures of the dota-type complexes. The reason for the exclusive O coordination is the presence of two protons in the cavity, as suggested in the above-mentioned complexation mechanism. Two water molecules are directly coordinated to each Er^{III} ion and complete its coordination sphere. The main difference between the two forms of the compound $[Er\{H_2do3aP^{Ph}\}(H_2O)_2]_2Cl_2\cdot xH_2O$ was found in the shape of coordination sphere of the Er^{III} ions. The coordination polyhedron found in the α form resembles more closely square-antiprismatic shape rather than dodecahedral one. However, the Er^{III} coordination polyhedron found in the β form is more properly described by dodecahedral geometry.[17]

In this work, preparation and X-ray diffraction studies of a series of intermediate lanthanide(III) complexes are described. The stereochemistry and the polymorphism of these compounds are discussed. These compounds extend the number of known and structurally characterised intermediates from the complexation mechanism in the systems of Ln^{III}-dota-type ligands.

Results and Discussion

Synthesis

The complexes were prepared from the corresponding metal chloride or nitrate as described in the Experimental Section. Standing of filtered aqueous solutions at 15–30 °C combined with very slow evaporation was necessary to obtain crystals suitable for X-ray diffraction. Crystallisation of complexes corresponding to the previously published β form of erbium(III) complex might be preferred at lower temperatures,[17] but this effect is not clear.

Crystal Structures of the Prepared Complexes

The set of ten obtained complexes can be divided into three groups according to their crystal structures. The first group consists of five isostructural compounds (for lattice parameters, see Table 1) of the overall formula $[Ln\{H_2do3aP^{Ph}\}(H_2O)_2]_2Cl_2\cdot xH_2O$ (Ln = Nd, Gd, Dy, Yb or Y); labelled as group GI. These complexes (labels I-Ln) crystallise in the space group $P\bar{1}$ with $Z = 1$, and the position of the Ln^{III} ion in the unit cell is about 0.509, 0.262, 0.637. The complexes I-Ln are isostructural with the previously reported β form of erbium(III) complex.[17] Two nitrates of the overall formula $[Ln\{H_2do3aP^{Ph}\}(H_2O)_2]_2(NO_3)_2\cdot xH_2O$ (Ln = Gd, Er) with the position of Ln^{III} approaching 0.253, 0.434, –0.056 are isostructural (see Table 1; group GII) as well as two complexes of overall formula $[Ln\{H_2do3aP^{Ph}\}(H_2O)_3]_2Cl_2\cdot xH_2O$ (Ln = La, Ce)

Table 1. Cell parameters *a*, *b*, *c* (Å; first row), *α*, *β*, *γ* (°; second row), fraction coordinates of Ln^{III} (third row) and cell volume (*U*, Å^3) for studied crystal structures; $Z = 1$ with the exception of the Eu^{III} complex IV-Eu ($Z = 2$).

Compound	*a*; *α*; *x*	*b*; *β*; *y*	*c*; *γ*; *z*
I-Dy	11.647(2)	12.144(1)	12.431(1)
$[Dy(H_2do3aP^{Ph})(H_2O)_2]_2Cl_2\cdot 10H_2O$	112.546(3)	94.621(3)	100.884(2)
$U = 1571.8(1)$	0.50750(2)	0.26213(2)	0.63802(2)
I-Gd	11.640(1)	12.162(1)	12.441(1)
$[Gd(H_2do3aP^{Ph})(H_2O)_2]_2Cl_2\cdot 11H_2O$	112.589(1)	94.533(2)	100.885(1)
$U = 1574.4(2)$	0.50746(1)	0.26303(2)	0.63838(1)
I-Nd	11.682(1)	12.270(1)	12.537(1)
$[Nd(H_2do3aP^{Ph})(H_2O)_2]_2Cl_2\cdot 10H_2O$	112.674(3)	94.645(3)	101.124(2)
$U = 1602.9(1)$	0.51031(2)	0.26452(2)	0.63886(2)
I-Y	11.633(1)	12.108(1)	12.396(1)
$[Y(H_2do3aP^{Ph})(H_2O)_2]_2Cl_2\cdot 12H_2O$	112.396(3)	94.667(3)	100.886(3)
$U = 1562.5(1)$	0.50744(3)	0.26165(3)	0.63774(3)
I-Yb	11.691(1)	12.210(1)	12.432(1)
$[Yb(H_2do3aP^{Ph})(H_2O)_2]_2Cl_2\cdot 12H_2O$	110.535(2)	95.207(1)	101.638(2)
$U = 1602.3(1)$	0.51272(1)	0.25376(2)	0.63180(1)
II-Er	11.302(1)	11.778(1)	12.173(1)
$[Er(H_2do3aP^{Ph})(H_2O)_2]_2(NO_3)_2\cdot 12H_2O$	84.885(1)	85.748(1)	84.486(1)
$U = 1603.0(1)$	0.25291(1)	0.43549(1)	–0.05708(1)
II-Gd	11.394(1)	11.765(1)	12.229(1)
$[Gd(H_2do3aP^{Ph})(H_2O)_2]_2(NO_3)_2\cdot 11H_2O$	84.985(2)	86.035(2)	84.558(2)
$U = 1622.6(2)$	0.25284(2)	0.43412(2)	–0.05679(2)
III-Ce	11.664(1)	11.877(1)	12.264(1)
$[Ce(H_2do3aP^{Ph})(H_2O)_3]_2Cl_2\cdot 11H_2O$	84.894(2)	85.550(2)	85.887(1)
$U = 1683.(1)$	0.25442(3)	0.43673(3)	0.43729(2)
III-La	11.667(1)	11.933(1)	12.221(1)
$[La(H_2do3aP^{Ph})(H_2O)_3]_2Cl_2\cdot 12H_2O$	85.300(2)	85.923(2)	85.778(2)
$U = 1687.5(1)$	0.2564(1)	0.4355(1)	0.4373(1)
IV-Eu	11.648(1)	12.151(1)	23.122(1)
$[Eu(H_2do3aP^{Ph})(H_2O)_2]_2Cl_2\cdot 11H_2O$	83.562(1)	79.341(1)	78.940(1)
$U = 3146.4(1)$, $Z = 2$			
α-ErCl[a]	11.351(1)	11.546(1)	12.475(1)
$[Er(H_2do3aP^{Ph})(H_2O)_2]_2Cl_2\cdot 9H_2O$	81.366(2)	87.353(1)	75.776(1)
$U = 1566.8(1)$	0.76351(1)	0.93369(1)	–0.04106(1)
β-ErCl[a] (probably " I-Er ")	11.631(3)	12.094(3)	12.380(3)
$[Er(H_2do3aP^{Ph})(H_2O)_2]_2Cl_2\cdot 11H_2O$	112.366(1)	94.678(2)	100.851(2)
$U = 1559.0(1)$	0.50725(2)	0.26145(2)	0.63762(2)

[a] Data from ref.[17]

with the position of the central ion in the unit cell near to 0.254, 0.438, 0.435 (see Table 1; group GIII).

Group GII (labelled II-Ln) and GIII (labelled III-Ln) contain only two isostructural compounds each; the only significant difference between the complexes from groups GII and GIII is the number of coordinated water molecules.

Compound $[Eu\{H_2do3aP^{Ph}\}(H_2O)_2]_2Cl_2\cdot 11H_2O$ (label IV-Eu) does not fit into the above-mentioned groups; the structure of this complex has a twofold unit cell with $Z = 2$.

The crystal structures of all these compounds consist of centrosymmetric dimeric complex cations $[Ln\{H_2do3aP^{Ph}\}(H_2O)_n]_2^{2+}$ (*n* is two for GI, GII and three for GIII), chloride or nitrate counteranions and solvate water molecules. The solvate water molecules as well as anions are localised in channels (diameters about 4.5–6.5 Å), which is common in similar structures (e.g. ref.[17–21]). Due to the size of the channels, it is not surprising that anions and water molecules have enough space to move along the channels and such structures have ample possibilities for both static and dynamic disorder of the channel contents. This feature is common for this type of compound[17–21] and made the structure solution difficult. In addition, the crystals outside the mother liquor (even under an inert atmosphere) are highly unstable (in scale of minutes) and thus it is understandable that solvation of a single crystal may vary during X-ray experiments, as observed for sets of similar complexes.[18,19]

Molecular structure of dimeric cations from GI is depicted in Figure 1 (for Ln = Dy); Table 2 lists selected bond lengths and angles in the coordination polyhedra of the lanthanide ions. The $(H_2do3aP^{Ph})^{2-}$ zwitterions are coordinated to the Ln^{III} ion by two oxygen atoms from two bridging phenylphosphinate groups, two oxygen atoms from bidentate carboxyl group, one oxygen atom from monodentate carboxyl group and one oxygen atom from a bridg-

ing monodentate carboxyl group. The CN is completed to eight by coordination of two water molecules (O1 and O2). The three carboxy groups of $(H_2do3aP^{Ph})^{2-}$ are coordinated to the metal ion by three different ways: as a monodentate ligand coordinated by oxygen O10, as a bidentate ligand coordinated by oxygens O7 and O8 and as a monodentate ligand to the second metal centre of the dimer by oxygen $O4^i$.

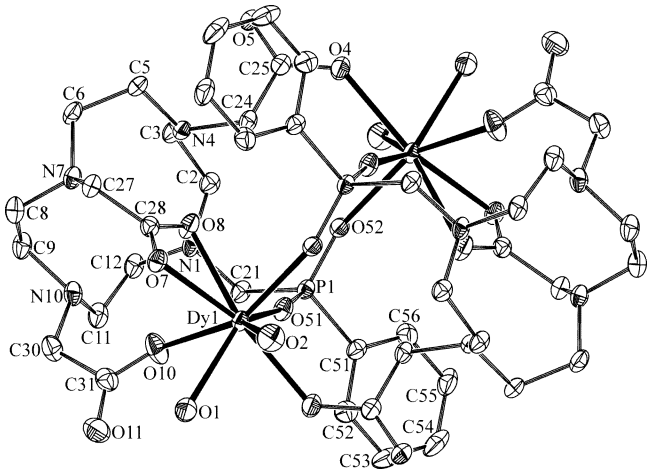

Figure 1. Molecular structure of $[Dy(H_2do3aP^{Ph})(H_2O)_2]_2^{2+}$ centrosymmetric cation in structure of $[Dy(H_2do3aP^{Ph})(H_2O)_2]_2Cl_2 \cdot 10H_2O$ (compound from group GI) with labelling scheme.

Two nitrogen atoms (N4 and N10) are protonated, two nitrogen atoms (N1 and N7) remain unprotonated; however, these nitrogen atoms do not participate on coordination, contributing only to the system of hydrogen bonds.

In order to describe properly the coordination polyhedra on the metal ions in compounds from GI and GII, we used an established approach described by Muetterties and Guggenberger.[22] The description of the eight-vertex polyhedron is based on calculation of the angles of diagnostic planes (ADP) according to a scheme given in the legend of Table 3, and on comparison of the calculated values of ADP with the ones tabulated for ideal polyhedra.[22] As can be seen in Table 3, the geometry of the lanthanide coordination polyhedra present in the structures from GI can be more properly described by dodecahedral geometry, as in the recently published isostructural compound β-$[Er\{H_2do3aP^{Ph}\}(H_2O)_2]_2Cl_2 \cdot 11H_2O$.[17]

Molecular structures of both crystallographically independent dimeric cations from the compound

Table 2. Selected bond lengths (Å) and corrected Ln–O bond lengths (Å) in studied complexes (Ln^{III} radius in parentheses).[a]

	III-Ce	(1.336)	III-La	(1.356)	IV-Eu (mol. A)	(1.206)	IV-Eu (mol. B)	(1.206)		
Ln-O1	2.567(4)	1.231	2.588(4)	1.232	2.428(3)	1.222	2.458(3)	1.252		
Ln-O2	2.620(7)	1.284	2.640(5)	1.284	2.436(3)	1.230	2.461(3)	1.255		
Ln-O3	2.588(5)	1.252	2.640(4)	1.284	–	–	–	–		
Ln-O51	2.352(4)	1.016	2.377(3)	1.021	2.284(2)	1.078	2.280(2)	1.074		
Ln-$O52^i$	2.415(4)	1.079	2.455(4)	1.099	2.344(2)	1.138	2.325(2)	1.119		
Ln-O7	2.662(4)	1.326	2.691(4)	1.335	2.498(2)	1.292	2.495(2)	1.289		
Ln-O8	2.593(4)	1.257	2.648(3)	1.292	2.498(2)	1.292	2.502(2)	1.296		
Ln-O10	2.479(2)	1.143	2.524(5)	1.168	2.407(3)	1.201	2.394(2)	1.188		
Ln-$O4^i$	2.415(4)	1.079	2.499(5)	1.143	2.427(2)	1.221	2.414(2)	1.208		
Ln···Ln^i	6.1290(8)	3.457	6.1846(7)	3.473	5.9640(4)	3.552	5.9558(4)	3.544		
	I-Dy	(1.167)	I-Gd	(1.193)	I-Nd	(1.249)	I-Y	(1.159)	I-Yb	(1.125)
Ln-O1	2.412(3)	1.245	2.435(3)	1.242	2.500(4)	1.251	2.402(3)	1.243	2.373(4)	1.248
Ln-O2	2.413(3)	1.246	2.430(3)	1.237	2.491(4)	1.242	2.403(3)	1.244	2.363(4)	1.238
Ln-O3	–	–		–	–	–	–	–	–	–
Ln-O51	2.245(3)	1.078	2.273(2)	1.193	2.313(4)	1.064	2.242(2)	1.083	2.202(3)	1.077
Ln-$O52^i$	2.300(3)	1.133	2.323(2)	1.130	2.364(3)	1.115	2.283(2)	1.124	2.233(3)	1.108
Ln-O7	2.453(3)	1.286	2.480(2)	1.287	2.549(4)	1.300	2.435(2)	1.276	2.418(3)	1.293
Ln-O8	2.473(3)	1.306	2.490(2)	1.297	2.532(3)	1.283	2.462(2)	1.303	2.420(3)	1.295
Ln-O10	2.377(3)	1.210	2.389(3)	1.196	2.441(4)	1.192	2.358(3)	1.199	2.350(3)	1.225
Ln-$O4^i$	2.377(3)	1.210	2.400(2)	1.207	2.458(4)	1.209	2.357(2)	1.198	2.321(4)	1.196
Ln···Ln^i	5.9220(5)	3.588	5.9483(6)	3.562	6.0128(6)	3.515	5.9025(7)	3.585	5.8360(4)	3.586
	II-Er	(1.144)	II-Gd	(1.193)	α-ErCl[b]	(1.144)	β-ErCl[b]	(1.144)		
Ln-O1	2.390(3)	1.246	2.430(4)	1.237	2.386(3)	1.242	2.386(4)	1.242		
Ln-O2	2.387(3)	1.243	2.437(4)	1.244	2.385(5)	1.241	2.385(4)	1.241		
Ln-O3	–	–	–	–	–	–	–	–		
Ln-O51	2.229(2)	1.085	2.270(3)	1.077	2.230(2)	1.086	2.229(3)	1.085		
Ln-$O52^i$	2.270(2)	1.126	2.322(3)	1.129	2.264(2)	1.120	2.277(3)	1.133		
Ln-O7	2.445(2)	1.301	2.482(3)	1.289	2.442(3)	1.298	2.427(3)	1.283		
Ln-O8	2.467(3)	1.323	2.512(3)	1.319	2.495(2)	1.351	2.456(3)	1.312		
Ln-O10	2.356(3)	1.212	2.403(3)	1.210	2.361(1)	1.217	2.350(4)	1.206		
Ln-$O4^i$	2.302(3)	1.158	2.368(4)	1.175	2.301(2)	1.157	2.348(3)	1.204		
Ln···Ln^i	5.8694(3)	3.581	5.9249(6)	3.431	5.8803(3)	3.592	5.8937(4)	3.606		

[a] i = $-x + 1, -y, -z + 1$ for I-Ln; $-x, -y + 1, -z$ for II-Ln; $-x, -y + 1, -z + 1$ for III-Ln; $-x + 1, -y + 2, -z$ and $-x + 1, -y + 1, -z + 1$ for IV-Eu. [b] Data from ref.[17]

Table 3. Diagnostic angles[22] of faces of coordination polyhedra (°) in studied compounds with CN 8 together with two erbium complexes from ref.[17][a]

	Ideal		I-Dy			I-Gd		
	DO	SA	obs.	ΔDO	ΔSA	obs.	ΔDO	ΔSA
δ1	29.5	0.0	22.5(2)	–7.0	22.5	21.9(1)	–7.6	21.9
δ2	29.5	52.4	35.3(3)	5.8	–17.1	35.6(1)	6.1	–16.8
δ3	29.5	0.0	29.8(2)	0.3	29.8	30.5(1)	1.0	30.5
δ4	29.5	52.4	38.3(1)	8.8	–14.1	38.4(1)	8.9	–14.0
	Ideal		I-Nd			I-Y		
	DO	SA	obs.	ΔDO	ΔSA	obs.	ΔDO	ΔSA
δ1	29.5	0.0	22.5(2)	–7.0	22.5	21.7(1)	–7.8	21.7
δ2	29.5	52.4	36.6(2)	7.1	–15.8	35.2(1)	5.7	–17.2
δ3	29.5	0.0	30.5(2)	1.0	30.5	29.6(1)	0.1	29.6
δ4	29.5	52.4	37.9(2)	8.4	–14.5	37.8(1)	8.3	–14.6
	Ideal		I-Yb					
	DO	SA	obs.	ΔDO	ΔSA			
δ1	29.5	0.0	20.8(2)	–8.7	20.8			
δ2	29.5	52.4	36.5(1)	7.0	–15.9			
δ3	29.5	0.0	26.6(2)	–2.9	26.6			
δ4	29.5	52.4	35.9(1)	6.4	–16.5			
	Ideal		II-Er			II-Gd		
	DO	SA	obs.	ΔDO	ΔSA	obs.	ΔDO	ΔSA
δ1	29.5	0.0	17.9(1)	–11.6	17.9	11.7(2)	–17.8	11.7
δ2	29.5	52.4	48.2(1)	13.3	–4.2	42.7(2)	13.2	–9.7
δ3	29.5	0.0	13.6(2)	–15.9	13.6	14.4(2)	–15.1	14.4
δ4	29.5	52.4	46.3(1)	16.8	–6.1	47.0(2)	17.5	–5.4
	Ideal		IV-Eu (mol. A)			IV-Eu (mol. B)		
	DO	SA	obs.	ΔDO	ΔSA	obs.	ΔDO	ΔSA
δ1	29.5	0.0	22.6(1)	–6.9	22.6	23.4(1)	–6.4	23.4
δ2	29.5	52.4	37.4(1)	7.9	–15.0	34.5(1)	5.0	–15.0
δ3	29.5	0.0	30.4(1)	0.9	30.4	31.8(1)	2.3	31.8
δ4	29.5	52.4	39.4(1)	9.9	–13.0	37.3(1)	7.8	–13.0
	Ideal		α-ErCl[b]*			β-ErCl[b] "I-Er"		
	DO	SA	obs.	ΔDO	ΔSA	obs.	ΔDO	ΔSA
δ1	29.5	0.0	22.6(1)	–6.9	22.6	25.2(2)	–4.3	25.2
δ2	29.5	52.4	40.7(2)	11.2	–11.7	35.2(2)	5.7	–17.2
δ3	29.5	0.0	15.5(2)	–14.0	15.5	30.0(2)	0.5	30.0
δ4	29.5	52.4	44.8(1)	15.3	–7.6	37.9(2)	8.4	–14.5

[a] δ1 = angle of O1, O4^{i}, O10 and O4^{i}, O10, O51 faces; δ2 = angle of O1, O7, O10 and O7, O10, O8 faces; δ3 = angle of O2, O7, O52^{i} and O7, O52^{i}, O8 faces; δ4 = angle of O2, O4^{i}, O52^{i} and O4^{i}, O52^{i}, O51 faces. i = $-x + 1, -y, -z + 1$ for I-Ln; $-x, -y + 1, -z$ for II-Ln; $-x + 1, -y + 2, -z$ and $-x + 1, -y + 1, -z + 1$ for IV-Eu. ΔDO = obs. – DO, ΔSA = obs. – SA; where DO is dodecahedron and SA is square antiprism. [b] Data from ref.[17]

[Eu{H_2do3aP^{Ph}}(H_2O)$_2$]$_2Cl_2$·11H_2O are identical to that of GI; the geometry of the coordination shell of Eu^{III} is dodecahedral (see Table 3).

The molecular structure of dimeric cations from compounds of GII is depicted in Figure 2 (for Ln = Er); Table 2 lists selected bond lengths and angles of the metal ion coordination shells. The coordination and protonation of the (H_2do3aP^{Ph})$^{2-}$ zwitterions are the same as in structures from GI described above. In order to describe properly the coordination polyhedra on the central ions, we used again the approach described by Muetterties and Guggenberger.[22] As can be seen in Table 3, the geometry of the Gd^{III} and Er^{III} coordination polyhedra present in the structures of GII correspond to the square-antiprismatic shape rather than the dodecahedral one. In particular, values of δ2 and δ4 are diagnostic in this case. The square-antiprismatic geometry can be more properly described by dodecahedral geometry, as in recently published α-[Er{H_2do3aPPh}-(H_2O)$_2$]$_2Cl_2$·9H_2O.[17] However, the α form of the erbium compound does not belong to the isostructural group GII.

The molecular structure of dimeric cations from GIII is depicted in Figure 3 (for Ln = Ce); Table 2 lists selected bond lengths and angles. The coordination and protonation of the (H_2do3aP^{Ph})$^{2-}$ zwitterions are again the same as that in structures from GI and GII described above. The ligand occupies six coordination positions in the coordination shell of La^{III} and Ce^{III} ions. The CN is completed to nine by coordination of three water molecules (O1, O2 and O3).

Two nitrogen atoms (N4 and N10) are protonated and two nitrogen atoms (N1 and N7) remain unprotonated; however, these two nitrogen atoms do not participate on

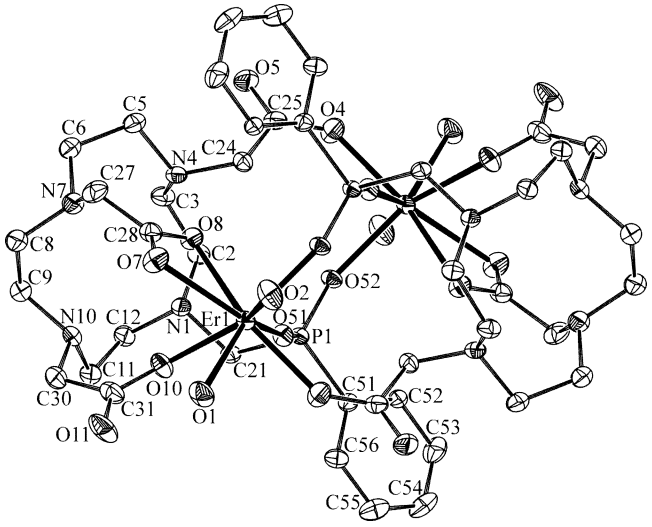

Figure 2. Molecular structure of $[Er(H_2do3aP^{Ph})(H_2O)_2]_2^{2+}$ centrosymmetric cation in structure of $[Er(H_2do3aP^{Ph})(H_2O)_2]_2(NO_3)_2 \cdot 12H_2O$(compound from group GII) with labelling scheme.

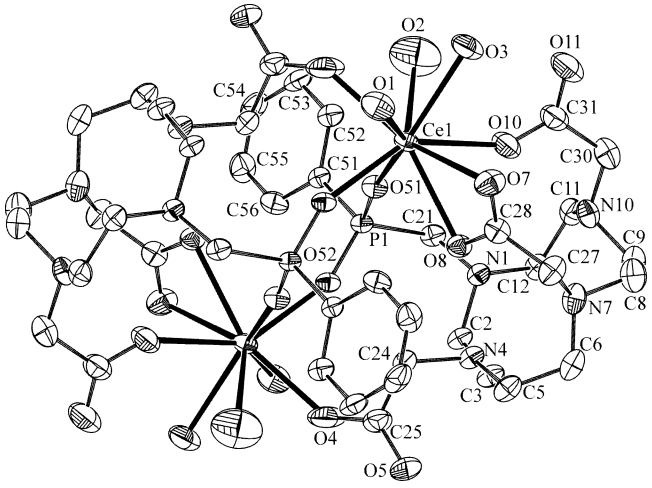

Figure 3. Molecular structure of $[Ce(H_2do3P^{Ph})(H_2O)_3]_2^{2+}$ centrosymmetric cation in structure of $[Ce(H_2do3P^{Ph})(H_2O)_3]_2Cl_2 \cdot 11H_2O$ (compound from group GIII) with labelling scheme.

coordination. The coordination polyhedra of Ln^{III} are irregular.

Selected bond lengths of all studied compounds are listed in Table 2 together with their "corrected" values. These values can be obtained simply by subtracting the ionic radii of lanthanide ions Ln^{III} with the corresponding CN:

$d_{cor} = d - r_M$;

where d_{cor} is the "corrected" bond length (or some distance selected for a geometry description) and d is the value of the corresponding distance obtained directly from structure determination. The r_M is the ionic radius of metal cation with the corresponding CN.[23]

Formation of typical eight-membered centrosymmetric $(-M–O–P-O-)_2$ rings is characteristic for complexes containing phosphinate donor groups; the bridging phenylphosphinate group is coordinated in the μ^2 mode in these rings (e.g. ref.[19,24]). The rings form the rigid frames of the dimeric complexes and together with μ-carboxylate groups fix the lanthanide ions in distances from 5.84 to 6.13 Å (see Table 2). In comparison to similar lanthanide dimeric complexes of 1,4,7,10-tetraazacyclododecane-10-methyl-1,4,7-tris(methylenephenylphosphinic) acid (H_3do3P^{Ph}-me, ref.[19,24]), a slight decrease in the Ln-Ln^i distance can be observed, probably due to the presence of additional carboxylate bridges in the structures of the O-coordinated intermediates presented in this work.

Hydrogen bonds are important for molecular structures of these compounds. The system of intramolecular H-bonds is identical in all prepared complexes regardless of the CN of the metal ion, geometry of the coordination sphere or crystal structure (groups GI–GIII). Both hydrogen atoms on the protonated nitrogen atoms N4 and N10 are located on the same side of the N1–N10 plane, towards the metal ion. Atom H4 participates on a trifurcated bond with atoms O8, N1 and N7 as acceptors; atom H10 participates on the same type of bond with acceptors O10, N1 and N7 as depicted in Figure 4. Bond lengths and angles of these hydrogen-bond systems important for the formation of the square N1, N4, N7, N10 are listed in Table 4 together with hydrogen bonds observed in previously reported structures.[19,25,26]

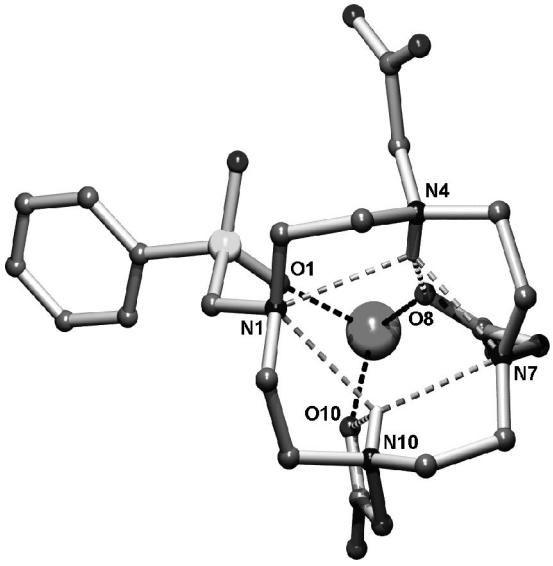

Figure 4. The frame of intramolecular H-bonds important for "N_4-square" formation in the structure of $[Dy(H_2do3P^{Ph})(H_2O)_2]_2Cl_2 \cdot 10H_2O$.

Discussion

The molecular structures of the studied complexes are very similar. In all complexes, the tetraazacyclododecane ring exists in the {3,3,3,3} conformation.[27] Nitrogen atoms N1, N4, N7 and N10 are coplanar with a deviation less than 0.015 Å, as documented in Table 5, exactly as in the case of previously published complexes with O,N-coordinated ligands.[18–21,24,28] No differences throughout the isostructural groups GI–GIII and the compound IV-Eu were

Table 4. Hydrogen bonds of protonated nitrogen atoms N4 and N10 (distances, Å; angles, °) in studied compounds.

	III-Ce		III-La		IV-Eu (mol. A)		IV-Eu (mol. B)	
	Distance	Angle on H	Distance	Angle on H	Distance	Angle on H	Distance	Angle on H
N4–H4···O8	2.762	140	2.760	140	2.756	148	2.752	144
N4–H4···N7	2.838	114	2.838	113	2.853	115	2.846	115
N4–H4···N1	3.013	106	3.032	106	2992	104	2.989	107
N10–H10···O10	2.613	114	2.606	114	2.641	109	2.660	107
N10–H10···N7	2.969	111	2.988	111	2.909	111	2.937	113
N10–H10···N1	3.020	107	3.034	107	3.060	111	3.053	105
	I-Dy		I-Gd		I-Nd		I-Y	
	Distance	Angle on H	Distance	Angle on H	Distance	Angle on H	Distance	Angle on H
N4–H4···O8	2.753	140	2.749	142	2.751	144	2.749	145
N4–H4···N7	2.843	117	2.848	118	2.861	120	2.831	122
N4–H4···N1	2.980	107	2.991	107	3.006	112	2.980	103
N10–H10···O10	2.665	111	2.651	111	2.656	104	2.653	119
N10–H10···N7	2.923	108	2.916	109	2.923	117	2.919	111
N10–H10···N1	3.050	113	3.055	110	3.067	114	3.043	111
	I-Yb		II-Er		II-Gd		α-ErCl[a]	
	Distance	Angle on H	Distance	Angle on H	Distance	Angle on H	Distance	Angle on H
N4–H4···O8	2.748	147	2.790	143	2.784	140	2.793	146
N4–H4···N7	2.829	113	2.828	117	2.835	116	2.834	113
N4–H4···N1	2.979	101	2.987	108	2.991	109	2.995	105
N10–H10···O10	2.664	120	2.653	111	2.637	117	2.694	105
N10–H10···N7	2.935	106	2.975	109	2.963	109	2.937	116
N10–H10···N1	3.034	108	2.974	112	2.988	106	2.988	108
	β-ErCl[a]		do3aph[b]		do3ap^{bisP}[c]			
	Distance	Angle on H	Distance	Angle on H	Distance	Angle on H		
N4–H4···O8	2.747	141	3.091	124	2.958	133		
N4–H4···N7	2.834	122	2.937	109	3.016	110		
N4–H4···N1	2.977	104	2.978	110	2.920	107		
N10–H10···O10	2.648	109	–	–	2.969	133		
N10–H10···N7	2.918	115	2.949	108	2.850	107		
N10–H10···N1	3.038	112	3.021	111	3.028	111		

[a] Data from ref.[17] [b] Data from ref.[15] [c] Data from ref.[26]

observed. Surprisingly, the geometry of the square formed by the four N atoms is the same in these "O-coordinated-only intermediates" as in O,N-coordinated complexes with the metal ion inside the cavity. The lengths of both diagonals (N1–N7, N4–N10) are nearly the same and differ only slightly from the ones in the O,N-coordinated complexes. In contrast, an almost identical arrangement of N atoms was also observed in the crystal structure of 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic-10-methylenephosphonic acid (H_5do3aP) (ref.[25]) and 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic-10-methylene-(ethyl-2,2-bisphosphonic) acid (ref.[26]) (H_8do3aP^{bisP}) (see Table 5).

The lanthanide ions are located between the N_4-plane and O_4-plane in O,N complexes, and the position of the ions toward the planes depends on the size of the lanthanide ions.[19,21,28] The vector Ln-Q(N) [where Q(N) is the centroid of the N_4-square] is perpendicular to the N_4-plane in all structures of the O,N-coordinated complexes (e.g. ref.[18–21,24,28]). The distances from N_4-planes [distances Q(N)–Ln] are in range of about 1.4–1.8 Å and depend on the ionic radii of Ln^{III}. After correction on the metal ion radius, values in range of about 0.38–0.5 Å were obtained for the O,N complexes.

Similarly, the vector Ln-Q(N) is perpendicular to the N_4-plane in all structures of the O-coordinated intermediates. The distances of the lanthanide ions from N_4-planes are in range of about 4.35–4.75 Å. Mean value of about 3.2 Å was obtained after correction on the Ln^{III} radius (see Table 5).

The comparison of the structures of O,N-coordinated complexes with O-coordinated intermediates point to some general conclusions. The interaction between the cation and protonated ligand is predominantly electrostatic, any individual influence of the lanthanide ion is negligible. Mean values of corrected bond lengths are 1.25 and 1.21 Å for the bonds Ln–O(H_2) and Ln–O(C) from monodentate carboxyl group, respectively, for all O-coordinated complexes. The same effect was observed also for Ln–O(P) bonds from the eight-membered (-M–O–P–O-)$_2$ rings formed by the phenylphosphinic groups; the mean value was 1.12 Å for O-coordinated complexes. Practically the same values were calculated for Ln–O(C) and Ln–O(P) bonds from the previously reported structures of N,O-coordinated complexes. A value of 1.25 Å for corrected bond length Ln–O(H_2) is close to the value 1.2 Å, which was calculated from the data for species $[Ln(H_2O)_9]^{3+}$ and $[Ln(H_2O)(L_x)]$, where L_x represents any ligand or ligands.[29] Similar values were found for water molecules in N,O-coordinated complexes with minimal steric hindrance on the O_4-plane. Higher values of these corrected bond lengths were found in some N,O complexes with phosphorus-bearing pendant arms.[20,24] We expect

Table 5. Selected parameters describing the position of Ln^{III} towards the N_4-plane of the ligand (distances in Å, angles in °).

	α-ErCl[a]	β-ErCl[a]	II-Er	II-Gd	III-La	III-Ce	IV-Eu (mol. A)	IV-Eu (mol. B)
r(Ln)	1.144	1.144	1.144	1.247	1.356	1.336	1.260	1.260
N1···N7	4.143(4)	4.100(5)	4.097(4)	4.104(5)	4.114(8)	4.121(6)	4.120(4)	4.109(4)
N4···N10	4–166(4)	4.217(6)	4.220(4)	4.223(5)	4.291(9)	4.249(7)	4.230(4)	4.249(4)
M.d. N_4-plane	0.0142	0.0014	0.0013	0.0041	0.0108	0.0025	0.0098	0.0009
N_4-plane···Ln	4.352(1)	4.354(2)	4.370(2)	4.394(2)	4.563(3)	4.487(2)	4.399(1)	4.383(1)
Corr.(N_4-plane···Ln)	3.208	3.210	3.226	3.147	3.207	3.151	3.139	3.123
Ln···QN	4.385(1)	4.384(1)	4.394(1)	4.416(2)	4.587(1)	4.510(2)	4.426(1)	4.416(1)
Corr.(Ln···QN)	3.241	3.240	3.250	3.169	3.231	3.174	3.166	3.156
Ln-QN–N1	86.0(1)	86.5(1)	86.7(1)	86.4(1)	85.0(1)	85.5(1)	86.2(1)	86.2(1)
Ln-QN–N4	95.3(1)	95.8(1)	95.0(1)	94.8(1)	94.0(1)	93.9(1)	95.4(1)	95.9(1)
Ln-QN–N7	94.9(1)	93.6(1)	93.4(1)	93.5(1)	94.5(2)	94.4(2)	93.4(1)	94.0(1)
Ln-QN–N10	84.1(1)	84.4(1)	85.1(1)	85.6(1)	86.8(2)	86.4(1)	85.3(1)	84.2(1)
	I-Dy	I-Gd	I-Nd	I-Y	I-Yb	do3aph[b]	[Yb]	[Dy]
r(Ln)	1.167	1.247	1.249	1.159	1.125	–	1.247	1.167
N1···N7	4.112(5)	4.117(4)	4.131(6)	4.099(4)	4.110(5)	3.994(2)	4.126(5)	4.174(2)
N4···N10	4.226(5)	4.231(4)	4.249(6)	4.222(5)	4.214(5)	4.334(2)	4.192(5)	1.411(2)
M.d. N_4-plane	0.0028	0.0013	0.0012	0.0027	0.0008	0.0051	0.0038	0.0010
N_4-plane···Ln	4.374(2)	4.382(2)	4.421(2)	4.364(2)	4.348(2)	–	1.574(2)	1.531(1)
Corr.(N_4-plane···Ln)	3.207	3.135	3.172	3.205	3.223	–	0.327	0.364
Ln···QN	4.403(1)	4.412(1)	4.450(1)	4.394(1)	4.372(1)	–	1.573(1)	1.531(2)
Corr.(Ln···QN)	3.236	3.165	3.201	3.235	3.247	–	0.326	0.364
Ln-QN–N1	86.3(1)	86.3(1)	86.0(1)	86.4(1)	86.6(1)	–	–	–
Ln-QN–N4	95.7(1)	95.6(1)	95.3(1)	95.7(1)	95.0(1)	–	–	–
Ln-QN–N7	93.7(1)	93.8(1)	94.0(1)	93.6(1)	93.6(1)	–	–	–
Ln-QN–N10	84.6(1)	84.6(1)	85.0(1)	84.6(1)	85.1(1)	–	–	–

[a] = Data from ref.[17] [b] = Data from ref.[15], [Yb] = $[Yb(do3P^{Ph}\text{-me})]_2 \cdot 6H_2O$, see ref.[19], [Dy] = $Li[Dy(Hdo3aph)] \cdot 5H_2O$, see ref.[21]

only a slight steric hindrance in O-coordinated complexes due to the position of metal ions out of the ligand cavities.

The mere fact that the nitrogen atoms N1, N4, N7 and N10 form almost the same squares in the structures of O-coordinated intermediates, O,N-coordinated complexes (e.g. ref.[19,21,24]) and even in uncoordinated H_5do3aP[25] and H_8do3aP^{bisP}[26] is enticing. The arrangement of the nitrogen atoms in space is determined by the coordination in structures of the O,N-coordinated compound. In the case of the O-coordinated complexes, the square-planar arrangement of the nitrogen atoms is probably caused by the system of intramolecular hydrogen bonds (see Table 4). The same system of hydrogen bonds was found in the structure of uncoordinated H_5do3aP[25] and H_8do3aP^{bisP}[26] in the solid state. These hydrogen bonds are therefore the cause of the analogical square-planar arrangement of the nitrogen atoms (Tables 4 and 5). Though our results from solid state and solution behaviour might be a little different, the formation of N,O-coordinated compounds can be considered as a "gradual approaching" of Ln^{III} to a preorganised N_4-plane of the ligand followed by a stepwise deprotonation.

Conclusion

In summary, the process of the interaction $[Ln(H_2O)_9]^{3+}$–ligand can be described as a "grabbing" of hydrated Ln^{III} ion by the pendant arms of the ligand in the first stadium, followed by approaching of the Ln^{III} ion to the preorganised N_4-plane of the ligand. The step is accompanied by deprotonation of the ligand. Gradual release of water molecules from the coordination shell of $[Ln(H_2O)_9]^{3+}$ is connected with all steps of coordination.

The isolation of the intermediate complexes reported in this paper was probably enabled by the stabilisation effect of the eight-membered phosphinate ring. This ring cannot be formed in the case of other dota-like ligands.

Experimental Section

2,2′,2′′-(10-{[Hydroxy(phenyl)phosphoryl]methyl}-1,4,7,10-tetraazacyclododecan-1,4,7-triyl)triacetic acid (H_4do3aP^{Ph}) and its ammonium salt were obtained as described previously.[17] Hydrated lanthanide(III) chlorides and nitrates were obtained from Strem Chemicals and used without further purification.

Preparation of the Complexes: The lanthanide complexes were prepared by starting from a reaction mixture of the corresponding lanthanide salt (0.050 g) and an aqueous solution of the ligand ammonium salt (0.35 mL), similarly as described previously.[17] The concentration of the ligand in the starting solution was about 0.4–0.5 g/mL. The resulting solution was carefully filtered through a nylon microfiltre (0.45 μm) into a cylindrical 5-mL vial to remove any dust particles that might disturb crystallisation. The vial was sealed by a tightly fitting stopper and left standing for crystallisation. The pH of the solutions was about 4.5; however, the pH value changed during complex formation and crystallisation. The crystalline complexes were obtained by crystallisation at temperature region 15–30 °C. In all cases, the complexes were obtained as single crystals of millimetre length. The crystals were relatively stable in the mother liquor but decomposed rapidly (2–4 min) upon exposure to ordinary laboratory atmosphere at room temperature.

Therefore, the single crystals for XRD experiments were selected in the mother liquor, quickly transferred into Fluorolube oil, mounted on glass fibres in random orientation and quickly cooled to 150(1) K. For analytical purposes, the crystals were isolated from mother liquor and air-dried on a filter paper. During this time, some loss of hydrate water occurred and the crystals became opaque. The opaque crystals thus formed did not yield XRD diffraction pattern any longer. The elemental analysis of this material proved equimolar Ln:P ratio for all complexes but the absolute values varied slightly due to variable amount of the hydrate water left.

X-ray Crystallography: XRD experiments were performed with a Nonius Kappa CCD diffractometer (Enraf – Nonius) at 150(1) K (Cryostream Cooler Oxford Cryosystem) and analysed by using the HKL program package.[30] The structures were solved by the direct methods and refined by full-matrix least-square techniques SIR92[31], SHELXL97.[32]. Scattering factors used for neutral atoms were included in the program SHELXL97. Hydrogen atoms of hydrate water molecules were not found in some structures. Hydrogen atoms of coordinated water molecules and protons on N4 and N10 were found on differential Fourier map; hydrogen atoms attached to C-atoms were locked in theoretical positions (SHELXL97). Final geometric calculations were carried out with SHELXL97 and a recent version of PLATON program[33] was used for visualisation. In all structures residual largest difference peaks were observed in range 1.57–3.13 e/Å^3 near to the Ln atom because of not very good quality of the crystals and/or because of utilising only empirical absorption corrections. Relevant crystallographic data are listed in Table S3 in the Supporting Information. CCDC-680386(for I-Nd), -680381 (for I-Gd), -680380 (for I-Dy), -680389 (for I-Yb), -680388 (for I-Y), -680383 (for II-Gd), -680382 (for II-Er), -680385 (for III-La), -680384 (for III-Ce) and 680387 (for IV-Eu) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Structures of various ligands discussed; list of previously published intermediates (with references); parameters of the coordination shells of Ln^{III} in previously published intermediates; X-ray diffraction data.

Acknowledgments

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[1] a) A. E. Merbach (Ed.), *The Chemistry of Contrast Agents in Medicinal Magnetic Resonance Imaging*, Wiley, Chichester, **2001**; b) W. Krause (Ed.), *Topics in Current Chemistry*, Springer, Heidelberg, **2002**, vol. 221; c) P. Caravan, R. B. Lauffer, *Chem. Rev.* **1999**, *99*, 2293.

[2] a) W. Li, L. Meyer, C. J. Anderson, *Top. Curr. Chem.* **2005**, *252*, 179; b) S. Liu, *Chem. Soc. Rev.* **2004**, *33*, 445; c) M. J. Welch, C. S. Redvanly (Eds.), *Handbook of Radiopharmaceuticals. Radiochemistry and Applications*, Wiley, Chichester **2003**; d) S. Liu, D. S. Edwards, *Bioconjugate Chem.* **2001**, *12*, 7.

[3] É. Tóth, E. Brücher, I. Lázár, I. Tóth, *Inorg. Chem.* **1994**, *33*, 4070.

[4] M. F. Tweedle in *Lanthanide Probes in Life; Chemical and Earth Sciences* (Eds.: J. C. Bünzli, G. G. Choppin), Elsevier, Amsterodam, **1989**, p. 127.

[5] J. Moreau, E. Guillon, J.-C. Pierrard, J. Rimbault, M. Port, M. Aplincourt, *Chem. Eur. J.* **2004**, *10*, 5218.

[6] S. L. Wu, W. DeW. Horrock Jr., *Inorg. Chem.* **1995**, *34*, 3724.

[7] E. Burai, I. Fábián, R. Király, E. Silágyi, E. Brücher, *J. Chem. Soc., Dalton Trans.* **1998**, 243.

[8] Y. H. Jang, M. Blanco, S. Dasgupta, D. A. Keire, J. E. Shively, W. A. Goddard III, *J. Am. Chem. Soc.* **1999**, *121*, 6142.

[9] E. Szilágyi, É. Tóth, Z. Kovács, J. Platzek, B. Radüchel, E. Brücher, *Inorg. Chim. Acta* **2000**, *298*, 226.

[10] C. A. Chang, Y.-L. Liu, Ch.-Y. Chen, X.-M. Chou, *Inorg. Chem.* **2001**, *40*, 3448.

[11] E. Brücher, G. Laurenczy, Z. S. Makra, *Inorg. Chim. Acta* **1987**, *130*, 141.

[12] K. Kumar, M. F. Tweedle, *Inorg. Chem.* **1993**, *32*, 4193.

[13] X. W. Wang, T. Jin, V. Comblin, A. Lopez-Mut, E. Merciny, J. F. Desreux, *Inorg. Chem.* **1992**, *31*, 1095.

[14] S. P. Kasprzyk, R. G. Wilkins, *Inorg. Chem.* **1982**, *21*, 3349.

[15] a) A. Bianchi, L. Calabi, C. Giorgi, P. Losi, P. Mariani, P. Paoli, P. Rossi, B. Valtancoli, M. Virtuani, *J. Chem. Soc., Dalton Trans.* **2000**, 697; b) A. Bianchi, L. Calabi, L. Ferini, P. Losi, F. Uggeri, B. Valtancoli, *Inorg. Chim. Acta* **1996**, *249*, 13.

[16] J. Moreau, E. Guillon, P. Aplincourt, J.-C. Pierrard, J. Rimbault, M. Port, M. Aplincourt, *Eur. J. Inorg. Chem.* **2003**, 3007.

[17] P. Vojtíšek, J. Rohovec, *Collect. Czech. Chem. Commun.* **2006**, *71*, 264.

[18] J. Rohovec, P. Vojtíšek, P. Hermann, J. Mosinger, Z. Žák, I. Lukeš, *J. Chem. Soc., Dalton Trans.* **1999**, 3585.

[19] J. Rohovec, P. Vojtíšek, I. Lukeš, P. Hermann, J. Ludvík, *J. Chem. Soc., Dalton Trans.* **2000**, 141.

[20] J. Rudovský, P. Cígler, J. Kotek, P. Hermann, P. Vojtíšek, I. Lukeš, J. A. Peters, L. V. Elst, R. N. Muller, *Chem. Eur. J.* **2005**, *11*, 2373.

[21] P. Vojtíšek, J. Cígler, J. Kotek, J. Rudovský, P. Hermann, I. Lukeš, *Inorg. Chem.* **2005**, *44*, 5591.

[22] E. L. Muetterties, L. J. Guggenberger, *J. Am. Chem. Soc.* **1974**, *96*, 1748.

[23] R. C. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

[24] P. Vojtíšek, J. Klimentová, *J. Mol. Struct.* **2007**, *826*, 82.

[25] P. Táborský, P. Lubal, J. Havel, J. Kotek, P. Hermann, I. Lukeš, *Collect. Czech. Chem. Commun.* **2005**, *70*, 1909.

[26] J. Kotek, prepared to publication.

[27] a) J. Dale, *Isr. J. Chem.* **1980**, *20*, 3; b) J. Dale, *Tetrahedron* **1974**, *30*, 1683.

[28] I. Lukeš, J. Kotek, P. Vojtíšek, P. Hermann, *Coord. Chem. Rev.* **2001**, *216–217*, 287 and references cited therein.

[29] D. Parker, R. S. Dickins, H. Puschmann, C. Crossland, J. A. K. Howard, *Chem. Rev.* **2002**, *102*, 1977.

[30] a) Z. Otwinovski, W. Minor, *HKL Denzo and Scalepack Program Package by Nonius BV*, Delft, **1997**; b) Z. Otwinovski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307.

[31] A. Altomare, M. C. M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[32] G. M. Sheldrick, *SHELXL97: Program for Crystal Structure Refinement from Diffraction Data*, University of Göttingen, Göttingen, **1997**.

[33] A. L. Spek, *PLATON: A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2003**.

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