

Poly[aqua- μ_3 -*p*-aminobenzoato- $\kappa^3 N:O:O'$ - μ_2 -*p*-aminobenzoato- $\kappa^2 O:O'$ -*p*-aminobenzoato- $\kappa^2 O,O'$ -gadolinium(III)]

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Key indicators

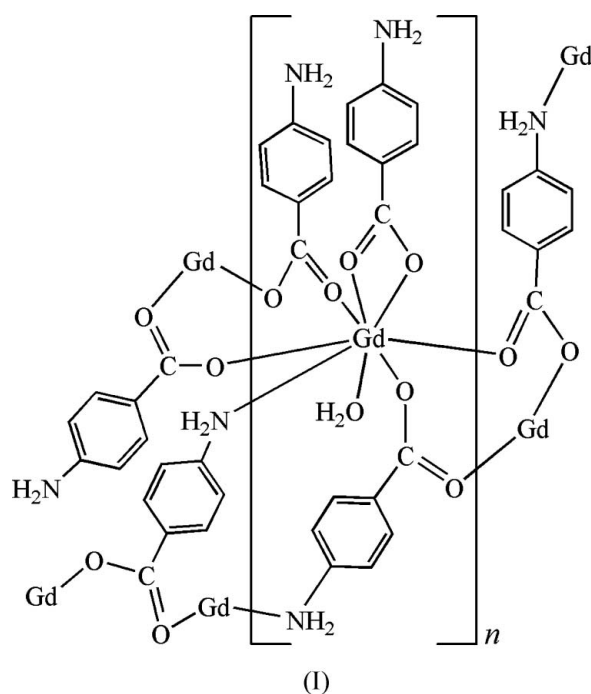
Single-crystal X-ray study
 $T = 291$ K
Mean $\sigma(C-C) = 0.004$ Å
 R factor = 0.023
 wR factor = 0.054
Data-to-parameter ratio = 15.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $[Gd(C_7H_6NO_2)_3(H_2O)]_n$, a two-dimensional coordination polymer, the eight-coordinate Gd^{III} ions are bridged by two carboxylate groups from two μ_2 -*p*-aminobenzoate ligands, forming a centrosymmetric dinuclear block. These blocks are further connected by μ_3 -*p*-aminobenzoate ligands, yielding a two-dimensional network. The coordination polymers thus formed are connected *via* hydrogen bonds, producing a three-dimensional supramolecular structure.

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Comment

Construction of metal-organic frameworks has attracted much attention owing to their fascinating structures and their potential applications as functional solid materials (Seo *et al.*, 2000; Swiegers & Malefetse, 2000; Pavlishchuk *et al.*, 2001; Kitaura *et al.*, 2002; Hagrman *et al.*, 1999). Most recent studies have concentrated on *d*-block transition metals, with much less research done on lanthanides because of their tendency for high coordination numbers (Sun *et al.*, 2005; Pan *et al.*, 2003; Chen *et al.*, 2006). We report here the synthesis and structure of a two-dimensional gadolinium(III) coordination polymer, (I), assembled with the *p*-aminobenzoate ligand.



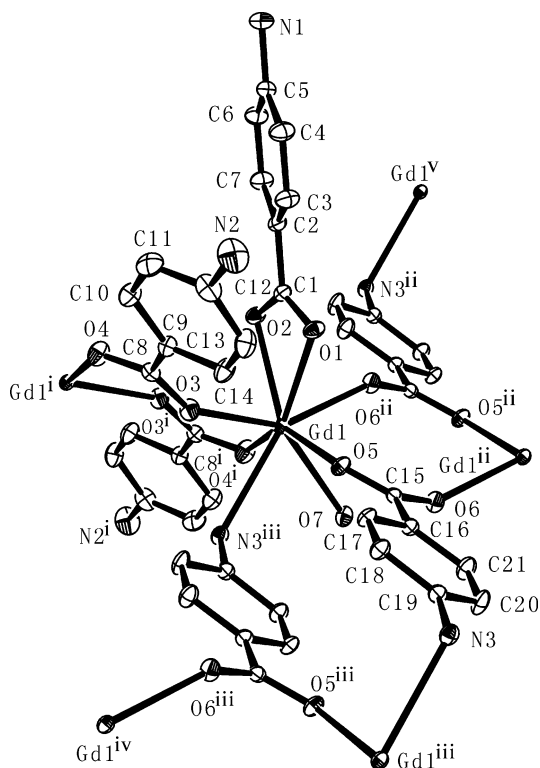


Figure 1

A view of part of the structure of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + 1, -y + 2, -z$; (iii) $-x, -y + 2, -z$; (iv) $1 + x, y, z$; (v) $-1 + x, y, z$.]

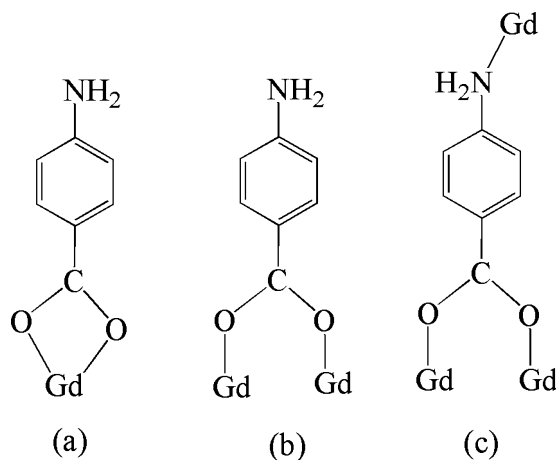


Figure 2

Coordination modes of *p*-aminobenzoate: (a) chelating mode, (b) μ_2 -bridging mode and (c) μ_3 -bridging mode.

Gd^{III} ion is connected to one terminal water molecule, the amino group from one *p*-aminobenzoate ligand and six carboxylate O atoms from five *p*-aminobenzoate ligands, forming a distorted dodecahedral geometry. Thus, each Gd^{III} ion in compound (I) is coordinated by six *p*-aminobenzoate ligands which show three types of coordination modes (chelating mode, μ_2 -bridging mode and μ_3 -bridging mode; Fig. 2). Two mononuclear units are bridged by two carboxylate

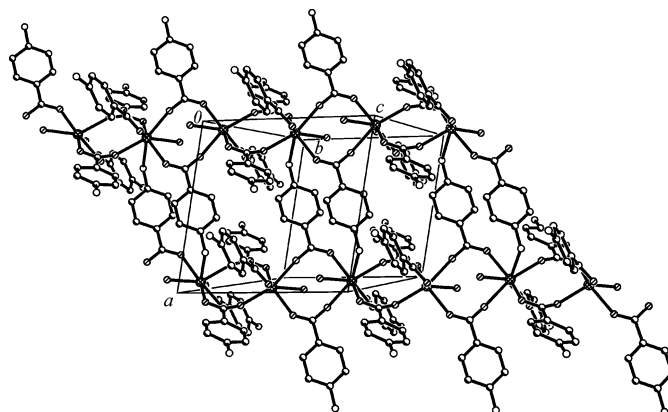


Figure 3

The two-dimensional coordination network in (I). H atoms have been omitted for clarity.

groups from the μ_2 -bridging *p*-aminobenzoate ligands, forming a dinuclear building block with an inversion centre located between the Gd^{III} ions and with a $\text{Gd} \cdots \text{Gd}$ separation of 4.7505 (9) Å. These dinuclear building blocks are further connected by μ_3 -bridging *p*-aminobenzoate ligands, yielding a two-dimensional coordination network parallel to the *ac* plane (Fig. 3). This connection leads to a $\text{Gd} \cdots \text{Gd}$ contact of 5.1271 (9) Å along the *c* axis. Hydrogen bonds (Table 2) further stabilize the two-dimensional networks and additionally connect them into a three-dimensional supramolecular structure.

Experimental

Gd_2O_3 (0.1813 g, 0.5 mmol) was dissolved in 0.3 ml of HClO_4 (70%) with heating. The solution was then transferred into a Young–Schlenk flask containing *p*-aminobenzoic acid (0.3429 g, 2.5 mmol) in 15 ml distilled water. The pH value of the resultant mixture was adjusted to 5 using NaOH solution and the reaction mixture was left to stand at 373 K for 4 d, and subsequently cooled and filtered. Red crystals of compound (I) were formed when the filtrate was allowed to evaporate at ambient temperature for one month. Elemental analysis, calculated for $\text{C}_{21}\text{H}_{20}\text{N}_3\text{O}_7\text{Gd}$ (%): C 43.22, H 3.45, N 7.20; found: C 43.40, H 3.80, N 7.93.

Crystal data

$[\text{Gd}(\text{C}_7\text{H}_6\text{NO}_2)_3(\text{H}_2\text{O})]$
 $M_r = 583.65$
 Monoclinic, $P2_1/n$
 $a = 9.7639$ (18) Å
 $b = 22.836$ (4) Å
 $c = 9.8496$ (18) Å
 $\beta = 99.908$ (4)°
 $V = 2163.4$ (7) Å³

$Z = 4$
 $D_x = 1.792$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 3.11$ mm⁻¹
 $T = 291$ (2) K
 Block, red
 $0.46 \times 0.33 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1998)
 $T_{\text{min}} = 0.310, T_{\text{max}} = 0.534$

13405 measured reflections
 4828 independent reflections
 3994 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.054$
 $S = 1.05$
 4828 reflections
 307 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0217P)^2 + 1.9268P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.006$
 $\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.17 \text{ e } \text{\AA}^{-3}$

Table 1

Selected bond lengths (\AA).

Gd1—O3	2.307 (2)	Gd1—O2	2.4672 (18)
Gd1—O4 ⁱ	2.3444 (19)	Gd1—O1	2.4720 (18)
Gd1—O5	2.3509 (16)	Gd1—O7	2.5260 (19)
Gd1—O6 ⁱⁱ	2.356 (2)	Gd1—N3 ⁱⁱⁱ	2.670 (2)

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + 1, -y + 2, -z$; (iii) $-x, -y + 2, -z$.

Table 2

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O7—H1W ⁱ ···O1 ⁱⁱ	0.85 (1)	2.58 (2)	3.184 (3)	129 (2)
O7—H1W ⁱ ···O6	0.85 (1)	2.00 (1)	2.786 (3)	153 (3)
N3—H3B···O2 ^{vi}	0.90	2.04	2.924 (3)	168
N3—H3A···N2 ^{vii}	0.90	2.48	3.374 (4)	175
O7—H2W ⁱⁱⁱ ···N1 ^{viii}	0.85 (1)	2.09 (2)	2.892 (3)	158 (2)
N2—H2A···O7 ^{ix}	0.85 (3)	2.36 (2)	3.135 (4)	151 (4)
N1—H1A···O1 ^x	0.86 (1)	2.23 (2)	2.985 (3)	147 (3)

Symmetry codes: (ii) $-x + 1, -y + 2, -z$; (vi) $x - 1, y, z - 1$; (vii) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (viii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ix) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (x) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.

The H atoms bound to N1, N2 and O7 were located in a difference Fourier map and were refined isotropically with $U_{\text{iso}}(\text{H}) = 1.2$ times

$U_{\text{eq}}(\text{N}, \text{O})$; O—H and H···H distances were restrained (O—H = 0.85, N—H = 0.86 and H···H = 1.45 \AA) to ensure a reasonable geometry for the coordinated water molecule and amino group. H atoms bound to N3 and to C atoms were placed in calculated positions, with N—H = 0.90 \AA and C—H = 0.93 \AA , and refined in riding mode, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{C})$. The deepest hole is located 0.76 \AA from Gd1.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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