

Syntheses and Crystal Structures of Lanthanide Complexes of New 15-Membered Macrocyclic Ligands with Three Pendant Acetato Groups

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Two new 15-membered functionalized macrocycles, dioxopolyazacycloalkanes with three pendant acetato groups, have been synthesized by the condensation reaction of DTPA dianhydride (DTPA = diethylenetriaminepentaacetic acid) with 1,2-diaminopropane, (15-DTPA-1,2-pn), or 1,2-diaminocyclohexane, (15-DTPA-1,2-cy). Their lanthanide complexes [Ln(15-DTPA-1,2-pn)·2H₂O] (Ln = Eu (1), Gd (2)) and [Ln(15-DTPA-1,2-cy)·2H₂O] (Ln = Eu (3), Gd (4)) were also prepared. Single crystal X-ray diffraction analyses of complexes 2 and 4 show that they have dimeric structures in solid state; each metal ion is nine-coordinated in a distorted tricapped-trigonal prism. In complex 4, the coexistence of two diastereoisomeric molecules in the crystal lattice was observed.

Keywords macrocyclic ligand, lanthanide complex, synthesis, crystal structure

Introduction

In recent years, the complexation chemistry of the lanthanides has received much attention due to the application of related paramagnetic gadolinium complexes as commercially important contrast agents in magnetic resonance imaging (MRI)¹ and the europium and terbium complexes as luminescent probes.² Acyclic and macrocyclic polyamino-polycarboxylate ligands have received the most attention for these purposes, since they form highly thermodynamic and kinetically stable complexes with lanthanide ions.³⁻⁵ Their Gd^{III} complexes, such as Gd^{III}(DTPA)³⁻ (DTPA = diethylenetriaminepentaacetic acid) and Gd^{III}(DOTA)⁻ (DOTA = 1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetic acid), have been used as MRI contrast agents in humans and are applied routinely nowadays.^{6,7} However, for specific applications there is the need to supply the patient with higher doses of contrast agents, while Gd(DTPA)³⁻ and Gd(DOTA)⁻ possess residual negative charge, a higher administered dose could provoke an osmotic shock to the red blood cells with consequent hemolysis. Thus, it was suggested that neutral Gd(III) complexes may represent a good alternative for this

kind of application.⁸ Trinegative ligands such as DTPA-bis (amide) are attractive as the ligands of MRI contrast agents because of its high binding constant for lanthanides, its excellent solubility, its relatively high coordination number, and formation of neutral complexes with Ln³⁺.⁹⁻¹¹

In this work, two new 15-membered dioxopolyazacycloalkane triacetic acids, (15-DTPA-1,2-pn)H₃ (1,2-pn = 1,2-diaminopropane) and (15-DTPA-1,2-cy)H₃ (1,2-cy = 1,2-diaminocyclohexane) were synthesized. Their neutral complexes of lanthanide ions, Ln(15-DTPA-1,2-pn)₂ (Ln = Eu (1) and Gd (2)), and Ln(15-DTPA-1,2-cy)₂ (Ln = Eu (3), and Gd (4)), were prepared, and complexes 2 and 4 have been characterized by single crystal X-ray diffraction analyses.

Experimental

All reagents were obtained from commercial sources unless otherwise stated. DTPA dianhydride was prepared according to the patent.¹² 1,2-Diaminopropane and 1,2-diaminocyclohexane were purchased from Aldrich and purified by distillation under reduced pressure. Carbon, hydrogen and nitrogen analyses were performed by direct combustion on a Carlo Erba-1110 instrument. NMR spectra were obtained from a Bruker DPX-300 spectrometer. Infrared spectra were recorded on a Biorad FTS-7 IR spectrophotometer (KBr pellets). FAB-MS spectra were recorded on a Finnigan Mat 95 mass spectrometer.

Syntheses of the macrocycles

A sample of (15-DTPA-1,2-pn)H₃ was synthesized by a condensation reaction between DTPA dianhydride and 1,2-diaminopropane. 0.68 mL (8 mmol) of 1,2-diaminopropane in 100 mL DMF was added dropwise to 2.98 g (8 mmol) of DTPA dianhydride in 300 mL DMF with vigorous stirring during a 4 h period under a nitrogen atmosphere.

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The resulting reaction mixture was allowed to stand overnight. The colorless solid formed was removed by filtration. The filtrate was concentrated to yield a pale yellow oil by a rotary evaporator. When THF was added to the oil, a colorless solid was obtained. The solid was solved in 4 mL of water resulting in a yellowish solution. The colorless product was formed in a few days and separated by filtration from the solution, washed successively with water and acetone, and dried in vacuum. Yield 1.05 g (30.4%); $^1\text{H NMR}$ (D_2O , assignments as in Scheme 1) δ : 4.09 (br, 1H, H_e), 3.68 (t, 10H, $\text{H}_a + \text{H}_c$), 3.38 (d, $J = 2$ Hz, 2H, H_d), 3.16—3.35 (m, 8H, H_b), 1.11 (d, $J = 6$ Hz, 3H, H_f); IR (KBr) ν : 3380, 3250, 3083, 2977, 2851, 1723, 1678, 1624, 1582, 1437, 1393, 1335, 1221, 1206, 1179, 1152, 1092, 920, 737 cm^{-1} . Anal. calcd for $\text{C}_{17}\text{H}_{29}\text{N}_5\text{O}_8$: C 47.33, H 6.78, N 16.23; found C 46.95, H 6.57, N 16.01.

The macrocycle (15-DTPA-1,2-cy) H_3 was prepared by the same method as described above but using 1,2-diaminocyclohexane instead of 1,2-diaminopropane. Yield 35.6%; $^1\text{H NMR}$ (D_2O) δ : 3.62—3.81 (m, 2H, H_{a2}), 3.21—3.43 (m, 10H, $\text{H}_{a1} + \text{H}_c + \text{H}_d$), 2.79—3.03 (m, 8H, H_b), 1.85 (br, 4H, H_e), 1.29 (br, 4H, H_f); IR (KBr) ν : 3443, 3073, 2938, 2869, 1723, 1678, 1641, 1561, 1393, 1221, 1146, 1088, 667 cm^{-1} . Anal. calcd for $\text{C}_{20}\text{H}_{33}\text{N}_5\text{O}_8$: C 50.95, H 7.05, N 14.85; found C 50.62, H 6.84, N 14.53.

Synthesis of [Eu(15-DTPA-1,2-pn)(H_2O) $_{12}$] $\cdot 13\text{H}_2\text{O}$ (**1** · $13\text{H}_2\text{O}$)

Solid europium carbonate (63 mg, 0.13 mmol) was added to a solution of the ligand (15-DTPA-1,2-pn) H_3 (86 mg, 0.20 mmol) in water (8 mL). The mixture was stirred for about 6 h at 60 °C, and the excess carbonate was removed by subsequent filtration. The colorless single crystals suitable for X-ray crystal analysis were grown from an aqueous solution by slow evaporation. Yield 78%; IR (KBr) ν : 3510, 2960, 2925, 2860, 1636, 1586, 1563, 1455, 1402, 1393, 1258, 1110, 1019, 803, 741 cm^{-1} ; FAB-MS m/z : 580 [Eu(15-DTPA-1,2-pn)] $^+$. Anal. calcd for $\text{C}_{34}\text{H}_{82}\text{N}_{10}\text{O}_{31}\text{Eu}_2$: C 28.54, H 5.78, N 9.78; found C 28.71, H 5.22, N 9.93.

Synthesis of [Gd(15-DTPA-1,2-pn)(H_2O) $_{12}$] $\cdot 13\text{H}_2\text{O}$ (**2** · $13\text{H}_2\text{O}$)

The synthesis of **2** was carried out as described for **1**, but using gadolinium carbonate instead of europium carbonate. The colorless single crystals suitable for X-ray crystal analysis were grown from an aqueous solution by slow evaporation. Yield 85%; IR (KBr) ν : 3516, 2960, 2925, 2854, 1636, 1586, 1560, 1420, 1393, 1327, 1258, 1107, 1049, 799, 741 cm^{-1} ; FAB-MS m/z : 585 [Gd(15-DTPA-1,2-pn)] $^+$. Anal. calcd for $\text{C}_{34}\text{H}_{82}\text{N}_{10}$ -

O_{31}Gd_2 : C 28.33, H 5.73, N 9.71; found C 28.67, H 5.04, N 9.85.

Synthesis of [Eu(15-DTPA-1,2-cy)(H_2O) $_{12}$] $\cdot 15.5\text{H}_2\text{O}$ (**3** · $15.5\text{H}_2\text{O}$)

Solid europium carbonate (63 mg, 0.13 mmol) was added to the ligand (15-DTPA-1,2-cy) H_3 (94 mg, 0.20 mmol) in water (5 mL). The mixture was stirred for about 6 h at 60 °C, and excess carbonate was removed by subsequent filtration. The colorless single crystals suitable for X-ray crystal analysis were grown from an aqueous solution by slow evaporation. Yield 74%; IR (KBr) ν : 3434, 3250, 3110, 2965, 2932, 1636, 1624, 1582, 1561, 1458, 1404, 1329, 1286, 1103, 1022, 968, 932 cm^{-1} ; FAB-MS m/z : 620 [Eu(15-DTPA-1,2-cy)] $^+$. Anal. calcd for $\text{C}_{40}\text{H}_{95}\text{N}_{10}\text{O}_{33.5}\text{Eu}_2$: C 30.87, H 6.15, N 9.00; found C 30.51, H 6.02, N 8.72.

Synthesis of [Gd(15-DTPA-1,2-cy)(H_2O) $_{12}$] $\cdot 15.5\text{H}_2\text{O}$ (**4** · $15.5\text{H}_2\text{O}$)

The synthesis of **4** was carried out as described for **3**, but using gadolinium carbonate instead of europium carbonate. The colorless single crystals suitable for X-ray crystal analysis were grown from an aqueous solution by slow evaporation. Yield 81%; IR (KBr) ν : 3422, 3245, 3094, 2971, 2938, 1636, 1624, 1582, 1560, 1455, 1404, 1329, 1292, 1103, 1022, 968, 931 cm^{-1} ; FAB-MS m/z : 625 [Gd(15-DTPA-1,2-cy)] $^+$. Anal. calcd for $\text{C}_{40}\text{H}_{95}\text{N}_{10}\text{O}_{33.5}\text{Gd}_2$: C 30.66, H 6.11, N 8.94; found C 30.42, H 5.83, N 9.07.

X-Ray crystal analyses

Single-crystal X-ray analyses were carried out for compounds **2** and **4**. Crystals of suitable quality were mounted in air in a capillary with epoxy resin. X-Ray diffraction data of these complexes were collected on a Rigaku AFC7R diffractometer equipped with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.071069$ nm) at room temperature using the ω - 2θ and ω scan techniques. All intensity data were corrected for Lorentz and polarization effects. In all data sets, reflections with $I \geq 1.5 \sigma(I)$ were considered observed and used in the structural analyses. Structures were solved by direct methods and expanded using Fourier techniques and subsequent refinement by full-matrix least squares analysis on F . All calculations were performed on a Silicon-Graphics workstation using the teXsan crystallographic software package from Molecular Structure Corporation.

The crystallographic data and other experimental details, including data collection parameters, structure solution, and refinement details, are summarized in Table 1.

Table 1 Crystal data and data collection parameters for complexes **2** and **4**

Complex	2 · 13H ₂ O	4 · 15.5H ₂ O
Empirical formula	C ₃₄ H ₈₂ N ₁₀ O ₃₁ Gd ₂	C ₄₀ H ₉₅ N ₁₀ O _{33.5} Gd ₂
<i>M_r</i>	1441.58	1566.74
Crystal color, habit	Colorless, block	Colorless, block
Crystal size (mm)	0.22 × 0.17 × 0.27	0.23 × 0.24 × 0.19
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (# 14)	<i>P</i> $\bar{1}$ (# 2)
<i>a</i> (nm)	1.1499(1)	1.4447(5)
<i>b</i> (nm)	2.0604(1)	1.9283(5)
<i>c</i> (nm)	1.2736(1)	1.2590(3)
α (°)	90	96.31(2)
β (°)	105.31(1)	99.32(2)
γ (°)	90	78.60(2)
<i>V</i> (nm ³)	2.9106(5)	3.381(1)
<i>Z</i>	2	2
<i>D_c</i> (g/cm ³)	1.645	1.539
μ (Mo K α) (cm ⁻¹)	23.59	20.40
<i>F</i> (000)	1464	1602
Reflections collected	4161	12401
Unique reflections	3936	11886
Observed reflections [<i>I</i> > 1.50 σ (<i>I</i>)]	3168	8529
<i>R</i>	0.039	0.058
<i>R_w</i>	0.049	0.073

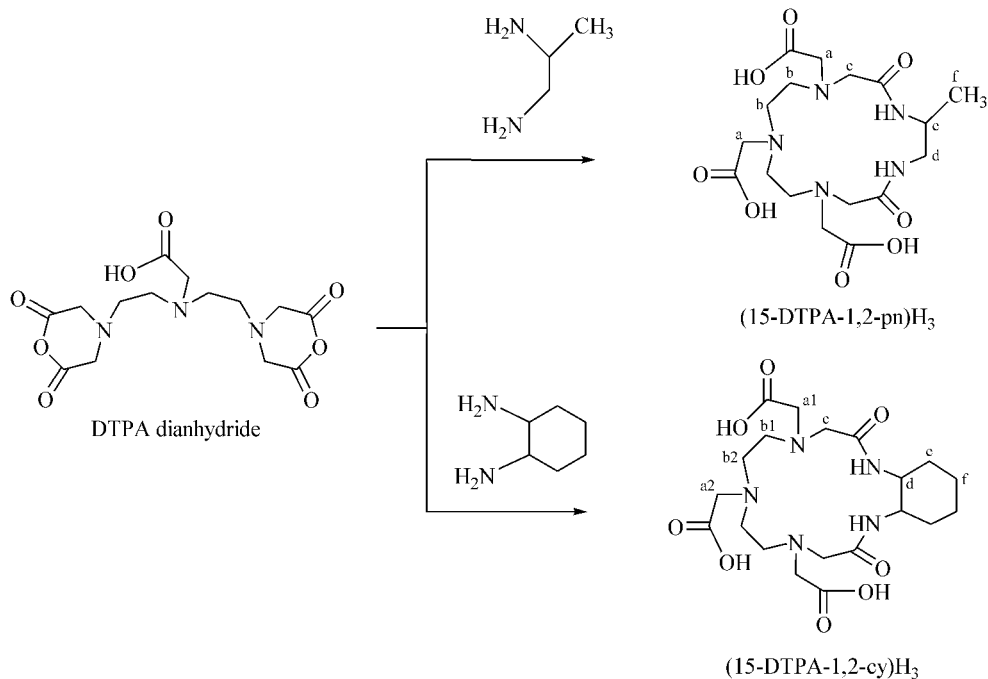
Results and discussion

Synthesis

The condensation reactions between DTPA dianhy-

dride and 1,2-diaminopropane (1,2-pn) or 1,2-diaminocyclohexane (1,2-cy) afforded two new 15-membered dioxopolycycloalkane triacetic acids, (15-DTPA-1,2-pn)₃ and (15-DTPA-1,2-cy)₃, which were identified by elemental analyses and NMR spectra, as shown in Scheme 1.

Scheme 1



These functionalized macrocycles reacted with lanthanide carbonate to give the corresponding neutral lanthanide complexes, which were characterized by elemental analyses, MS and IR spectroscopy. The elemental analyses are consistent with the proposed formula of these complexes. The IR spectra of **1** to **4** show sharp bands at about 1630 and 1580 cm^{-1} , which can be assigned to amide carbonyl stretch and carboxylate stretches.

Crystal structures of **2** · 13H₂O

Fig. 1 shows the molecular structure of **2** together with the atomic numbering scheme. Selected bond distances and angles are summarized in Table 2. The X-ray results have demonstrated that a 15-membered macrocyclic ligand with three pendant acetato groups is obtained by the reaction as shown in Scheme 1, and that the new ligand forms a neutral non-ionic metal complex with lanthanide ion. Two lanthanide metal ions are located between two ligands, forming a binuclear centrosymmetric metal complex, in which the average molecular planes of the two macrocyclic rings are parallel to each other, the symmetric center lies in the midpoint between Gd and Gd*. Each metal ion is bonded to an amide oxygen atom O(8), two carboxylate oxygen atoms O(4) and O(6), and two amine nitrogen atoms, N(4) and N(5) from one ligand molecule; one amide oxygen atom O(1*), a carboxylate oxygen atom O(2*) and an amine nitrogen atom N(3*) from another macrocycle as well as to an oxygen from water O(9).

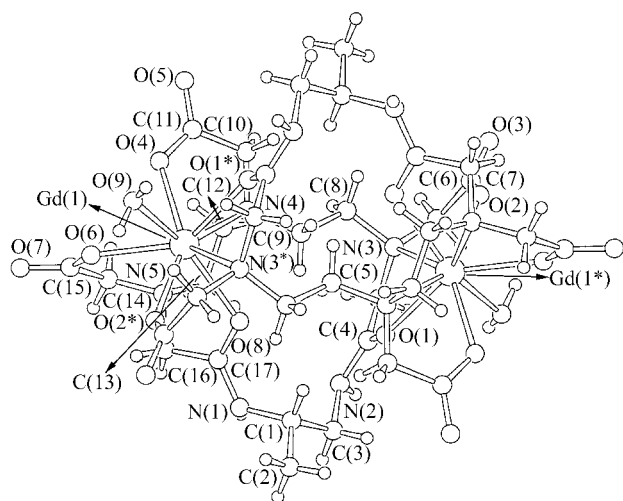


Fig. 1 Molecular structure of $[\text{Gd}(15\text{-DTPA-1,2-pn})_2(\text{H}_2\text{O})]_2$

The central lanthanide ion lies in a distorted, tri-capped-trigonal prismatic environment. The two triangular faces of the prism are constituted by O(1*), O(4), O(9) and O(2*), O(8), N(5), respectively, while O(6), N(3*) and N(4) are in capping position with respect to the three rectangular faces. The dihedral angles between the O(2*)O(8)N(5) and O(6)N(3*)N(4) planes is 15.90° , and 4.35° between the O(1*)O(4)O(9) and

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for complexes **2** and **4**.

Complex	2	4 (A)	4 (B)
Li(1)—O(1*)	0.240(6)	0.242(7)	0.240(7)
Li(1)—O(2*)	0.236(6)	0.238(7)	0.236(8)
Li(1)—O(4)	0.240(6)	0.239(7)	0.234(7)
Li(1)—O(6)	0.235(6)	0.238(7)	0.232(7)
Li(1)—O(8)	0.243(6)	0.247(7)	0.241(7)
Li(1)—O(9)	0.241(7)	0.241(7)	0.246(8)
Li(1)—N(3*)	0.289(7)	0.290(8)	0.282(10)
Li(1)—N(4)	0.274(7)	0.274(8)	0.276(1)
Li(1)—N(5)	0.263(6)	0.261(8)	0.263(9)
O(1*)—Li(1)—O(2*)	123.4(2)	123.4(2)	124.2(3)
O(1*)—Li(1)—O(4)	76.5(2)	75.3(2)	75.5(3)
O(1*)—Li(1)—O(6)	142.3(2)	143.0(3)	138.5(3)
O(1*)—Li(1)—O(8)	103.3(2)	103.9(2)	104.7(3)
O(1*)—Li(1)—O(9)	77.9(2)	75.7(2)	75.8(3)
O(1*)—Li(1)—N(3*)	61.5(2)	61.2(2)	61.7(3)
O(1*)—Li(1)—N(4)	72.1(2)	69.8(2)	74.7(3)
O(1*)—Li(1)—N(5)	138.1(2)	136.3(2)	141.1(3)
O(2*)—Li(1)—O(4)	146.8(2)	147.0(2)	145.0(3)
O(2*)—Li(1)—O(6)	73.6(2)	73.1(3)	71.8(3)
O(2*)—Li(1)—O(8)	70.0(2)	70.0(2)	71.7(3)
O(2*)—Li(1)—O(9)	79.8(2)	81.1(3)	80.3(3)
O(2*)—Li(1)—N(3*)	62.5(2)	62.9(2)	63.5(3)
O(2*)—Li(1)—N(4)	144.2(2)	145.9(3)	145.1(3)
O(2*)—Li(1)—N(5)	90.6(2)	92.8(3)	89.0(3)
O(4)—Li(1)—O(6)	75.6(2)	76.9(3)	75.2(3)
O(4)—Li(1)—O(8)	136.0(2)	136.5(2)	136.1(3)
O(4)—Li(1)—O(9)	79.3(2)	77.9(3)	77.4(3)
O(4)—Li(1)—N(3*)	133.6(2)	132.6(2)	132.8(3)
O(4)—Li(1)—N(4)	62.8(2)	62.4(2)	62.4(3)
O(4)—Li(1)—N(5)	87.5(2)	86.9(3)	88.2(3)
O(6)—Li(1)—O(8)	114.4(2)	113.0(2)	116.8(3)
O(6)—Li(1)—O(9)	72.4(2)	75.0(2)	69.5(3)
O(6)—Li(1)—N(3*)	128.2(2)	129.0(2)	125.7(3)
O(6)—Li(1)—N(4)	115.4(2)	116.9(2)	115.5(3)
O(6)—Li(1)—N(5)	64.8(2)	64.9(2)	65.9(3)
O(8)—Li(1)—O(9)	144.5(2)	145.0(2)	146.3(3)
O(8)—Li(1)—N(3*)	75.9(2)	75.6(2)	76.9(3)
O(8)—Li(1)—N(4)	75.1(2)	76.4(2)	75.1(3)
O(8)—Li(1)—N(5)	63.0(2)	63.4(2)	63.8(3)
O(9)—Li(1)—N(3*)	73.8(2)	73.9(2)	74.0(3)
O(9)—Li(1)—N(4)	135.9(2)	132.3(3)	134.6(3)
O(9)—Li(1)—N(5)	137.2(2)	139.4(2)	135.2(3)
N(3*)—Li(1)—N(4)	116.3(2)	114.0(2)	118.8(3)
N(3*)—Li(1)—N(5)	137.0(2)	137.9(2)	137.8(3)
N(4)—Li(1)—N(5)	66.1(2)	66.6(2)	66.5(3)

O(6)N(3*)N(4) planes in **2**, respectively. The geometry is distorted from the ideal D_{3h} geometry in which the three planes are parallel. The coordination sphere about Gd(III) in this complex was apparently strained by the

macrocyclic ligand, since the five atoms of each amide group $-\text{C}-\text{CO}-\text{N}-\text{C}-$ are located on a plane: the maximum deviation from the least-squares plane is 0.00096 nm in the group $\text{C}(16)\text{C}(17)\text{O}(8)\text{N}(1)\text{C}(1)$ and 0.00312 nm in $\text{C}(5)\text{C}(4)\text{O}(1)\text{N}(2)\text{C}(3)$, respectively. This planarity in the amide groups generates inflexibility in the ligand, which generates the distortion geometry around the lanthanide ion. The dihedral angle between the neighboring amide planes is 60.89° for **2**, which is smaller than the corresponding value in $\text{Gd}(\text{16-DTPA-pn})\text{J}^3(99.7^\circ)$ because the introduction of an additional $-\text{CH}_2-$ group into the macrocyclic ring increases the flexibility of the ligand.

The $\text{Gd}-\text{N}(3^*)$ bond length [0.2897(7) nm] is extremely long compared with the bond distances of $\text{Gd}-\text{N}(4)$ and $\text{Gd}-\text{N}(5)$, due to the coordination of Gd to $\text{N}(3^*)$ from another macrocycle. The average distances of $\text{Ln}-\text{O}_{\text{carboxylate}}$ (0.2375 nm) and $\text{Ln}-\text{N}_{\text{amine}}$ (0.2759 nm) are apparently longer than those in the monomeric macrocyclic lanthanide complexes.^{5,14}

Crystal structure of **4** · 15.5H₂O

The crystal structure of **4** is similar to that of **2**. However, there are two crystallographically nonequivalent molecules in the unit cell, as shown in Fig. 2 (A and B), A and B are diastereoisomer. Selected bond distances and angles are summarized in Table 2. The coordination geometry around one gadolinium atom in the diastereoisomers is similar, but the coordination fashion of the pendant acetato groups is different. In molecule A,

two acetato groups adopt clockwise fashion around one central metal ion, while another acetate is arranged around the metal ion counterclockwise. In molecule B, only one acetato group adopts clockwise fashion around the metal ion $\text{Gd}(2)$, the other two acetato groups adopt the opposite coordination fashion. For most of the macrocyclic polyamino-polycarboxylate lanthanide complexes, the coordination fashion of the three or four acetato groups in one macrocyclic ring is the same.^{5,14-16}

The coordination geometry can be described as a distorted tricapped-trigonal prism with two amine nitrogen atoms and one carboxylate oxygen atom as the rectangular face caps. This coordination geometry is different from those in monomeric macrocyclic or acyclic DTPA-bis(amide) lanthanide complexes, in which two amine nitrogen atoms and the coordinated water oxygen atom occupy the capping positions.^{5,14} The dihedral angles between the $\text{O}(2^*)\text{O}(8)\text{N}(5)$ and $\text{O}(6)\text{N}(3^*)\text{N}(4)$ planes are 22.88° , and 6.29° between the $\text{O}(1^*)\text{O}(4)\text{O}(9)$ and $\text{O}(6)\text{N}(3^*)\text{N}(4)$ planes in molecule A; in molecule B, the corresponding dihedral angles are 17.69° and 2.99° , respectively. The two amide groups in each of molecules A and B are also coplanar, which resembles those in **2**.

The average $\text{Gd}-\text{X}$ distances for carboxymethyl oxygen, amide oxygen, and amine nitrogen atoms are slightly shorter in molecule B than those in molecule A. But the $\text{Gd}-\text{O}_{\text{water}}$ bond length is longer in B than that in A. The $\text{Gd}-\text{N}$ bond lengths vary from 0.2615(8) to 0.2907(8) nm in molecule A and from 0.2638(9) to 0.2823(10) nm in molecule B (Table 2), leading to the slight distorted coordination polyhedron in molecule B.

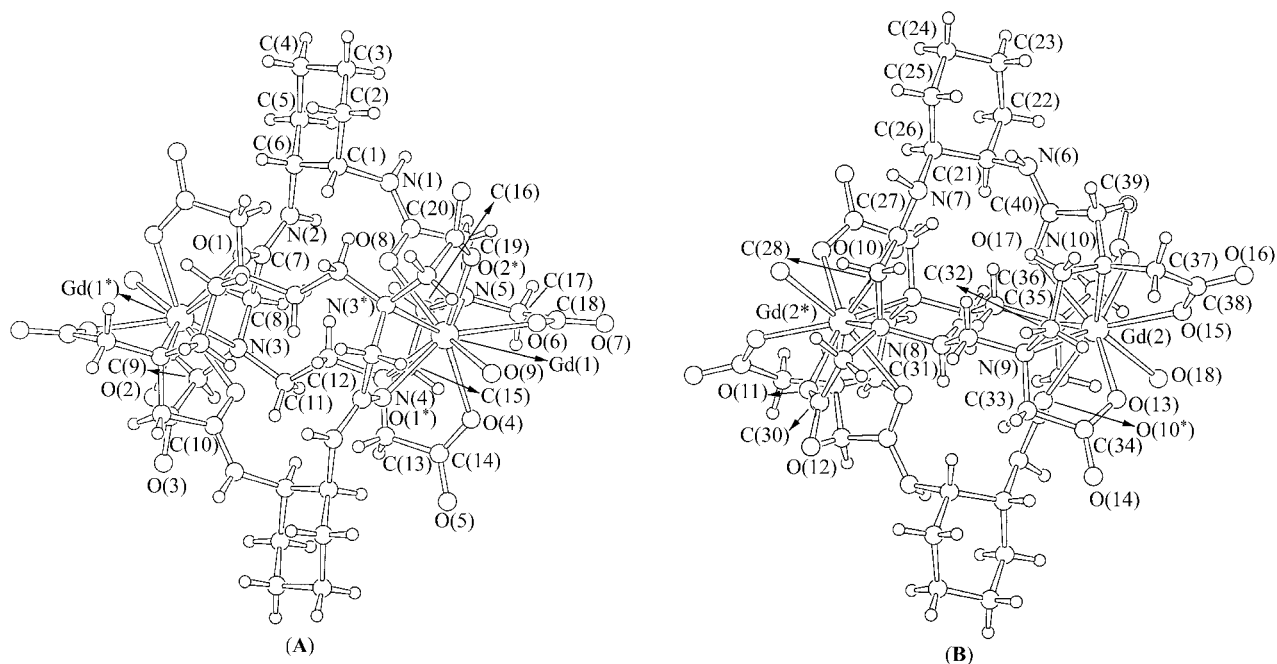


Fig. 2 Structures of two $[\text{Gd}(\text{15-DTPA-1,2-cy})(\text{H}_2\text{O})](\mathbf{4})$ molecules: (A) molecule A. (B) molecule B.

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