

Poly[*diaqua*(μ_4 -benzene-1,2-dicarboxylato)(isonicotinato- κ^2 O,O')-gadolinium(III)]

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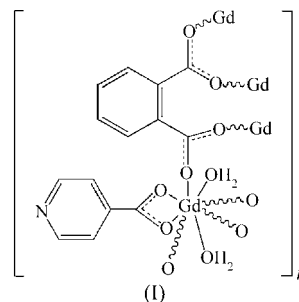
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The title neutral polymer, $[\text{Gd}(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2]_n$, contains an extended two-dimensional wave-like lanthanide carboxylate layer decorated by isonicotinate (IN) ligands. The Gd^{III} atom is eight-coordinated by four carboxylate O atoms from four benzene-1,2-dicarboxylate (1,2-bdc) ligands, two 1,2-bdc carboxylate O atoms from one chelating IN ligand and two terminal water molecules, forming a bicapped trigonal-prismatic coordination geometry. The wave-like layers are stacked in an $\dots ABAB \dots$ packing mode along the c -axis direction. Strong hydrogen-bonding interactions further stabilize the structure of the title compound.

Comment

Considerable attention has been paid to the design of multi-dimensional metal-organic frameworks (MOFs), owing to their intriguing structural topological properties and potential magnetism (Noro *et al.*, 2000; Banfi *et al.*, 2004). The rational choice of appropriate metal ions and organic linkers is an important issue for the design and synthesis of predictable MOFs. The lanthanide ions are good candidates for the construction of MOFs, because of their high coordination numbers, with variable coordination geometries, and unique magnetism and luminescent properties. The aromatic polycarboxylate ligands, possessing multidentate functional groups and versatile coordination modes, have been demonstrated as useful organic linkers for the construction of MOFs (Fan *et al.*, 2003; Wang *et al.*, 2004). Many extended one-, two- and three-dimensional coordination compounds have been reported to be assembled by the three isomeric benzenedicarboxylate (bdc) ligands (Groenman *et al.*, 1998; Chen *et al.*, 2007). Among them, the 1,2-bdc ligand, when used as the sole organic linker, often forms zero-dimensional isolated structures or one-dimensional chains (Ma *et al.*, 2004; Wang *et al.*, 2007), but occasionally results in a higher dimensionality

metal-carboxylate framework, as demonstrated by several reports concerning two-dimensional layers in metal-carboxylate coordination polymers (Natarajan & Thirumuran, 2005; Wang *et al.*, 2003). We present here a new two-dimensional MOF assembled by Gd^{III} atoms and 1,2-bdc ligands in the presence of isonicotinate (IN) ligands, in which 1,2-bdc acts as the only organic linker.



The title compound, (I), consists of an extended two-dimensional wave-like lanthanide carboxylate layer decorated by the isonicotinate ligands. The asymmetric unit (Fig. 1) contains one gadolinium(III) ion, one bdc ligand, one IN ligand and two aqua ligands. Each Gd^{III} ion is eight-coordinated with a bicapped trigonal-prismatic coordination geometry consisting of four carboxylate O atoms (O_{COO}) from four 1,2-bdc ligands, two O_{COO} atoms from one chelating IN ligand and two terminal water molecules. $\text{O1/O2}^{\text{iii}}/\text{O3}^{\text{ii}}$ and O4/O6/O8 define the two basal planes of the trigonal prism [symmetry codes: (ii) $-x, -y + 3, -z$; (iii) $-x, -y + 2, -z$], while atoms O5 and O7 cap the sides defined by O1/O2/O4/O6 and O1/O3/O8/O6 , respectively. The $\text{Gd}-\text{O}$ bond lengths range from 2.310 (3) to 2.499 (3) Å (Table 1), comparable to

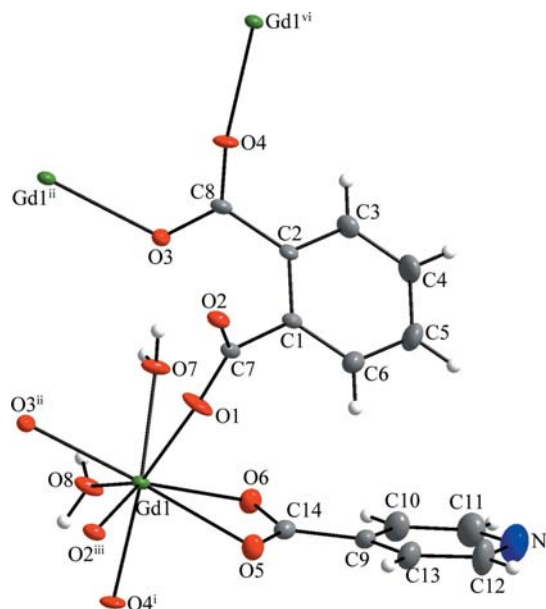


Figure 1

A view of the molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $-x, -y + 3, -z$; (iii) $-x, -y + 2, -z$; (vi) $x - \frac{1}{2}, y + \frac{1}{2}, z$.]

those of other gadolinium(III)–carboxylate complexes (Natarajan & Thirumurugan, 2005).

Although abundant and versatile coordination modes have been found in IN and bdc ligands, only a single bidentate chelating (for IN) and a unique tetradentate bridging (for bdc) mode are adopted in the crystal structure of the title compound. This suggests a high co-operativity between the IN and bdc ligands (Wang *et al.*, 2007) in the formation of the framework.

The Gd^{III} centers are bridged by carboxylate groups of bdc ligands so as to form eight-membered rings (Fig. 2, rings *A* and *B*). Such rings are further connected to one another by sharing common Gd atoms, and form an extended wave-like chain propagating approximately along the *a*-axis direction. The

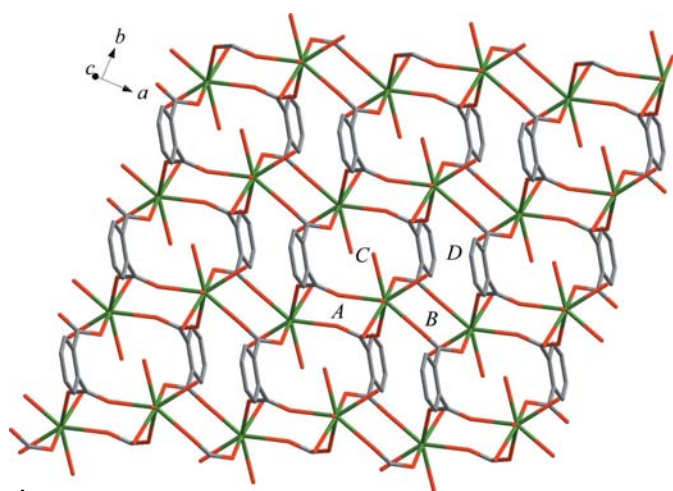


Figure 2
A perspective view of the two-dimensional layer structure. The pyridyl C and N atoms of the IN ligands and all H atoms have been omitted for clarity.

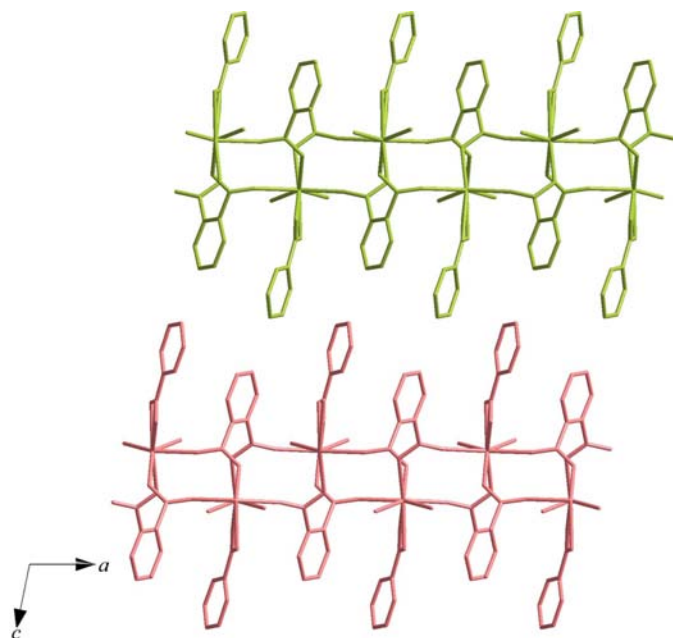


Figure 3
A view along the *b* axis showing the stacking of layers in the *c*-axis direction. All H atoms have been omitted for clarity.

Gd··Gd distances between neighboring Gd centers, bridged by C7OO and C8OO groups, are 5.530 (4) and 4.846 (4) Å, respectively. The aromatic rings of the bdc ligands link neighboring one-dimensional wave-like chains to construct a two-dimensional undulating layer in the *ab* plane and form two 14-membered rings with dimensions of $5.896 \times 7.457 \text{ \AA}^2$ (ring *C*) and $7.520 \times 7.014 \text{ \AA}^2$ (ring *D*).

The IN ligand in the title compound does not serve as an organic linker or raise the dimensionality of the structure, but only decorates the two-dimensional layer, owing to its coordination mode chelating a single Gd center. Each of the two coordinated water molecules on the Gd atom forms two O—H··O hydrogen bonds (Table 2) with neighboring carboxylate groups. These hydrogen-bonding interactions help to consolidate the layer structure. The undulating layers are stacked together in an *...ABAB...* packing mode along the *c*-axis direction, with the pyridyl rings of the IN ligands projecting into the interlamellar region (Fig. 3).

(H₂PIP)[Gd₂(bdc)₂(H₂O)₂] (PIP is piperazine; Natarajan & Thirumurugan, 2005) is another example of a two-dimensional network constructed from Gd^{III} ions linked by a single organic linker, *viz.* 1,2-bdc, in the presence of piperazine. In this compound, the Gd center is eight-coordinated by five bdc anions and one aqua ligand, while the Gd center in the title compound is eight-coordinated by four bdc ligands, one IN anion and two aqua ligands. The two carboxylate units of the bdc ligand in (H₂PIP)[Gd₂(bdc)₂(H₂O)₂] have three coordination modes, namely chelating to one Gd center, bridging two Gd centers and monodentate connecting to only one Gd center. The H₂PIP counter-anions are isolated and located in the voids within the sheet. By contrast, both carboxylate groups of 1,2-bdc in the title compound bridge two Gd centers, and the IN ligands are covalently connected to the two-dimensional lanthanide carboxylate framework.

Experimental

A mixture of Gd₂O₃ (0.036 g, 0.1 mmol), benzene-1,2-dicarboxylic acid (0.135 g, 0.8 mmol), isonicotinic acid (0.098 g, 0.8 mmol) and water (8 ml) was placed in an 18 ml Teflon-lined Parr acid digestion bomb. The pH of the reaction mixture was adjusted to *ca.* 5.0 with 10% sodium hydroxide. The mixture was then heated for 4 d at 443 K under autogenous pressure and slow cooling to room temperature gave colorless prismatic crystals (yield *ca.* 42%, based on Gd).

Crystal data

[Gd(C ₆ H ₄ NO ₂)(C ₈ H ₄ O ₄)(H ₂ O) ₂]	$V = 3123.9 (4) \text{ \AA}^3$
$M_r = 479.50$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 16.6086 (15) \text{ \AA}$	$\mu = 4.29 \text{ mm}^{-1}$
$b = 6.1031 (3) \text{ \AA}$	$T = 298 \text{ K}$
$c = 31.450 (3) \text{ \AA}$	$0.10 \times 0.10 \times 0.05 \text{ mm}$
$\beta = 101.495 (6)^\circ$	

Data collection

Rigaku Mercury CCD diffractometer	11364 measured reflections
Absorption correction: multi-scan (<i>CrystalClear</i> ; Rigaku, 2002)	3566 independent reflections
$T_{\min} = 0.673$, $T_{\max} = 0.814$	3308 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	6 restraints
$wR(F^2) = 0.073$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\max} = 1.20 \text{ e } \text{\AA}^{-3}$
3566 reflections	$\Delta\rho_{\min} = -0.97 \text{ e } \text{\AA}^{-3}$
217 parameters	

Table 1

Selected bond lengths (Å).

Gd1—O1	2.310 (3)	Gd1—O5	2.499 (3)
Gd1—O2 ⁱ	2.434 (3)	Gd1—O6	2.410 (3)
Gd1—O3 ⁱⁱ	2.402 (3)	Gd1—O7	2.393 (3)
Gd1—O4 ⁱⁱⁱ	2.323 (3)	Gd1—O8	2.403 (3)

Symmetry codes: (i) $-x, -y + 2, -z$; (ii) $-x, -y + 3, -z$; (iii) $x + \frac{1}{2}, y - \frac{1}{2}, z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O7—H7A ^{iv} ···O5 ^{iv}	0.82	1.89	2.682 (4)	163
O7—H7B ^v ···O3	0.82	1.92	2.737 (4)	172
O8—H8A ^v ···O2 ^v	0.82	2.04	2.841 (4)	165
O8—H8B ^v ···O5 ^{iv}	0.82	2.21	2.893 (4)	140

Symmetry codes: (iv) $x, y + 1, z$; (v) $x + \frac{1}{2}, y + \frac{1}{2}, z$.

The water H atoms were located in difference Fourier maps and refined as riding in their as-found relative positions, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. Other H atoms were placed geometrically and refined as riding [$C-H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3207). Services for accessing these data are described at the back of the journal.

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