PREPARATION AND STRUCTURAL CHARACTERIZATION OF THE INTERMEDIATE COMPLEX $[Er\{H_2C_8H_{16}N_4(CH_2COO)_3(CH_2(Ph)PO_2)\}(H_2O)_2]_2Cl_2\cdot xH_2O$ IN THE REACTION OF Er^{3+} AND THE DOTA-TYPE LIGAND. AN INTERESTING EXAMPLE OF TWO STEREOFORMS OF A LANTHANIDE COMPLEX

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Dedicated to Professor Jaroslav Podlaha on the occasion of his 70th birthday.

The synthesis of a new H_4do3aPPh ligand related to the 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate (dota) family is described together with its erbium(III) complexes. The complexes constitute a new type of coordination compounds within the Ln-dota family, with the macrocycle protonated and erbium ions above the ring. They represent an intermediate stage on the way from the ligand to the classical in-cavity complexes. In addition, the erbium complexes have been isolated in two stereoforms, differing mainly in the arrangement on the erbium ion. The coordination polyhedra found are dodecahedron and square antiprism.

Keywords: X-ray diffraction; Lanthanoids; Lanthanide complexes; Erbium; Stereochemistry; Dota ligand; Azacrown compounds.

The chemistry of lanthanide ions in aqueous solutions obtained in the past few years a great impetus due to the synthesis and utilization of chelating macrocyclic ligands of the dota-type, where dota denotes the 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate anion[1]. Reaction of the ligands with lanthanide ions produces stable lanthanide complexes, widely used in magnetic resonance imaging. Some of the complexes were characterized by XRD, leading invariably to the N_4O_4 coordination sphere of the lanthanide ion, with square antiprismatic or twisted square antiprismatic geometry, occasionally enriched by one coordinated water molecule[2]. So far, no other coordination polyhedron has been observed for this type of complexes.

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The mechanism of complexation involving lanthanide ions and dota-type macrocyclic ligands has not been well elucidated. It is widely accepted that the reaction proceeds via several stages, as suggested by results of kinetic measurements[3]. The kinetic data suggested existence of an O-coordinated intermediate, but were lacking idea about its exact stoichiometry or structure.

Generally, the interactions of lanthanide ions with ligands in complexes are mainly of an electrostatic nature, without appreciable directional character. Due to this fact, the coordination polyhedron on Ln is typically very flexible and observations of geometrical isomers of lanthanide complexes are very rare, even in the solid state. Minor changes in preparation (reaction or crystallization) conditions can easily lead to profound changes in the coordination polyhedron type and geometry. The eight-vertex coordination polyhedra are similar, and their interconversion is accompanied by only small changes in bonding distances and angles. It is usually possible to isolate only one form of a complex, as the other forms present in the reaction systems (typically in solutions) are isomerising quickly. Because of a low stereochemical rigidity of the lanthanide coordination sphere, isomers of Ln complexes are usually observed in solid phase, while isomerizing in solution.

We will present here such an intermediate compound $[Er(H_2do3aPPh)(H_2O)_2]_2Cl_2$ arising from the reaction of the Er^{3+} ion and the $H_4do3aPPh$ ligand, and its solid-state structure. The abbreviation $H_4do3aPPh$ denotes 1,4,7,10-tetraazacyclododecane-1-methylene(phenyl phosphinic)-4,7,10-tris(acetic) acid (Chart 1).

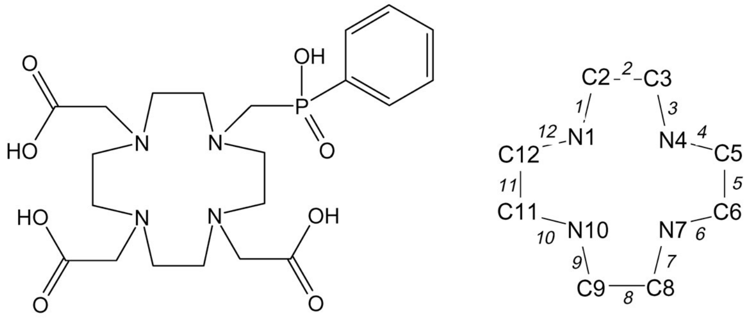

CHART 1
Structural formula of $H_4do3aPPh$ and the numbering scheme of torsion angles in the macrocyclic ring. Bonds numbers are given in italics

Moreover, we were lucky to obtain two stereoforms of the compound $[Er(H_2do3aPPh)(H_2O)_2]_2Cl_2$. They were crystallized in the course of our study of isostructural series of the chloride and nitrate complexes of this type. In this article, the two forms of the $[Er(H_2do3aPPh)(H_2O)_2]_2Cl_2$ complex, denoted here α and β, will be described. Special attention will be paid to the stereochemistry of the lanthanide complexes with the dota-type ligand, with a special accent on the coordination polyhedron on the lanthanide ion and the geometry of the macrocycle.

EXPERIMENTAL

Phenylphosphinic acid, polyformaldehyde and 1,4,7,10-tetraazacyclododecane-1,4,7-tris-(acetic) acid (H_3do3a) were obtained from Aldrich. Erbium chloride octahydrate was obtained from Strem Chemicals and was used without purification.

XRD experiments were performed on a Nonius Kappa CCD diffractometer (Enraf–Nonius) at 150(1) K (Cryostream Cooler Oxford Cryosystem) and analyzed using the HKL program package[4]. The structures were solved by the direct methods, and refined by full-matrix least-square techniques (SIR92 [5], SHELXL97 [6]). Scattering factors used for neutral atoms were included in the program SHELXL97. The hydrogen atoms of hydrate water molecules were not found in these structures. The hydrogen atoms of coordinated water molecules and protons on N4 and N10 were found on differential Fourier map; the hydrogen atoms attached to C-atoms were kept in theoretical positions (SHELXL97). Final geometric calculations were carried out with SHELXL97 and a recent version of the PLATON program[7] was used for visualization. The residual largest difference peaks were observed near to the Er atom (0.85 and 0.80 Å in stuctures of the α and β form, respectively) due to a worse quality of the crystals and/or using only empirical absorption corrections. CCDC 282760 (α form) and 282761 (β form) contain the supplementary crystallographic data (included cif-files) for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Elemental analyses of the α and β forms of the complex $[Er(H_2do3aPPh)(H_2O)_2]_2Cl_2$ were performed by the emission optical spectroscopy (EOS) technique. NMR spectra (δ, ppm; *J*, Hz) of the ligand were obtained on a Varian Inova 400 spectrometer, using aqueous (10% D_2O) solutions at pH 14. The infrared spectra (DRIFTS, diluted in KBr) were recorded with a Nicolet Magna 760 FTIR spectrometer (4 cm^{-1} resolution, Happ–Genzel apodization) in the 400–4000 cm^{-1} range, and the Raman spectrum of a polycrystalline sample with a Nicolet Magna 760 FTIR spectrometer equipped with a Nexus FT-Raman module (4 cm^{-1} resolution, Happ–Genzel apodization, 1064 nm Nd:YVO_4 laser excitation, 300 mW power at sample) in the 100–3700 cm^{-1} region.

Synthesis of the Ligand $H_4do3aPPh$

H_3do3a (0.74 g, 2 mmol) was dissolved in 20% aqueous hydrochloric acid at room temperature and phenylphosphinic acid (1.00 g, 7 mmol) was added in one portion. The mixture was heated to 70–80 °C. Upon stirring, solid polyformaldehyde (0.39 g, 13 mmol) was added at the same temperature over a period of 6 h. The solution was heated for another 16 h.

Volatiles were evaporated in vacuum and the resulting yellow glassy solid was co-evaporated twice with water to remove the excess of formaldehyde. The pure product was isolated by ion exchange chromatography on a Dow 50WX8 ion exchanger, using gradient elution with hydrochloric acid/water, followed by elution with water and finally with aqueous ammonia. Evaporation in vacuo gave an aqueous solution of the ammonium salt of the ligand, which was concentrated and used for complex preparation. When needed, it could be converted to $H_4do3aPPh \cdot xH_2O$, an off-white glassy solid. ^{13}C NMR (D_2O): 180.91, 180.32, 176.47, 175.49, 137.35 (d, J_{PC} = 117.1); 129.64 (d, J_{PC} = 8.0); 129.23, 126.93 (d, J_{PC} = 11.1); 56.65, 56.28 (d, J_{PC} = 150.3); 56.26, 51.37, 49.44, 48.67, 48.40. $^{31}P\{^1H\}$ NMR (D_2O): 30.80. IR (DRIFTS, diluted in KBr, room temperature): 442 (vw), 497 (m), 542 (m), 556 (m), 580 (m), 618 (m), 650 (w), 705 (w), 753 (s), 822 (w), 898 (w), 1021 (vw), 1036 (s), 1087 (s), 1125 (m), 1159 (s), 1181 (w), 1220 (vw), 1330 (s), 1353 (s), 1396 (vs), 1436 (m), 1459 (s), 1586 (vs), 1618 (vs), (1650–1660 sh), 1910 (m, b), 2185 (w, b), 2849 (vs), 2966 (vs), 3000–3350 (vs, vb). Raman (powder sample, room temperature): 139 (s), 302 (w), 338 (vw), 483 (vw), 590 (w), 618 (m), 691 (w), 711 (w), 760 (vw), 823 (m), 902 (s), 913 (sh), 998 (vs), 1035 (w), 1057 (vw), 1126 (m), 1157 (w), 1179 (w), 1288 (w), 1323 (m), 1388 (s), 1460 (s), 1572 (w), 1590 (s), 1625 (vw), 1701 (vw), 2858 (s), 2966 (vs), 3053 (s). Futher spectroscopic data are given in Supplementary (http://dx.doi.org/10.1135/cccc20060264).

Preparation of Erbium Complexes

The α and β stereoforms of $[Er(H_2do3aPPh)(H_2O)_2]_2Cl_2$ were prepared from a reaction mixture of erbium chloride (0.05 g) and the aqueous solution of the ligand ammonium salt (0.35 ml). The concentration of the ligand in the starting solution was ca. 0.4–0.5 g ml^{-1}. The resulting solution was carefully filtered through a nylon microfilter (0.45 μm) into a cylindrical 5-ml vial to remove possible dust particles disturbing crystallization. The vial was sealed by a tightly fitting stopper and left standing for crystallization. The solution pH was initially ca. 4.5. The pH value changed during the complex formation and crystallization.

The β form of the complex was obtained by crystallization at temperatures slightly below 20 °C, typically between 10 and 15 °C. The α form was obtained at elevated temperatures, typically at 30 °C.

In both cases, the complexes were obtained as pink single crystals of a millimeter length. The crystals were inherently stable in the mother liquor, but decomposed quite rapidly within 2–4 min when exposed to ordinary laboratory atmosphere at room temperature. Therefore, the single crystals for XRD experiments were selected in the mother liquor, quickly transferred into the Fluorolub 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 filter paper. During this time, some loss of hydrate water occurred and the crystals became opaque. The opaque crystals formed did not yield the XRD diffraction pattern any longer. The elemental analysis of this material proved the Er:P 1:1 ratio for both forms of the complex, but the absolute values varied slightly due to the variable amount of the remaining hydrate water.

RESULTS AND DISCUSSION

The new macrocyclic ligand H_4do3aPPh was prepared by an adapted Mannich-type reaction, attaching the phenylphosphinic acid moiety to the H_3do3a backbone via the methylene bridge. The product was purified by ion exchange chromatography and obtained as the ammonium salt, which is a good starting material for the preparation of lanthanide complexes. The identity and purity of the isolated ligand were checked by ^{13}C and ^{31}P NMR spectroscopies that proved to be more feasible for the characterization and purification check than ^1H NMR and IR spectroscopies (see Supplementary). The organic C, H analysis of the ligand samples did not give satisfactory results due to the glassy character of the compound, containing a variable amount of water.

The α and β forms of the Er complex were obtained starting from the same reaction mixture in a slightly acidic pH region. The only variable parameter was the temperature; the concentration and pH were the same for both compounds. Different temperatures used for crystallization led to separation of the α or β stereoforms, yielding single crystals suitable for the XRD study. The temperature difference causing the α or β form separation was quite small, ca. 15 °C, giving an impression how delicate the factors governing the crystallization of various stereoforms are. Based on this observation, we assume that the energy difference between the α and β forms is very small.

It would be interesting to detect whether the pure stereoforms α and β, or a mixture of both stereoforms crystallize from solutions. To tackle this problem, powder-XRD or IR techniques are typically used. However, the nature of both forms of $[Er(H_2do3aPPh)(H_2O)_2]_2Cl_2$ precludes using of these methods in this case. Powder-XRD is inconvenient because of an easy liberation of hydrate water and a loss of crystallinity of dry samples in a very short time (2–4 min) and/or in the process of pulverization. IR and similar spectroscopic methods suffer of low sensitivity to small changes of molecular structure and need similar requirements for sample preparation. This point was partially elucidated during the single-crystal XRD measurement. Several crystals were randomly selected from each batch for this experiment. The macroscopic shapes of the crystals were uniform in each batch. In oder to find the most suitable crystal for data collection, several crystals were tested. The lattice parameters obtained were the same for all tested crystals of a certain batch. Thus it is probable that only one stereoform was presented in each batch.

Common Features of the α and β Forms of [Er(H_2do3aPPh)(H_2O)$_2$]Cl_2

Both α and β stereoforms of [Er(H_2do3aPPh)(H_2O)$_2$]$_2$$Cl_2$ crystallize in the centrosymmetric space group *P*-1 (No. 2). Basic crystallographic data of the structures are given in Table I. The structures consist of centrosymmetric dimeric complex cations [Er(H_2do3aPPh)(H_2O)$_2$]$_2^{2+}$, chloride counter-anions and hydrate water molecules. The numbering scheme of the complex cation is presented in Fig. 1. Selected bond distances and angles are collected in Table II. The heavy atom connectivities in both structures are the same, the coordination number of the erbium centers being eight in both cases.

The most striking feature in both structures is the exclusive O-coordination of the erbium central ions. This is the most remarkable difference from the N4O4 coordination known from structures of the dota-type complexes. The reason why the lanthanide ion remained halfway is that the cavity is occupied by two protons, as will be discussed below. Thus, the Er^{3+} ion cannot enter the cavity and remains coordinated only by oxygen atoms from the pendant arms. This stuctural motive is completely new in the field of lanthanide complexes of dota-type ligands. The compounds α- and β-[Er(H_2do3aPPh)(H_2O)$_2$]$_2$$Cl_2$ represent the expected intermediate in the formation of the Ln-dota-type complexes.

Another interesting attribute of both structures is the presence of two water molecules directly coordinated to the lanthanide ion. This is also noteworthy with respect to applications of Ln complexes in MRI diagnos-

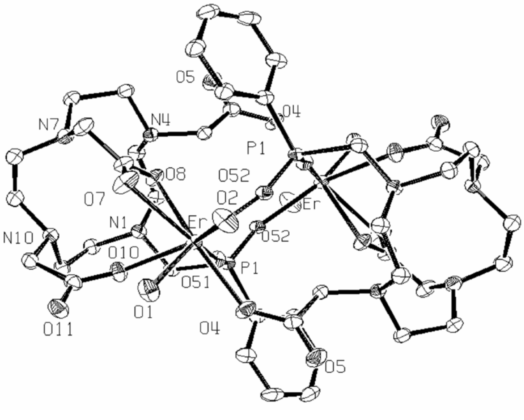

FIG. 1
Atom numbering scheme of the cation [Er(H_2do3aPPh)(H_2O)$_2$]$_2^{2+}$, common for the α and β stereoforms

TABLE I
Experimental data from the X-ray diffraction studies of α- and β-$[Er(H_2do3aPPh)(H_2O)_2]_2Cl_2 \cdot xH_2O$

Parameter	Form α	Form β
Formula	$C_{42}H_{88}Cl_2Er_2N_8O_{29}P_2$	$C_{42}H_{88}Cl_2Er_2N_8O_{31}P_2$
x	9	11
Molecular weight	1636.56	1672.60
T, K	150(1)	150(1)
Crystal size, mm	0.23 × 0.25 × 0.27	0.20 × 0.15 × 0.10
Shape and color	irregular, pale rose	irregular, pale rose
Crystal system	triclinic	triclinic
Space group	P-1 (No. 2)	P-1 (No. 2)
a, Å	11.3510(3)	11.6310(3)
b, Å	11.5460(3)	12.0940(3)
c, Å	12.4750(3)	12.3800(3)
α, °	81.366(2)	112.366(1)
β, °	87.3529(1)	94.678(2)
γ, °	75.776(1)	100.851(2)
V, Å^3; Z	1566.80(7); 1	1558.98(7); 1
D_{calcd}, g cm^{-3}	1.734	1.782
λ, Å	0.71073	0.71073
μ, mm^{-1}	2.89	2.91
F(000)	828.0	848.0
θ range of data collection, °	2.27–27.53	2.27–27.53
Index ranges	–14,14; –14,15; –16,16	–15,15; –15,15; –16,16
No. of measured reflections	25711	29290
$R_σ$	0.0282	0.0307
No. of observed reflections [$I > 2σ(I)$]	6763	6844
No. of independent reflections	7178	7155
R_{int}	0.0337	0.0454
Coefficients in weighting scheme[a]	0.0337; 3.9115	0.0203; 10.5169
Data, restraints, parameters	7178/0/445	7155/0/435
Goodness-of-fit on F^2	1.129	1.160
Final R, R' indices [$I \geq 2σ(I)$][b]	0.0286, 0.0769	0.0381, 0.0928
Maximum shift, e.s.d.	0.002	0.001
Largest difference peak and hole, e Å^{-3}	1.606, –1.347	4.320, –2.395

[a] $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (F_o^2 + 2F_c^2)/3$ (SHELXL97). [b] $R = \Sigma|F_o - F_c|/\Sigma|F_c|$, $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (SHELXL97).

TABLE II
Selected bonds (in Å) and angles (in °) in α- and β-$[Er(H_2do3aPPh)(H_2O)_2]_2Cl_2$

Bond	Form α	Form β
Er–O51	2.230(2)	2.229(3)
Er–O52[a]	2.264(2)	2.277(3)
Er–O10	2.361(3)	2.350(4)
Er–O7	2.495(3)	2.427(3)
Er–O8	2.442(2)	2.456(3)
Er–O4[a]	2.301(2)	2.348(3)
Er–O1	2.386(3)	2.386(4)
Er–O2	2.385(5)	2.385(4)
Er···Er[a]	5.8803(3)	5.8937(4)
P1–O51	1.501(2)	1.504(3)
P1–O52	1.514(2)	1.505(3)
P1–C21	1.822(2)	1.821(4)
P1–C51	1.807(3)	1.806(4)
C25–O4	1.273(4)	1.272(5)
C25–O5	1.238(4)	1.238(5)
C25–C24	1.520(5)	1.520(6)
O4–C25–O5	125.7(3)	125.4(4)
C28–O7	1.260(4)	1.260(5)
C28–O8	1.258(4)	1.267(5)
C28–C27	1.524(5)	1.519(6)
O7–C28–O8	120.0(3)	120.5(4)
C31–O10	1.254(4)	1.264(6)
C31–O11	1.250(4)	1.228(6)
C31–C30	1.525(5)	1.524(7)
O10–C31–O11	127.0(3)	127.2(5)

[a] i = $-x + 1, -y + 2, -z$ and $-x + 1, -y, -z + 1$ for the α and β forms, respectively.

tics, as the performance of MRI contrast agent is generally improved with increasing number of coordinated water molecules (the *q* number). The complexes of the type presented here are of a new structure type in the recent trend of seeking for new complexes with an increased *q* number for MRI applications.

The macrocyclic ligand bears four pendant arms, each of them being deprotonated and coordinated to the erbium ion. Their outstanding feature is the presence of three carboxylic pendant arms in three different coordination modes. One of them is coordinated in the simple $Ln–O–C(O)–CH_2$ mode, while the second one acts as a bidentate carboxylate $Ln(O)_2C–CH_2$ and the third one plays a role of a bridging group to the erbium ion (Er^i) in the symmetrically equivalent position. All of the coordination modes presented here are well known from the literature and the CCDC database, but the presence of all of them in one structure is quite rare. The geometrical parameters of acetate groups and the phosphinic acid unit in both structures are very similar. Thus, the reason for separation of different stereoforms of the complex studied does not reside in the system of pendant arms.

The inspection of the geometry of the macrocycle in the α and β forms is more laborious. It appears useful to define the torsion angles according to Chart 1. The values of the torsion angles are collected in Table III and

TABLE III
The τ values (in °) for α- and β-$[Er(H_2do3aPPh)(H_2O)_2]_2Cl_2$, and for $[Er\{MeC_8H_{16}N_4\text{-}(CH_2(Ph)PO_2)_3\}]_2$. The bond numbering scheme is given in Fig. 2

Bond No.	Form α	Form β	$[Er\{MeC_8H_{16}N_4\text{-} (CH_2(Ph)PO_2)_3\}]_2$[a]
1	82.8	81.4	159
2	61.6	61.5	–62
3	–172.4	–171	–73
4	74.1	75.2	–174
5	47.4	47.6	–60
6	–158	–161.3	–82
7	95.6	94.5	162
8	59	60.2	–60
9	–163.8	–160.8	–71
10	70	69.2	167
11	60.9	62.6	–66
12	–157.5	–159.2	–75

[a] Ref.[10]

graphically presented in Fig. 2. It is evident that the α and β forms have the same pattern of the dependence of the torsion angle τ on the bond number. The macrocyclic part of the ligand is of the same geometry and shape in both stereoforms.

The data set obtained on our crystals made it possilble to localize only the hydrogen atoms present in the macrocyclic cavity. This information is useful to get a better insight into factors influencing the macrocyclic ring geometry. The same behavior was found for the α and β forms of the compound studied; the data are collected in Table IV. The cavity is doubly protonated, the hydrogen atoms H4 and H10 being bound to N4 and N10, respectively. For both forms, a very similar hydrogen-bond system was found in the macrocyclic cavity. The hydrogen atom H4 takes part in two hydrogen bonds with the non-protonated N7 macrocyclic nitrogen atom and O8 of the bidentate carboxylic pendant arm. The H10 atom displays only a long and weak interaction with the non-protonated N1 atom, together with a weak hydrogen bond to the N7 atom. We can conclude that the shape and geometry of the macrocyclic ligand are almost the same in both α and β forms, being fixed by protonation and intraannular hydrogen bonds rather than coordination to lanthanide ion.

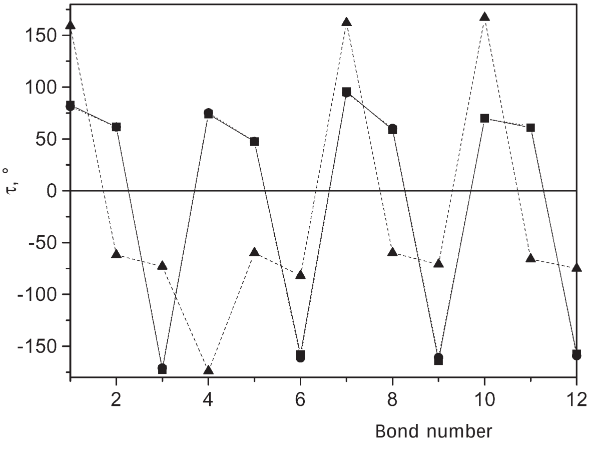

FIG. 2

The conformation pattern analysis of the macrocyclic ring in α- (■) and β-$[Er(H_2do3aPPh)(H_2O)_2]_2^{2+}$ (●), and in $[Er\{MeC_8H_{16}N_4(CH_2(Ph)PO_2)_3\}]_2$ (▲). The torsion angles τ around the twelve-membered ring (defined as the torsion angle X(i – 1)–**Xi**–**X**(**i** + 1)–X(i + 2) for the bond **Xi**–**X**(**i** + **1**) where X = N or C) are plotted against the ordinal number of bonds around the macrocycle ring (N1–C2 = 1, etc.)

For comparison purposes, we present in Fig. 2 also the torsion angle pattern for similar centrosymmetrical $[Er\{MeC_8H_{16}N_4(CH_2(Ph)PO_2)_3\}]_2$ already described in literature[10]. In this compound, Er^{3+} is located inside the macrocyclic cavity with the N4O4-type coordination sphere and the structure does not contain intraannular hydrogen bonds. As can be seen in Fig. 2, the τ pattern is completely different, demonstrating a profound geometrical change in the macrocyclic part of the ligand required for in-cavity coordination of the lanthanide ion.

The complexes containing phosphinate donor groups are characterized by formation of typical eight membered $(M–O–P–O)_2$ rings, in which the phosphinic group is coordinated in the μ^2-mode. For example, this typical structural feature is also present in the $[Er\{MeC_8H_{16}N_4(CH_2(Ph)PO_2)_3\}]_2$ mentioned above. This unit can be also seen in both α and β forms, Fig. 3. The α and β structures resemble each other also in this respect. The erbium ions are fixed by μ-phosphinate and μ-carboxylate bridges in the distances 5.8803(3) and 5.8937(4) Å in α and β form, respectively. The difference between them seems to be negligible. Comparing with $[Er\{MeC_8H_{16}N_4(CH_2(Ph)PO_2)_3\}]_2$, we can observe a slight increase in the $Er–Er^i$ distance due to the presence of only phosphinate bridges, while no carboxylate bridges are found in this structure.

TABLE IV
Hydrogen bonds (in Å) and angles (in °) in α- and β-$[Er(H_2do3aPPh)(H_2O)_2]_2Cl_2$

	Form α		Form β	
	D–H···A	Angle	D–H···A	Angle
N4–H4···O8	2.79	146	2.75	141
N4–H4···N7	2.83	113	2.83	122
N10–H10···N7	2.94	118	2.92	115
N10–H10···N1	3.12	108	3.04	112
O1–H11···O11	2.68	160	2.68	162
O1–H11···O10	–	–	2.74	136
O1–H12···Osolv1[a]	2.83	175	2.82	166
O2–H21···O7[b]	2.79	172	–	–
O2–H21···Osolv2[a]	–	–	2.90	148
O2–H21···Cl2[c]	–	–	3.11	154
O2–H22···Osolv3[a]	2.82	164	2.86	153

[a] Osolv1, Osolv2, Osolv3: three different solvate water molecules. [b] i = –*x* + 2, –*y* + 2, –*z*. [c] ii = –*x* + 1, –*y* + 1, –*z* + 1.

Differences in Structures of the α and β Forms of [Er(H_2do3aPPh)(H_2O)$_2$]Cl_2

As follows from the above discussion, the similarities between the α and β structures of [Er(H_2do3aPPh)(H_2O)$_2$]Cl_2 are extensive. The most prominent difference is found in the coordination sphere of the erbium centers.

In order to describe properly the coordination polyhedra on the central atoms, we use the established approach described in the literature[8]. The description of the eight-vertex coordination polyhedron is based on the calculation of the so called diagnostic angles according to the scheme given in the legend of Table V, and on comparison of the calculated diagnostic angles for the structure studied with the values tabelated for ideal polyhedra. The atom numbering scheme is given in Figs 4a and 4b. As can be seen in Table V, the geometry of the Er coordination polyhedron present in the α form of the complex closely approaches the square-antiprismatic shape rather than the dodecahedral one. In particular, the values δ2 and δ4 are diagnostic in this case. In contrast, the Er coordination polyhedron found in the β form is more properly described by dodecahedral geometry because the δ2 and δ4 values approximate the theoretical values for dodecahedron. The same conclusion is obtained studying the differences Δδ, also given in Table V. The coordination polyhedra of α and β form cations are depicted in Figs 4a and 4b.

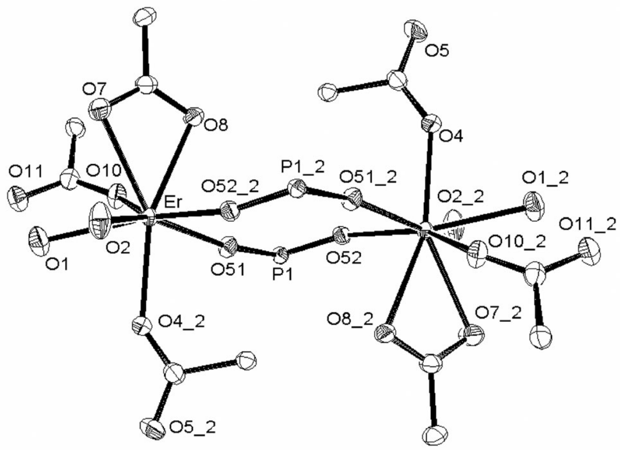

FIG. 3
Eight-membered phosphinate ring in the α-$[Er(H_2do3aPPh)(H_2O)_2]_2^{2+}$ structure

The presence of dodecahedral coordination shell on the Er ion in the β form is surprising. Generally, the dodecahedral geometry is quite rare, both in the d-block element complexes and lanthanide complexes. Thus, the structures of the α and β forms of the complex represent a rare example of compounds known in both coordination geometries fully characterized by XRD. Moreover, the α and β forms could be treated as an example of a pair of geometrical isomers. The observation of an isomeric pair of lanthanide ion complexes is quite scarce, due to very fast ligand exchange reactions on lanthanide ions in solution, preventing any attempts of their

TABLE V
Diagnostic angles of the faces of the coordination polyhedron (in °) in α- and β-$[Er(H_2do3aPPh)(H_2O)_2]_2Cl_2$

	Ideal DD[a]	Ideal SA[b]	α Form	β Form	Δδ α-DD	Δδ α-SA	Δδ β-DD	Δδ β-SA
δ1[c]	29.5	0.0	22.6(1)	25.2(2)	–6.9	22.6	–4.3	25.2
δ2[d]	29.5	52.4	40.7(2)	35.2(2)	11.2	–11.7	5.7	–17.2
δ3[e]	29.5	0.0	15.5(2)	30.0	–14	15.5	0.5	30
δ4[f]	29.5	52.4	44.8(1)	37.9(2)	15.3	–7.6	8.4	–14.5

[a] Dodecahedron. [b] Square antiprism. [c] Angle of O1, O4[g], O10 and O4[g], O10, O51 faces. [d] Angle of O1, O7, O10 and O7, O10, O8 faces. [e] Angle of O2, O7, O52[g] and O7. O52[g], O8 faces. [f] Angle of O2, O4[g], O52[g] and O4[g], O52[g], O51 faces. [g] i = –x + 1, –y + 2, –z and –x + 1, –y, –z + 1 for the α and β forms, respectively.

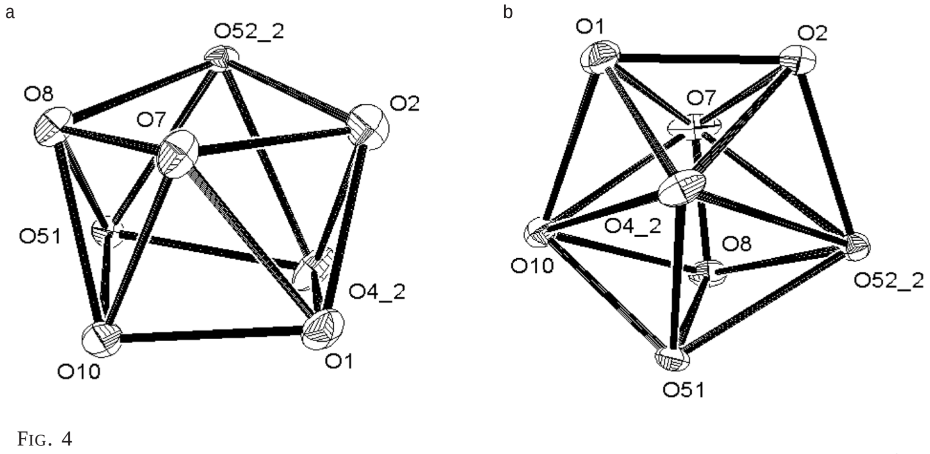

FIG. 4
Square antiprismatic arrangement of the coordination sphere in α-$[Er(H_2do3aPPh)(H_2O)_2]_2^{2+}$ (a). Dodecahedral arrangement of the coordination sphere in β-$[Er(H_2do3aPPh)(H_2O)_2]_2^{2+}$ (b)

isolation. Clearly, the existence of such isomeric pair is restricted to the solid state only, as fast isomerization is expected in solution.

Some differences between the α and β forms of the studied complex were also found in the hydrogen-bond systems (visualized in Supplementary) with participation of coordinated water molecules. The H12-atom at the coordinated water oxygen O1 participates in a bond to one water solvate molecule in both forms (2.83 and 2.82 Å in the α and β forms, respectively). The second hydrogen atom attached to O1 (H11) forms a short single H-bond to non-coordinated oxygen O11 of the monodentate carboxyl attached to N10 in the form α. This bond is relatively short (2.68 Å). The same H-atom (H11) forms a bifurcated H-bond (2.67 Å to O11 and 2.74 Å to O10) in the form β, see Table IV. Both H-atoms at O2 of the second coordinated water molecule form two single linear H-bonds, O2–H21···O7 (2.79 Å) and O2–H22···O99 (hydrate water; 2.82 Å) in the form α. No contact O2–H21···O7 shorter than 3 Å was observed in the β form structure. The hydrogen atom H22 attached to O2, forms a H-bond to the hydrate water molecule (2.86 Å) similarly as in the form α, but the second hydrogen, H21, participates in a bifurcate H-bond to another hydrate water molecule (2.90 Å) and to the chloride counter-anion (3.11 Å).

The direct influence of the different hydrogen-bond systems on the coordination polyhedron of Er^{3+} in both stereoforms is difficult to approve. It seems that the changes in the H-bond system can cause the change of the coordination sphere of cation. However, other effects can also contribute. On the other hand, the different shape of the coordination sphere affects the H-bond system due to small shifts in the O atom positions, as the O atoms paticipate in these hydrogen bonds.

CONCLUSIONS

The crystal structures of the α and β forms of the complex $[Er(H_2do3aPPh)(H_2O)_2]_2Cl_2$ represent a delicate example of the lanthanide ion coordination chemistry and stereochemistry realized with a ligand of the dota-type.

Their isolation proved the existence of the intermediate structure in the lanthanide ion complexation reaction with the macrocyclic ligand. The XRD measurements gave detailed structural information about this intermediate. This kind of intermediates were postulated and studied in solutions[9], while the solid-state characterization was outstanding.

The α and β forms exemplify a pair of stereoforms of a lanthanide complex differing in the coordination polyhedron. The dodecahedral geometry found around the Er center in the β form is quite unique.

The presence of the three different coordination modes of the carboxylate groups in one of the structures is not only appealing. We can also understand it as a reference to Prof. Podlaha work that focused mainly on coordination behavior of ligands with phosphine and carboxylic groups.

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