Syntheses of new 15-membered and 16-membered macrocyclic ligands with three pendant acetato groups and the structures of the gadolinium(III) complexes

Michiko B. Inoue[a,b], Motomichi Inoue[b], Iliana C. Muñoz[b], Michael A. Bruck[a] and Quintus Fernando[a]

[a]Department of Chemistry, University of Arizona, Tucson, AZ 85721 (USA)
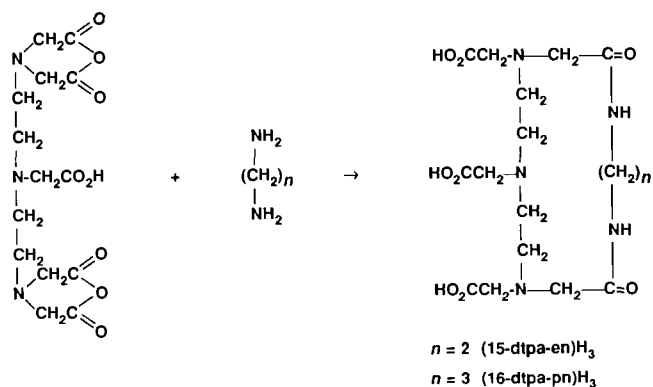[b]CIPM, Universidad de Sonora, Apartado Postal 130, Hermosillo, Sonora (Mexico)

Abstract

A condensation of diethylenetriaminepentaacetic dianhydride with ethylenediamine gave a 15-membered macrocyclic ligand with three pendant acetato groups, $(15\text{-dtpa-en})H_3 = C_{10}H_{18}N_5O_2(CH_2CO_2H)_3$; a 16-membered analogue, $(16\text{-dtpa-pn})H_3 = C_{11}H_{20}N_5O_2(CH_2CO_2H)_3$, was obtained by the use of propanediamine instead of ethylenediamine. The structures of their gadolinium(III) complexes, $Gd_2(15\text{-dtpa-en})_2 \cdot 16H_2O$ and $Gd(16\text{-dtpa-pn}) \cdot 4H_2O$, were determined by X-ray analyses. $Gd_2(15\text{-dtpa-en})_2 \cdot 16H_2O$ crystallized in the orthorhombic space group $Pbca$ with: $a = 18.205(1)$, $b = 18.930(1)$ and $c = 15.609(1)$ Å. Two Gd(III) ions are located between two ligand molecules, forming a binuclear metal chelate molecule with a center of inversion. The coordination geometry around a metal ion is described as a distorted tricapped trigonal prism that consists of nine coordinated atoms. $Gd(16\text{-dtpa-pn}) \cdot 4H_2O$ crystallized in the monoclinic space group $P2_1/c$ with: $a = 8.246(2)$, $b = 14.995(3)$, $c = 19.367(4)$ Å and $\beta = 90.258(2)°$. In this compound, a water molecule and a single ligand molecule are coordinated to a Gd(III) ion, forming a mononuclear chelate with a tricapped trigonal prism. The structural differences between the two Gd(III) complexes are a result of the differences in the favorable conformations assumed by the two macrocyclic ligands.

Introduction

The synthesis of metal complexes of macrocyclic ligands with pendant functional groups has attracted a large number of investigators [1–12]. Special attention has been directed to neutral non-ionic gadolinium(III) chelates of macrocyclic ligands, because they are potential magnetic resonance imaging agents [6–12]. In our previous paper [13], we reported that macrocyclic ligands with pendant acetato groups can be prepared by a condensation between ethylenediaminetetraacetic dianhydride and ethylenediamine. The formation of neutral metal chelates of these new ligands with copper(II) and manganese(II) ions has been confirmed by X-ray crystal analyses [13]. A possible route in the synthesis of a non-ionic metal chelate of a trivalent metal ion is the formation of a complex with a macrocyclic ligand that has three pendant acetato groups. In this study, therefore, the condensation of diethylenetriaminepentaacetic (abbreviated as dtpa) dianhydride with ethylenediamine (en) has been carried out, and a new 15-membered macrocyclic ligand with three pendant acetato groups ((15-dtpa-en)H₃ in Scheme 1) has been obtained. Since the structural properties of a metal chelate with a macrocyclic ligand are sensitively dependent on the geometrical properties of the ligand (such as the size and the flexibility of the ring), a 16-membered analogue, (16-dtpa-pn)H₃ in Scheme 1, was also synthesized by a condensation between dtpa and propanediamine (pn). The X-ray crystal analyses of

Scheme 1.

$n = 2$ (15-dtpa-en)H₃
$n = 3$ (16-dtpa-pn)H₃

their gadolinium(III) complexes have shown that both ligands form non-ionic metal chelates. Their molecular structures are quite different from each other.

Experimental

Materials

Diethylenetriaminepentaacetic dianhydride, ethylenediamine (99% + grade) and propanediamine (99% + grade) were supplied from Aldrich Chemical Co. and were used without further purification. Gadolinium(III) carbonate was supplied from Johnson Matthey, Rare Earth Products.

Syntheses of ligands

(15-dtpa-en)H$_3$ was synthesized as follows. To 2.45 g of diethylenetriaminepentaacetic dianhydride that was suspended in 350 ml of dry dimethylformamide (DMF) was added dropwise a DMF solution (50 ml) containing 0.413 g of ethylenediamine over a period of 4 h with vigorous stirring under a nitrogen atmosphere. The reaction mixture was heated at 50 °C for 3 h and then left to stand for c. 16 h at room temperature. The precipitate formed was removed by filtration. Concentration of the filtrate at a temperature below 40 °C resulted in the formation of a light yellow solid and a viscous liquid. To this reaction mixture, a small amount of water was added to dissolve the solid. When the resulting solution was mixed with tetrahydrofuran (THF), (15-dtpa-en)H$_3$ was obtained as a colorless solid. The product was purified by mixing an aqueous solution with THF. *Anal.* Calc. for C$_{16}$H$_{27}$N$_5$O$_8$·2H$_2$O: C, 42.38; H, 6.89; N, 15.44. Found: C, 42.41; H, 6.81; N, 15.31%.

(16-dtpa-pn)H$_3$ was obtained under essentially the same reaction conditions that were used for (15-dtpa-en)H$_3$, by using propanediamine instead of ethylenediamine. The product was purified by precipitation from a concentrated aqueous solution by the addition of THF, successively washed with a very small amount of water. *Anal.* Calc. for C$_{17}$H$_{29}$N$_5$O$_8$·3H$_2$O: C, 42.06; H, 7.27; N, 14.42. Found: C, 41.80; H. 6.94; N, 14.06%. The elemental analyses were performed by Desert Analytics, Tucson, AZ, USA.

Syntheses of gadolinium(III) complexes

To (15-dtpa-en)H$_3$·2H$_2$O suspended in a small amount of water, a slight excess of gadolinium(III) carbonate was added with stirring. The resulting mixture was heated at c. 40 °C with stirring overnight. From the resulting solid, the product was extracted with water at c. 40 °C. By evaporation of water, Gd(15-dtpa-en)·8H$_2$O was obtained as colorless crystals, which were suitable for X-ray analyses.

Gd(16-dtpa-pn)·4H$_2$O was prepared by essentially the same method that was employed for Gd(15-dtpa-en)·8H$_2$O. The product was purified by adding ethanol to the aqueous solution. Single crystals suitable for X-ray analyses were obtained as a tetrahydrate by diffusion of acetone into an aqueous solution of the complex in a narrow bore tube.

X-ray analyses

A crystal of Gd(15-dtpa-en)·8H$_2$O was sealed in a glass capillary together with the mother liquor for X-ray analysis; the crystal was found to readily effloresce. A crystal of Gd(16-dtpa-pn)·4H$_2$O was mounted on a glass fiber. Table 1 summarizes the crystal data and the data collection for the Gd(III) complexes. Empirical absorption corrections based on ψ-scans were applied to the data. Each structure was solved by the Patterson heavy-atom method, which revealed the position of the metal atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms bonded to carbon or nitrogen were included in the refinement at standardized positions with a fixed X–H distance of 0.95 Å; those of the water molecules were located in the difference Fourier map, and constrained to ride on the atoms to which they are bonded.

Results and discussion

The positional parameters of Gd(15-dtpa-en)·8H$_2$O are presented in Table 2. Selected bond lengths are given in Table 3. Figure 1 shows the structure of the Gd(III) chelate molecule. The X-ray results have demonstrated that a 15-membered macrocyclic ligand with three pendant acetato groups is obtained by the reaction shown in Scheme 1, and that the new ligand forms a neutral non-ionic metal chelate. Two gadolinium ions are located between two ligand molecules, forming a binuclear centrosymmetric metal chelate, [Gd$_2$(15-dtpa-en)$_2$(H$_2$O)$_2$], in which the averaged molecular planes of the two macrocyclic rings are parallel to each other. Each metal ion has nine coordination bonds with: an amide oxygen atom O(1), two carboxylato oxygen atoms O(3) and O(5), and two amine nitrogen atoms N(1) and N(2) from one ligand molecule; an amide oxygen atom O(2), a carboxylato oxygen atom O(7) and an amine nitrogen atom N(3) from the second ligand molecule; and a water oxygen atom O(w1). The coordination geometry around a Gd(III) ion is described as a distorted tricapped trigonal prism (i.e., tetradecahedron), as shown in Fig. 2(a).

The positional parameters of Gd(16-dtpa-pn)·4H$_2$O are collected in Table 4, and the selected bond lengths in Table 5. The molecular structure is shown in Fig. 3. Each metal ion has nine coordination bonds with:

TABLE 1. Crystal data and data collections for $Gd_2(15\text{-dtpa-en})_2 \cdot 16H_2O$ (I) and $Gd(16\text{-dtpa-pn}) \cdot 4H_2O$ (II)

	I	II
Chemical formula	$Gd_2C_{32}H_{48}N_{10}O_{16} \cdot 16H_2O$	$GdC_{17}H_{26}N_5O_8 \cdot 4H_2O$
Formula weight	1431.54	657.74
Crystal dimensions (mm)	0 46×0.30×0.22	0.50×0.37×0.34
T (°C)	21	23
$F(000)$	2904	1324
Space group	orthorhombic	monoclinic
	$Pbca$ (No. 61)	$P2_1/c$ (No. 14)
Cell parameters		
a (Å)	18.205(1)	8.246(2)
b (Å)	18.930(1)	14.995(3)
c (Å)	15.609(1)	19.367(4)
β (°)		90.258(2)
V (Å^3)	5379(1)	2395(1)
Z	4	4
ρ_{calc} (g cm^{-3})	1.77	1.82
μ (cm^{-1})	25.5	28.5
Diffractometer used	Enraf-Nonius CAD 4	Syntex P2$_1$
λ (Å) (monochromated Mo Kα)	0.71073	0.71073
Scan method	ω–2θ	θ–2θ
Maximum 2θ (°)	50	50
Transmission coefficient	0.77–1.00	0.77–1.00
No. reflections with $I > 3.0\sigma_I$	3974	3661
No. variables	343	316
$R = \Sigma|F_o - F_c|/\Sigma F_o$	0.026	0.021
$R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$	0.042	0.035
GOF	1.68	1.13
Highest peak (e$^-$ Å^{-3})	0.79(8)	0.49(7)
Min. negative peak (e$^-$ Å^{-3})	−0.14(8)	−0.42(7)
Computer and program used	VAX/MolEN	VAX/MolEN

two amide oxygen atoms O(1) and O(2), three carboxylato oxygen atoms O(3), O(5) and O(7), and three amine nitrogen atoms N(1), N(2) and N(3) from a single molecule, and a water oxygen atom O(w1). Thus, a ligand molecule and a water molecule occupy the tetradecahedral coordination sites around a Gd(III) ion (Fig. 2(b)), forming a mononuclear structure.

The structures of the Gd(15-dtpa-en) and the Gd(16-dtpa-pn) complexes are quite different from each other. First, Gd(15-dtpa-en) is a binuclear chelate whereas Gd(16-dtpa-pn) is mononuclear. Second, the sequences of the coordinated atoms in the tetradecahedrons are quite different from each other, as shown in Fig. 2. In addition, the tetradecahedron in the $Gd_2(15\text{-dtpa-en})_2$ chelate is highly distorted from the ideal D_{3h} geometry when compared with that in Gd(16-dtpa-pn). For example, the dihedral angle between the O(1)N(1)O(7) and O(3)N(2)N(3) planes in the $Gd_2(15\text{-dtpa-en})_2$ chelate (Fig. 2(a)) is 22.4°, and 4.9° between the O(2)O(5)O(w1) and O(3)N(2)N(3) planes; the three planes are parallel in the regular tetradecahedron. The corresponding dihedral angles in the Gd(16-dtpa-pn) chelate (Fig. 2(b)) are: 5.6° between the O(5)O(7)N(2) and N(1)N(3)O(w1) planes; and 7.3° between the O(1)O(2)O(3) and N(1)N(3)O(w1) planes.

These structural differences are explained by the geometrical properties of the two macrocyclic ligands. In both ligands, the five atoms, –C–CO–N–C–, of each amide group are located on a single plane: for $Gd_2(15\text{-dtpa-en})_2$, the maximum deviation from the least-squares plane is 0.010 Å in the group C(2)C(1)O(1)N(5)C(10) and 0.08 Å in C(7)C(8)O(2)N(4)C(9); for Gd(16-dtpa-pn), 0.009 Å in C(2)C(1)O(1)N(5)C(11) and 0.14 Å in C(7)C(8)O(2)N(4)C(9). This planarity of the amide groups generates inflexibility in the ligand. The geometry is affected to a greater extent in the 15-dtpa-en metal chelate in which C(9) and C(10) are directly bonded. The planarity of the amide groups and the coordination of the amide oxygen atoms define the conformation of the ligand. The dihedral angle between the neighboring amide planes is 60.8° in $Gd_2(15\text{-dtpa-en})_2$; the ligand is oriented in a manner that facilitates bridging between the two metal ions. The extreme distortion of the tetradecahedron around a Gd(III) ion is also attributable to the rigidity of the ligand. The extremely long Gd–N(3) distance is also due to the steric constraints of the macrocyclic ring. The introduction of an additional –CH$_2$– group into the macrocyclic ring increases the flexibility of the ligand, and results in the mononuclear structure in Gd(16-dtpa-pn) $\cdot$ 4H$_2$O. In this chelate mol-

TABLE 2. Positional parameters and isotropic thermal parameters for $Gd_2(15\text{-dtpa-en})_2 \cdot 16H_2O$

Atom	x	y	z	B_{eq} (Å²)ª
Gd	0.42584(1)	0 45223(1)	0.30709(1)	2.163(4)
O(1)	0.5543(1)	0.4714(1)	0.3476(2)	2 63(5)
O(2)	0.6391(1)	0.5538(1)	0.5589(2)	2 62(5)
O(3)	0.4089(2)	0.4461(1)	0.1561(2)	3.27(6)
O(4)	0.4035(2)	0.4949(2)	0.0272(2)	3 54(6)
O(5)	0.3209(1)	0.5243(2)	0.2820(2)	3.14(5)
O(6)	0.2309(1)	0.5899(2)	0.3335(2)	4.16(6)
O(7)	0.5011(1)	0.6419(1)	0.7477(2)	3.24(5)
O(8)	0.4135(1)	0.7199(2)	0.7200(2)	3.71(6)
N(1)	0.4980(2)	0.5467(2)	0.2190(2)	2.59(6)
N(2)	0.4240(1)	0.5850(2)	0.3804(2)	2.24(5)
N(3)	0.5337(1)	0.6574(1)	0.5705(2)	2.28(5)
N(4)	0.6849(2)	0.5990(2)	0.4372(2)	2.96(6)
N(5)	0.6695(2)	0.4940(2)	0 3003(2)	2.92(6)
C(1)	0 5983(2)	0.4898(2)	0 2899(2)	2.45(6)
C(2)	0.5680(2)	0.5102(2)	0 2032(2)	2.77(7)
C(3)	0.5121(2)	0.6146(2)	0.2646(2)	2.84(7)
C(4)	0.4469(2)	0.6372(2)	0.3156(2)	2.73(7)
C(5)	0.4719(2)	0.5844(2)	0.4577(2)	2.39(6)
C(6)	0.4679(2)	0.6498(2)	0.5147(2)	2.46(6)
C(7)	0.6004(2)	0.6697(2)	0.5188(2)	2.53(7)
C(8)	0 6427(2)	0.6025(2)	0.5056(2)	2.32(6)
C(9)	0.7383(2)	0.5432(2)	0.4230(3)	3.29(8)
C(10)	0.7061(2)	0.4781(2)	0.3806(2)	3.02(7)
C(11)	0.4603(2)	0.5599(2)	0.1368(2)	2.98(7)
C(12)	0.4220(2)	0.4948(2)	0.1035(2)	2.74(7)
C(13)	0.3468(2)	0.5989(2)	0.4013(2)	2.76(7)
C(14)	0.2957(2)	0.5687(2)	0.3335(2)	2.72(7)
C(15)	0.5186(2)	0.7168(2)	0.6293(2)	2.72(7)
C(16)	0.4727(2)	0.6914(2)	0.7043(2)	2.88(7)
O(w1)	0.3343(1)	0.3623(2)	0.2829(2)	3.66(6)
O(w2)	0.1181(2)	0.3667(2)	0.4733(2)	4.69(7)
O(w3)	0.4857(2)	0.3137(2)	0.0768(2)	4.78(7)
O(w4)	0.3547(2)	0.1352(2)	0.4782(2)	5 94(8)
O(w5)	0.1803(2)	0.2127(2)	0.1090(3)	7.9(1)
O(w6)	0.2944(2)	0 3047(3)	0.1229(3)	8.1(1)
O(w7)	0.1991(2)	0 3315(3)	0.3323(3)	10.0(1)
O(w8)	0.3362(3)	0 1872(3)	0.2119(3)	8.9(1)

ª$B_{eq} = (4/3)[a^2\beta_{1,1} + b^2\beta_{2,2} + c^2\beta_{3,3} + ab(\cos \gamma)\beta_{1,2} + ac(\cos \beta)\beta_{1,3} + bc(\cos \alpha)\beta_{2,3}]$.

TABLE 3 Selected bond distances (Å) in $Gd_2(15\text{-dtpa-en})_2 \cdot 16H_2O$

Gd–X distances

Gd–O(1)amide	2.449(2)	Gd–N(1)amine	2 611(3)
Gd–O(2)amide	2.406(2)	Gd–N(2)amine	2 761(3)
Gd–O(3)carboxylato	2.380(3)	Gd–N(3)amine	2 915(3)
Gd–O(5)carboxylato	2 381(3)	Gd–O(w1)water	2 412(3)
Gd–O(7)carboxylato	2 381(3)		

Carboxylato groups

C(12)–O(3)	1.257(5)	C(12)–O(4)	1.238(4)
C(14)–O(5)	1.249(5)	C(14)–O(6)	1.246(4)
C(16)–O(7)	1.267(4)	C(16)–O(8)	1.230(5)

Amide groups

C(1)–O(1)	1.255(4)	C(1)–N(5)	1.308(5)
C(8)–O(2)	1.243(4)	C(8)–N(4)	1.316(4)
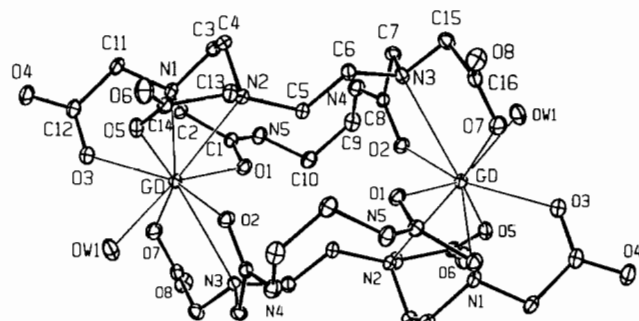
Fig 1. Molecular structure of $Gd_2(15\text{-dtpa-en})_2$ 16H₂O. Atoms are shown at the 20% probability level.

(a)   (b)
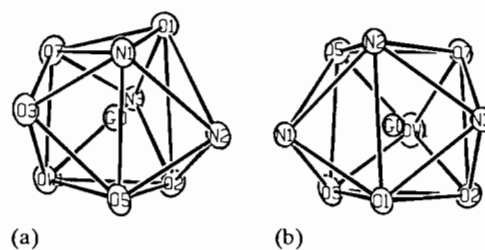
Fig. 2. Tetradecahedron around a gadolinium ion in $Gd_2(15\text{-dtpa-en})_2 \cdot 16H_2O$ (a) and that in $Gd(16\text{-dtpa-pn}) \cdot 4H_2O$ (b).

ecule, three amine nitrogen atoms have almost the same Gd–N distances. The dihedral angle between the amide groups is 99.7°, and the tetradecahedral coordination geometry is close to the ideal D_{3h} geometry. The extent of distortion is as small as that reported for the Gd(III) complex of dtpa–bis(ethylamide) that is an open chain ligand, although the sequences of the coordinated atoms in the tetradecahedrons are different from each other [14]: in the dtpa–bis(ethylamide) complex, the dihedral angles between neighboring planes with the quasi-C_3 axis are 6.2 and 8.9°. This shows that (16-dtpa-pn) has adopted a molecular conformation that enabled it to occupy the coordination positions around a Gd(III) ion.

In the two complexes, hydrogen bondings are well developed. In $Gd_2(15\text{-dtpa-en})_2 \cdot 16H_2O$, each of the O(4) and O(8) atoms forms hydrogen bonds with two water molecules, and each O(6) and O(7) is hydrogen-bonded to a water molecule. O(4) is linked with O(6) from the adjacent chelate through a water molecule. A hydrogen atom bonded to the amide nitrogen N(4) forms a hydrogen bond with a water oxygen, and the other amide hydrogen H–N(5) is hydrogen-bonded to O(6) of the adjacent metal chelate. In $Gd(16\text{-dtpa-pn}) \cdot 4H_2O$, each of the O(3), O(4), O(6) and O(8) atoms is hydrogen-bonded to a water molecule, and O(4) is linked with O(6) from the adjacent metal chelate through a water molecule. The amide hydrogen H–N(5)

TABLE 4 Positional parameters and isotropic thermal parameters for Gd(16-dtpa-pn)·4H₂O

Atom	x	y	z	B_{eq} (Å²)[a]
Gd	0.18531(2)	0.14340(1)	0.17534(1)	1.783(3)
O(1)	0.3071(2)	0.2896(2)	0.1528(1)	2 59(4)
O(2)	−0 0280(2)	0.2527(1)	0.1539(1)	2.44(4)
O(3)	0.2354(3)	0.1406(2)	0.0549(1)	3.13(5)
O(4)	0.3865(3)	0.1159(2)	−0.0373(1)	4.28(6)
O(5)	0 2757(3)	−0.0037(2)	0.1825(1)	2.87(4)
O(6)	0.3601(4)	−0.1218(2)	0.2411(2)	4.59(6)
O(7)	0.0206(2)	0.0792(2)	0.2636(1)	2.55(4)
O(8)	−0.1099(3)	0.0816(2)	0.3632(1)	3.33(5)
N(1)	0.5058(3)	0.1441(2)	0.1371(1)	2.32(5)
N(2)	0.3788(3)	0.1159(2)	0.2807(1)	2.30(5)
N(3)	0.1149(3)	0.2554(2)	0.2777(1)	2.05(5)
N(4)	−0.0123(3)	0.4018(2)	0.1377(1)	2.72(5)
N(5)	0.4187(4)	0.3522(2)	0.0582(2)	2.92(6)
C(1)	0.4198(4)	0.2956(2)	0.1097(2)	2.37(6)
C(2)	0.5639(4)	0.2353(2)	0.1199(2)	2.80(6)
C(3)	0.6033(4)	0.1053(3)	0.1934(2)	2.90(7)
C(4)	0.5475(4)	0.1426(2)	0.2626(2)	2.77(7)
C(5)	0.3277(4)	0.1705(3)	0.3409(2)	2.80(6)
C(6)	0.2647(4)	0.2613(2)	0.3214(2)	2.71(6)
C(7)	0.0711(4)	0.3431(2)	0.2486(2)	2.42(6)
C(8)	0.0035(3)	0.3295(2)	0.1762(2)	2.31(6)
C(9)	−0.0293(4)	0.3987(3)	0.0630(2)	3.38(7)
C(10)	0.1222(5)	0.3640(2)	0.0270(2)	3.33(8)
C(11)	0.2789(4)	0.4132(2)	0.0476(2)	3.38(7)
C(12)	0.5042(4)	0.0897(2)	0.0740(2)	2.99(7)
C(13)	0.3673(4)	0.1180(2)	0.0263(2)	2.95(7)
C(14)	0.3739(4)	0.0195(2)	0.2975(2)	3.09(7)
C(15)	0.3355(4)	−0.0404(2)	0.2355(2)	2.89(6)
C(16)	−0.0233(4)	0.2196(2)	0.3175(2)	2.43(6)
C(17)	−0.0380(4)	0.1193(2)	0.3157(2)	2.31(6)
O(w1)	−0.0326(3)	0.0590(2)	0.1163(1)	3.62(5)
O(w2)	0 6739(4)	0.1671(2)	0.9075(2)	5.57(7)
O(w3)	0.6665(3)	0.1605(2)	0.4542(1)	4.18(6)
O(w4)	0 9772(6)	0.0995(3)	0.9544(3)	12.1(1)

[a] $B_{eq} = (4/3)[a^2\beta_{1,1} + b^2\beta_{2,2} + c^2\beta_{3,3} + ab(\cos \gamma)\beta_{1,2} + ac(\cos \beta)\beta_{1,3} + bc(\cos \alpha)\beta_{2,3}]$.

TABLE 5. Selected bond distances (Å) in Gd(16-dtpa-pn) 4H₂O

Gd–X distances

Gd–O(1)_amide	2.451(2)	Gd–N(1)_amine	2.748(3)
Gd–O(2)_amide	2.439(2)	Gd–N(2)_amine	2.618(2)
Gd–O(3)_carboxylato	2.371(2)	Gd–N(3)_amine	2.664(2)
Gd–O(5)_carboxylato	2.332(2)	Gd–O(w1)_water	2.474(2)
Gd–O(7)_carboxylato	2.391(2)		

Carboxylato groups

C(13)–O(3)	1.270(4)	C(13)–O(4)	1.242(4)
C(15)–O(5)	1.264(4)	C(15)–O(6)	1.242(4)
C(17)–O(7)	1.272(4)	C(17)–O(8)	1.234(4)

Amide groups

C(1)–O(1)	1.256(4)	C(1)–N(5)	1.310(4)
C(8)–O(2)	1.257(4)	C(8)–N(4)	1.322(4)

forms a hydrogen bond with a water molecule, and the other amide hydrogen constructs a N(5)–H···O(8) bond with the adjacent metal chelate.
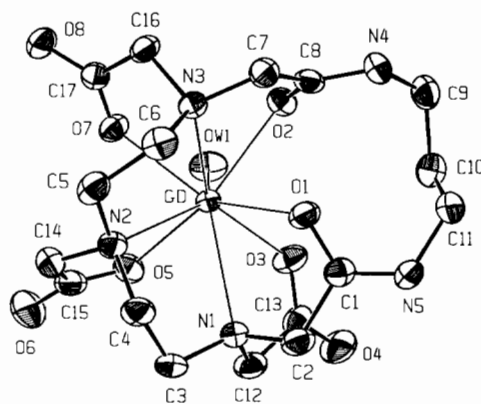

Fig. 3. Structure of a Gd(16-dtpa-pn)·4H₂O. Atoms are shown at the 50% probability level.

Conclusions

This study demonstrates that the condensation of dtpa dianhydride with a diamine is a versatile method for the preparation of a variety of macrocyclic ligands with three pendant acetato groups. The metal chelates of the resulting macrocycles are highly sensitive to the geometrical properties of the coordinated ligands. The structural difference between Gd₂(15-dtpa-en)₂ and Gd(16-dtpa-pn) is expected to result in different physical properties. In fact, the water solubility of the latter complex is much higher than that of the former.

Acknowledgement

References

1 R. M. Izatt and J. J. Christensen (eds.), *Synthetic Multidentate Macrocyclic Compounds,* Academic Press, New York, 1978.

2 G. A. Melson, *Coordination Chemistry of Macrocyclic Compounds,* Plenum, New York, 1979.

3 P. V Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.,* 104 (1990) 297.

4 D. Parker, *Chem. Br,* (1990) 942.

5 J. P. L. Cox, K. J. Jankowski, R. Kataky, D. Parker, N. R. A. Beeley, R. A. Boyce, M. A. W. Eaton, K. Millar, A T. Millican, A Harrison and C. Walker, *J. Chem. Soc., Chem. Commun,* (1989) 797.

6 P. Clark, S. F. Lincoln and K. P. Wainwright, *Inorg. Chem,* 30 (1991) 134.

7 D. D. Dischino, E. J. Delaney, J. E. Emswiler, G. T. Gaughan, J. S. Prasad, S. K. Srivastava and M. F. Tweedle, *Inorg Chem., 30* (1991) 1265.

8 M. Kodama, T. Koike, A B. Mahatma and E. Kimura, *Inorg Chem , 30* (1991) 1270.

9 E. Brucher, S. Cortes, F. Chavez and A. D Sherry, *Inorg. Chem., 30* (1991) 2092.

10 M. W. Perkovic, M. J. Heeg and J. F. Endicott, *Inorg. Chem*, *30* (1991) 3140.

11 I. Lazar, A. D. Sherry, R. Ramasamy, E. Brucher and R. Kiraly, *Inorg. Chem*, *30* (1991) 5016.

12 S Aime, M. Botta, G. Ermondi, F. Fedeli and F. Uggeri, *Inorg. Chem.*, *31* (1992) 1100.

13 M. B. Inoue, C. A. Villegas, K. Asano, M. Nakamura, M. Inoue and Q. Fernando, *Inorg Chem*, *31* (1992) 2480.

14 M. S Konings, W C. Dow, D. B. Love, K N. Raymond, S. C Quay and S. M Rocklage, *Inorg. Chem*, *29* (1990) 1488.