

Poly[[tetraaquad- μ_4 -glutarato- μ_2 -terephthalato-dineodymium(III)] heptadecahydrate]

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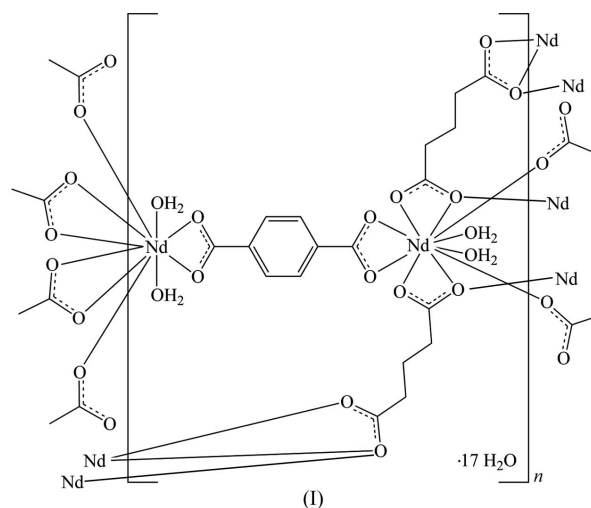
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The title compound, $[\text{Nd}_2(\text{C}_5\text{H}_6\text{O}_4)_2(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_4] \cdot 17\text{H}_2\text{O}$, obtained *via* hydrothermal reaction of Nd_2O_3 with glutaric acid and terephthalic acid, assembles as a three-dimensional open framework with ten-coordinate Nd–O polyhedra. The asymmetric part of the unit cell contains half a glutarate anion, a quarter of a terephthalate dianion, half an Nd^{III} cation, one coordinated water molecule and 4.25 solvent water molecules. Each $[\text{NdO}_{10}]$ coordination polyhedron is comprised of six O atoms originating from four glutarate anions, two others from a terephthalate carboxylate group, which coordinates in a bidentate fashion, and two from water molecules. The Nd–O distances range from 2.4184 (18) to 2.7463 (18) Å. The coordination polyhedra are interconnected by the glutarate anions, extending as a two-dimensional layer throughout the *bc* plane. Individual two-dimensional layers are interlinked *via* terephthalate anions along the *a* axis. This arrangement results in rectangular-shaped cavities with interstices of approximately $3.5 \times 6 \times 6.5$ Å (approximately 140 \AA^3), which are occupied by water molecules. The Nd^{III} cations, terephthalate anions, glutarate anions and one of the interstitial water molecules are located on special crystallographic positions. The Nd–terephthalate–Nd units are located across twofold rotation axes parallel to [100], with the Nd^{III} cations located directly on these axes. In addition, the terephthalate anion is bisected by a crystallographic mirror plane perpendicular to that axis, thus creating an inversion centre in the middle of the aromatic ring. The glutarate ligand is bisected by a crystallographic mirror plane perpendicular to (001). One of the solvent water molecules lies on a site of $2/m$ symmetry, and the symmetry-imposed disorder of its H atoms extends to the H atoms of the other four solvent water molecules, which are disordered over two equally occupied and mutually exclusive sets of positions.

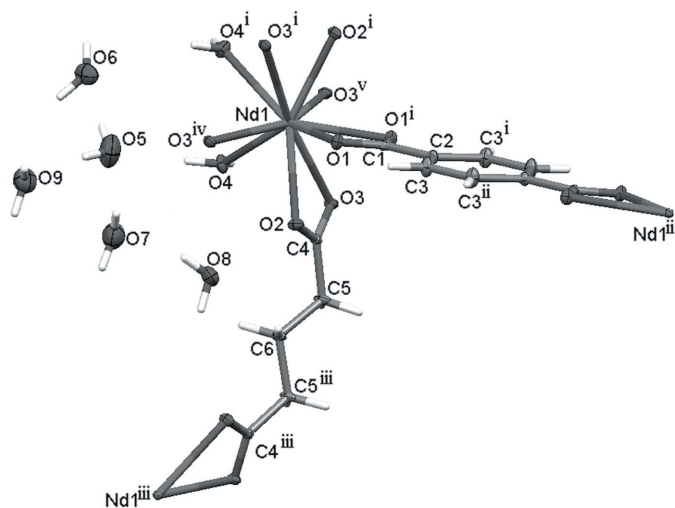
Comment

The synthesis of metal–organic frameworks (MOFs) has received increased consideration in recent years (Bradshaw *et al.*, 2005; Kawano *et al.*, 2007) because of their applications in diverse areas, *e.g.* gas storage (Eddaoudi *et al.*, 2002; Férey *et al.*, 2005; Liu *et al.*, 2007), drug delivery (Horcajada *et al.*, 2006, 2008; Vallet-Regi *et al.*, 2007) and electronics (Férey *et al.*, 2007), and also for the possible advancement of magnetic (Dietzel *et al.*, 2005; Kahn & Martinez, 1998), sensing (Chen *et al.*, 2008; Wong *et al.*, 2006) and catalytic (Gándara *et al.*, 2008; Müller *et al.*, 2008) systems. Terephthalic acid (TP) has become a very popular spacer ligand often used in MOFs, since it confers a high level of rigidity on the resulting compounds. In a recent paper (Zehnder *et al.*, 2010), we compared a number of lanthanide terephthalates with some of their already known counterparts, pointing out that the carboxylate groups experience an increased out-of-plane torsion for compounds of lanthanides with smaller ionic radii. For instance, $[\text{Nd}_2(\text{TP})_3(\text{H}_2\text{O})_4]$ exhibits maximum torsion angles between 25.1 (7) and 25.6 (7)° (Zehnder *et al.*, 2010). The Tb analogue experiences larger torsion angles of up to 28° (Reinecke *et al.*, 1999), while the Er counterpart, with the smallest ion radius, shows the highest degree of torsion at 30.6 (10)° (Pan *et al.*, 2001; Zehnder *et al.*, 2010).

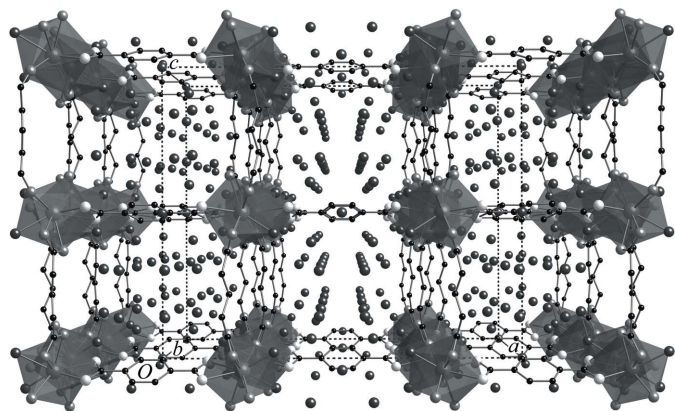
The combination of aliphatic dicarboxylates with more rigid building blocks, such as aromatic systems with two or more carboxylate groups, has led to the creation of stable framework structures with larger channels or solvent-filled voids (Borkowski & Cahill, 2004; He *et al.*, 2006; Serpaggi & Férey, 1998; Vaidhyanathan *et al.*, 2001) and to the development of unique network topologies (Li *et al.*, 2009; Wang *et al.*, 2009). The title compound, (I), represents another excellent example in this regard. To our knowledge, the single-crystal X-ray structural characterization of a lanthanide bis-glutarate terephthalate is unprecedented. Here, we describe the synthesis and characterization of (I), a lanthanide mixed-ligand complex incorporating two different organic components.



Compound (I) (Fig. 1) crystallizes in the orthorhombic crystal system in the space group *Cmcm* and assembles as a three-dimensional open framework. In this framework, the


Figure 1

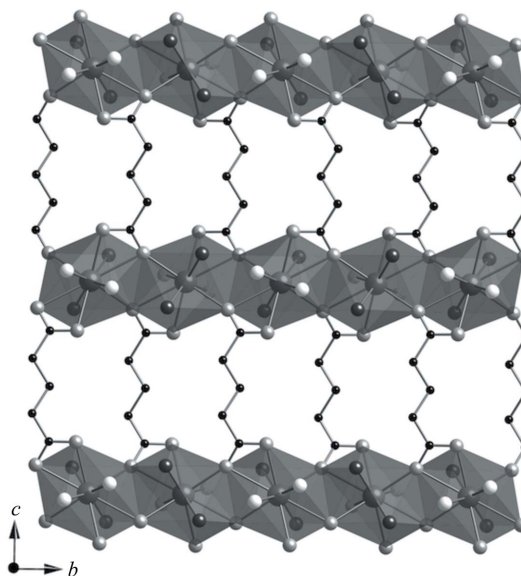
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Only the positions of one of the two alternative sets of disordered water H atoms are shown for clarity. Atoms Nd1 and O6 occupy sites of 2 and $2/m$ symmetry, respectively. [Symmetry codes: (i) $x, -y + 1, -z + 1$; (ii) $-x, y, z$; (iii) $x, y, -z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (v) $-x + \frac{1}{2}, y + \frac{1}{2}, z$.]


Figure 2

The packing of the $[\text{NdO}_{10}]$ polyhedra in (I), viewed along the b axis, showing interstitial water molecules. Light-grey spheres denote carboxylate O atoms from terephthalate anions, medium-grey spheres carboxylate O atoms from glutarate anions, dark-grey spheres water molecules, grey polyhedra $[\text{NdO}_{10}]$ units and small black spheres C atoms.

Nd^{III} cations, terephthalate anions, glutarate anions and one of the solvent water molecules are all located on special crystallographic positions. The Nd–terephthalate–Nd units are located on crystallographic twofold axes parallel to $[100]$, with the Nd^{III} cations located directly on these axes. In addition, the terephthalate anion is bisected by a crystallographic mirror plane perpendicular to that axis, thus creating an inversion centre in the middle of the aromatic ring. The glutarate ligand is bisected by a crystallographic mirror plane perpendicular to (001) .

Each central Nd^{III} cation is coordinated by ten O atoms, forming $[\text{NdO}_{10}]$ coordination polyhedra with the geometric shape of a bicapped square antiprism. Individual polyhedra


Figure 3

The arrangement of the glutarate anions in (I). Light-grey spheres denote carboxylate O atoms (O1) from terephthalate anions, medium-grey spheres carboxylate O atoms from glutarate anions (O2 and O3), dark-grey spheres water O atoms (O4), grey polyhedra $[\text{NdO}_{10}]$ units, small white spheres H atoms and small black spheres C atoms.

are stacked on top of each other. They share edges *via* two O atoms (O3) and form infinite chains running along the b axis in a staggered formation. The coordinating O atoms originate from two water molecules (O4), four glutarate carboxylate groups (six O atoms, two O2 and four O3) and one terephthalate carboxylate group (O1). Each terephthalate anion connects two $[\text{NdO}_{10}]$ polyhedra along the a axis in a bidentate fashion. Along the b axis, the $[\text{NdO}_{10}]$ polyhedra form AB layers as they alternate their orientation by 180° . As a result, terephthalate anions alternate with coordinated water molecules along the b direction (Fig. 2). Each glutarate carboxylate group connects two $[\text{NdO}_{10}]$ coordination polyhedra, with one O atom (O2) coordinating in a κ^1 fashion to a central Nd^{III} cation. The second O atom of each glutarate carboxylate group (O3) connects in a μ_2 fashion to two adjacent Nd^{III} central cations. All corresponding Nd1–O bond distances are summarized in Table 1. The glutarate anions infinitely link the Nd^{III} cations along the c axis. Simultaneously, they connect adjacent Nd^{III} metal centres along the b axis, creating highly interconnected two-dimensional layers of Nd^{III} cations and glutarate anions (Fig. 3). These layers are tied together by the terephthalate anions along the a axis.

The combination of two glutarate anions and one terephthalate anion per pair of Nd^{III} cations results in the formation of larger rectangular channels that stretch infinitely along the c axis. These channels have an approximate size of $3.5 \times 6 \text{ \AA}$. This arrangement of terephthalate and glutarate anions also results in the formation of nearly square-shaped infinite channels stretching along the b axis, with side lengths of approximately $6.5 \times 6 \text{ \AA}$. These channels bisect the others in a

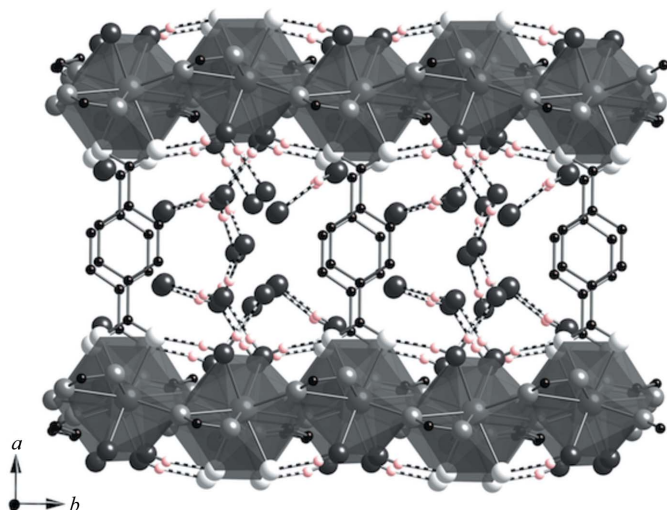


Figure 4

O—H...O hydrogen-bonding interactions (black-and-white dashed lines) between coordinated and interstitial water molecules in (I). Light-grey spheres denote carboxylate O atoms (O1) from terephthalate anions, medium-grey spheres carboxylate O atoms from glutarate anions (O2 and O3), dark-grey spheres water O atoms (O4), grey polyhedra [NdO₁₀] units, small white spheres H atoms and small black spheres Nd atoms.

perpendicular fashion, creating rectangular interstices of approximately 140 Å³. These interstices are occupied by water molecules, which are connected to the framework backbone and each other through O—H...O hydrogen-bonding interactions (Table 2). Fig. 4 shows how the two coordinated water molecules of one [NdO₁₀] polyhedron connect *via* O—H...O hydrogen bonds (H...O = 1.93 Å) to the carboxylate O atoms of the terephthalate anions that belong to the two adjacent coordination polyhedra. Additionally, these water molecules connect *via* O—H...O hydrogen bonds (H...O = 1.91 Å) to the interstitial water molecules within the channels. The hydrogen-bonding interactions between the interstitial water molecules themselves are disordered, due to one of the water O atoms (O6) being located at the centre of the unit cell at $(x, y, z) = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ on a special position that does not agree with the point symmetry of a water molecule. Two sets of half-occupied water H atoms were thus refined (see *Refinement* section for details). These water molecules connect *via* hydrogen bonds with H...O bond distances in the range 1.89–1.93 Å (Table 2).

The terephthalate anions hardly experience any tension, as their carboxylate groups are aligned in-plane with the conjugated π system, and they show only minor out-of-plane torsions not exceeding 3.4°. This is supported by the fact that most of the bond angles involving the Csp³ atoms in the glutarate anions are very close to the tetrahedral angle (108.7–109.1°) and only the C—C—C angles are slightly stretched, to 112.6 (3) and 114.1 (2)°. The resulting solvent-accessible areas are significantly larger than in the regular lanthanide terephthalates. Therefore, we expect that the interstices in related structures can be tuned by replacing the glutaric acid units with longer or shorter aliphatic dicarboxylates, such as adipates, pimelates, suberates, *etc.*

Experimental

Neodymium oxide (Acros Organics, 99.90%) (0.25 g, 0.75 mmol), terephthalic acid (Aldrich) (0.25 g, 1.5 mmol) and glutaric acid (Eastman) (0.10 g, 0.75 mmol) were suspended in deionized water (~15 ml) and placed in a Teflon liner inside a Parr acid-digestion vessel (model 4744; 45 ml capacity). The vessel was sealed and placed in a conventional laboratory oven at 443 K for 5 d. At the end of the heating period, the vessel was removed from the hot oven and allowed to cool to room temperature before opening. A solid material was obtained, submerged in the mother liquor. The solid product was pale purple in colour. It was rinsed four times with deionized water in order to remove any soluble by-products. A large quantity of the product, (I), had formed crystals in the form of large rectangular blocks. Small amounts of the product were stored in a scintillation vial with small quantities of deionized water until a single crystal was chosen for X-ray structural analysis (yield 0.23 g, 0.21 mmol; 56%). FT-IR (KBr, ν , 4000–500 cm⁻¹): 3454 (*br*), 3230 (*sh*) 3058 (*w*), 1608 (*sh*), 1596, (*sh*), 1549 (*sh*), 1540 (*vs*), 1516 (*sh*), 1504 (*vs*), 1418 (*vs*), 1403 (*vs*), 1310 (*s*), 1245 (*sh*), 1155 (*m*), 1101 (*w*), 1064 (*w*), 1050 (*w*), 1020 (*m*), 988 (*w*), 968 (*w*), 883 (*m*), 827 (*m*), 761 (*sh*), 750 (*s*), 576 (*sh*), 554 (*sh*), 528, (*m*), 509 (*m*). The FT-IR spectrum exhibits the strong bands one expects to see for the symmetric and asymmetric vibrations of terephthalate and glutarate (1700–1470 and 1460–1220 cm⁻¹), as well as those of the interstitial water molecules (3300–3600 cm⁻¹). The vibrations of the carboxylate groups can be observed at around 1600 cm⁻¹. They are shifted to somewhat lower frequencies, which can be attributed to the coordination of the carboxylate groups to the Nd^{III} atoms.

Analysis calculated for (C₁₈H₅₈O₃₃Nd₂)Nd₂(TP)(Glut)₂(H₂O)₄·17H₂O: C 19.82, H 5.36, N 0.00%; found: C 31.07, H 2.46, N 0.05%. Based on these data, we assume that we did not obtain a pure phase of this compound. The results would be close to the water-free compound, (C₁₈H₁₆O₁₂Nd₂)Nd₂(TP)(Glut)₂ (C 30.33, H 2.26%). This is rather unlikely, however, since we did not use high drying temperatures (<353 K), and the IR spectrum exhibits a broad band between 3400 and 3500 cm⁻¹, which suggests the presence of water.

Crystal data

[Nd ₂ (C ₅ H ₆ O ₄) ₂ (C ₈ H ₄ O ₄)(H ₂ O) ₄ ·17H ₂ O]	$V = 4082.6 (5) \text{ \AA}^3$
$M_r = 1091.12$	$Z = 4$
Orthorhombic, <i>Cmcm</i>	Mo $K\alpha$ radiation
$a = 24.0265 (16) \text{ \AA}$	$\mu = 2.62 \text{ mm}^{-1}$
$b = 8.7253 (6) \text{ \AA}$	$T = 100 \text{ K}$
$c = 19.4746 (13) \text{ \AA}$	$0.31 \times 0.29 \times 0.10 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer	36277 measured reflections
Absorption correction: multi-scan (APEX2; Bruker, 2009)	3403 independent reflections
$T_{\min} = 0.622$, $T_{\max} = 0.746$	2941 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	125 parameters
$wR(F^2) = 0.083$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\max} = 2.45 \text{ e \AA}^{-3}$
3403 reflections	$\Delta\rho_{\min} = -0.84 \text{ e \AA}^{-3}$

The H atoms of the interstitial water molecules located in the channels of the structure are disordered, due to hydrogen bonds across elements of symmetry that create mutually exclusive H-atom positions. The disorder originates with the water molecule of atom O6

Table 1

Independent Nd—O bond distances (Å) in the [NdO₁₀] polyhedron of (I).

Bond	Bond distance	Description
Nd1—O3	2.4184 (18)	Carboxylate groups from glutarate units (μ_2)
Nd1—O2	2.5130 (18)	Carboxylate groups from glutarate units (κ^1)
Nd1—O4	2.5164 (19)	Coordinating H ₂ O
Nd1—O1	2.5434 (18)	Carboxylate groups from terephthalate units
Nd1—O3	2.7463 (18)	Carboxylate groups from glutarate units (μ_2)

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O4—H4A...O5	0.84	1.91	2.750 (3)	176
O4—H4B...O1 ⁱ	0.84	1.93	2.762 (3)	168
O5—H5A...O9	0.84	1.92	2.751 (4)	168
O5—H5B...O6	0.84	1.92	2.764 (3)	178
O5—H5C...O7	0.84	1.91	2.720 (5)	161
O6—H6A...O5	0.84	1.97	2.764 (3)	156
O7—H7A...O8	0.84	1.90	2.699 (4)	158
O7—H7B...O5	0.84	1.91	2.720 (5)	163
O7—H7C...O7 ⁱⁱ	0.84	1.93	2.756 (6)	167
O7—H7D...O7 ⁱⁱⁱ	0.84	1.93	2.760 (6)	171
O8—H8A...O7	0.84	1.89	2.699 (4)	162
O8—H8B...O2 ⁱ	0.84	1.92	2.741 (3)	167
O8—H8C...O8 ⁱⁱⁱ	0.84	1.90	2.734 (5)	174
O9—H9A...O8 ^{iv}	0.84	1.92	2.727 (4)	162
O9—H9B...O9 ⁱⁱ	0.84	1.92	2.749 (6)	169
O9—H9C...O9 ⁱⁱⁱ	0.84	2.01	2.846 (6)	177

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

located at the centre of the unit cell at $(x, y, z) = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ on an inversion centre at the intersection of a mirror and a glide plane, and a twofold rotation and a screw axis, a site symmetry that does not agree with the point symmetry of a water molecule. Atom O6 was thus refined as being bonded to one crystallographically independent H atom (located in a difference density Fourier map). Application of the site symmetry creates four equivalent H atoms, which were refined as half-occupied to form two differently oriented water molecules located at the site of O6. The disorder of the H atoms around O6 induces disorder of the H atoms bonded to atoms O5, O7, O8 and O9, the other interstitial water molecules. H atoms were tentatively located in difference density Fourier maps. In the initial refinement cycles, H-atom positions were restrained using O—H distance restraints of 0.84 (2) Å and variable H...O distance restraints between 1.90 (2) and 2.01 (2) Å based on hydrogen-bonding considerations, taking the disorder into account. In the final refinement cycles, water H atoms were set to ride on their carrier O atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Carbon-bound H atoms were placed in calculated positions, with C—H = 0.95 Å for aromatic H atoms and 0.99 Å for methylene H atoms, and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *CrystalMaker for Mac* (Palmer, 2010); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3367). Services for accessing these data are described at the back of the journal.

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