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A gadolinium-based metal–organic framework, poly[[tris(μ_4-benzene-1,4-dicarboxylato)-bis(μ_2-*N*,*N*-diethylformamide)digadolinium(III)] monohydrate]

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
H-atom completeness 95%
Disorder in main residue
R factor = 0.022
wR factor = 0.054
Data-to-parameter ratio = 41.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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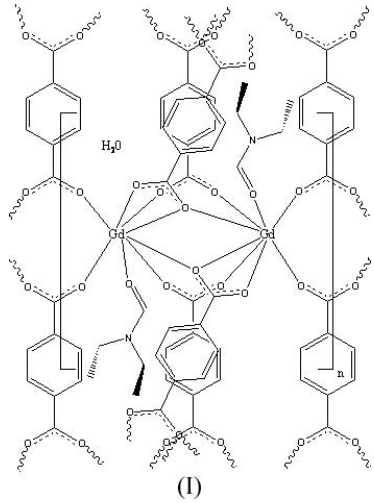
The crystal structure of the title compound, $\{[Gd_2(C_8H_4O_4)_3(C_5H_{11}NO)_2]\cdot H_2O\}_n$, consists of chains of Gd atoms interconnected by a benzene-1,4-dicarboxylate (BDC) linker. The chains are also intraconnected by carboxylate groups from the BDC linker, thus generating a three-dimensional framework with large cavities. The coordination of the eight carboxylate O atoms around the Gd^{III} ion is distorted dodecahedral, due to the steric constraints of the carboxylate groups. The large anisotropic displacement parameters of the atoms of the coordinated diethylformamide (DEF) and the disorder in their positions indicate loose bonding to the framework, and hence solvent exchange may be possible. Additionally, one water molecule is located in the cavity.

Comment

Metal–organic frameworks (MOFs) are of great scientific interest (Kitahawa *et al.*, 2004; Lu, 2003; O′Keeffe *et al.*, 2000). Their potential use in gas storage has gained enormous attention worldwide. Our main research effort has so far been focused on the magnetic properties of these compounds (Zhang *et al.*, 2005), and in this context the title structure, (I), is the first in a series of new MOFs which may combine interesting magnetic effects and potential gas storage, due to their electron-rich metal centres.



(I)

The structure of (I) consists of chains of carboxylate-bridged Gd^{III} atoms interconnected by benzene-1,4-dicarboxylate (BDC) linkers. The Gd chains are aligned along the *c* axis and thus there appears to be a unique magnetic direction, as interchain distances (>9.7 Å) are much larger than the intrachain Gd···Gd distance of 4.0363 (1) Å.

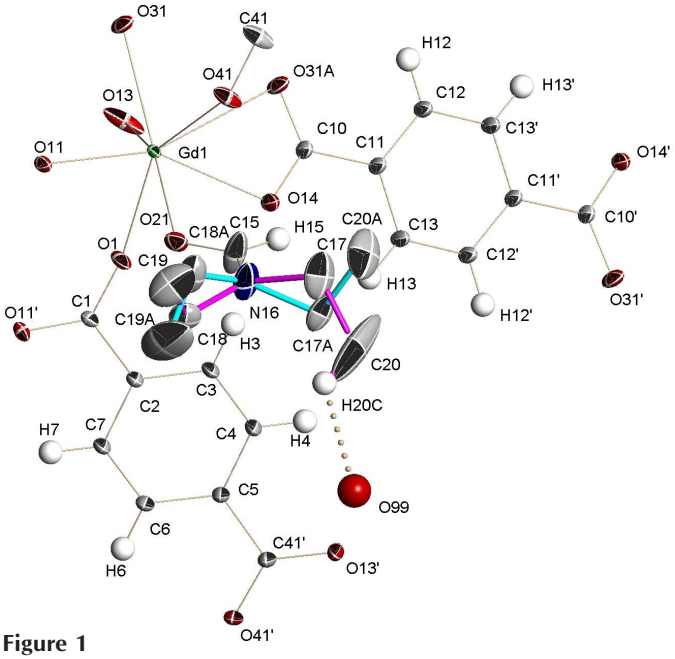


Figure 1
Part of the structure of the title compound. The disorder of the ethyl groups is shown with purple and turquoise bonds. For clarity, all ethyl H atoms except H20*C* have been omitted. Displacement ellipsoids are drawn at the 50% probability level.

The Gd^{III} ion is coordinated by seven O atoms from the carboxylate groups and one O atom from the diethylformamide (DEF) molecule. There is one μ-bridging carboxylate atom, O31, which bridges two Gd atoms with a long [Gd—O 2.818 (1) Å] and a short [Gd—O 2.381 (1) Å] bond. Not taking the long bond into account, the average bond length of the remaining carboxylate O atoms, <Gd—O(carboxylate)>, is 2.339 (1) Å, while <Gd—O(DEF)> is 2.428 (1) Å. The intraconnection of the Gd atoms by bridging carboxylate $(OCO)^-$ groups and only one bridging O31 atom gives rise to a disrupted Gd—O—Gd coupling.

The carboxylate groups in (I) are all delocalized, with an average C—O bond length of 1.260 (2) Å. This gives a net charge of -0.5 e$^-$ for each unique O atom. A formal electron count suggests that the Gd atom has a charge of +3, which is in agreement with the synthesis conditions.

In the crystal structure of (I), the inner parts of the voids are occupied by DEF molecules, which are bonded directly to the Gd atoms. As previously reported (Poulsen *et al.*, 2004, 2005) DEF solvent molecules do not only occupy the voids but also bond directly to the metal centres. The ethyl groups of the DEF molecule are disordered, with no overlap of atoms in the two positions [occupancy factors of 0.622 (6) and 0.378 (6)]. A single water molecule is found in the void, disordered over two crystallographically equivalent positions (50:50%) only 1.086 Å apart. The two H atoms of this water molecule were not located or included in the refinement.

Due to the bonding of the DEF molecule to the framework, it has been possible to refine the anisotropic displacement parameters of all non-H atoms. The displacement ellipsoid of the methyl group atom C20 is highly elongated towards H20*C*. This is probably due to further unresolved disorder.

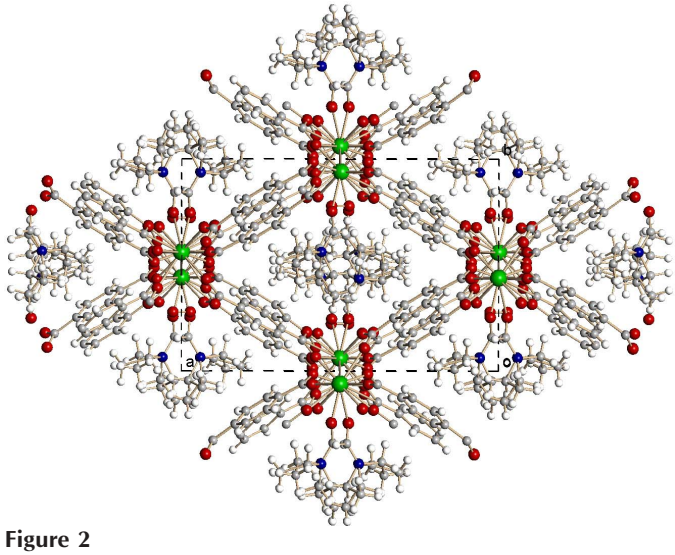


Figure 2
A packing diagram for (I).

Experimental

The title compound was prepared in an autoclave by adding a mixture of benzene dicarboxylic acid (BDC; 1 mmol, 0.166 g) and diethylformamide (DEF; 7 ml) to a solution of $Gd(NO_3)_3\,5H_2O$ (1.0 mmol, 0.434 g) in DEF (3 ml). The mixture was kept at 383 K for 72 h. White crystals of (I) suitable for single-crystal X-ray analysis were formed.

Crystal data

$[Gd_2(C_8H_4O_4)_3(C_5H_{11}NO)_2]\cdot H_2O$	D_x = 1.864 Mg m^{-3}
M_r = 1025.13	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 7811 reflections
a = 18.0582 (5) Å	θ = 2.8–42.4°
b = 11.4381 (3) Å	μ = 3.67 mm^{-1}
c = 18.6791 (4) Å	T = 100 (2) K
β = 108.796 (1)°	Block, white
V = 3652.44 (16) Å^3	0.20 × 0.05 × 0.05 mm
Z = 4	

Data collection

Bruker X8 APEXII CCD-based diffractometer	11366 independent reflections
φ and ω scans	9378 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	R_{int} = 0.039
T_{min} = 0.741, T_{max} = 0.830	θ_{max} = 43.0°
61459 measured reflections	$h = -33 \rightarrow 29$
	$k = -20 \rightarrow 20$
	$l = -33 \rightarrow 32$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.022	$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.054	$(\Delta/\sigma)_{max}$ = 0.001
S = 0.95	$\Delta\rho_{max}$ = 2.59 e Å^{-3}
11366 reflections	$\Delta\rho_{min}$ = −0.96 e Å^{-3}
277 parameters	

H atoms bonded to C atoms were included in calculated positions (C—H = 0.95–0.99 Å) and refined in a riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(C) for methyl groups. The disorder in the DEF molecule has no overlapping positions, and the sum of the two disordered occupancies was fixed to unity. The nine largest residual peaks were distributed within 0.75 Å around the Gd atoms.

Data collection: *APEX2* (Bruker–Nonius, 2004); cell refinement: *SAINT-Plus*; data reduction: *SAINT-Plus* (Bruker–Nonius, 2004);

program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XSHELL* (Bruker, 2004); software used to prepare material for publication: *enCIFer* (version 1.1; Allen *et al.*, 2004).

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