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Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in main residue
 R factor = 0.028
 wR factor = 0.057
Data-to-parameter ratio = 23.3

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

Poly[sesqui(μ_4 -biphenyl-4,4'-dicarboxylato- $\kappa^4\text{O}:\text{O}':\text{O}'':\text{O}'''$)(diethylformamide- κO)gadolinium]

The crystal structure of the title compound, $[\text{Gd}(\text{C}_{14}\text{H}_8\text{O}_4)_{1.5}(\text{C}_5\text{H}_{11}\text{NO})]_n$, comprises chains of Gd atoms intra-connected by the carboxylate groups of the biphenyl-4,4'-dicarboxylate (BPDC) linkers, one of which is disposed about a twofold axis. The Gd atom chains are aligned along the b axis and are interconnected by BPDC linkers, creating a three-dimensional framework. A single diethylformamide (DEF) molecule is bonded to each Gd atom. This molecule is positioned in the cavities formed by the interconnection of the Gd atom chains *via* the BPDC linkers. Due to the steric constraints of the carboxylate groups, the square antiprismatic coordination geometry of eight O atoms (one from the DEF molecule and seven from carboxylate groups) around Gd is distorted.

Received 16 September 2005
Accepted 10 October 2005
Online 15 October 2005

Comment

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

The structure of (I) comprises chains of 4,4'-biphenyl-dicarboxylate (BPDC)-bridged Gd atoms interconnected by BPDC linkers. The Gd chains are aligned along the b axis, and thus there appears to be a unique magnetic direction, as the interchain Gd...Gd distances (> 8.8 Å) are much longer than the intrachain Gd...Gd distance of 4.5553 (1) Å.

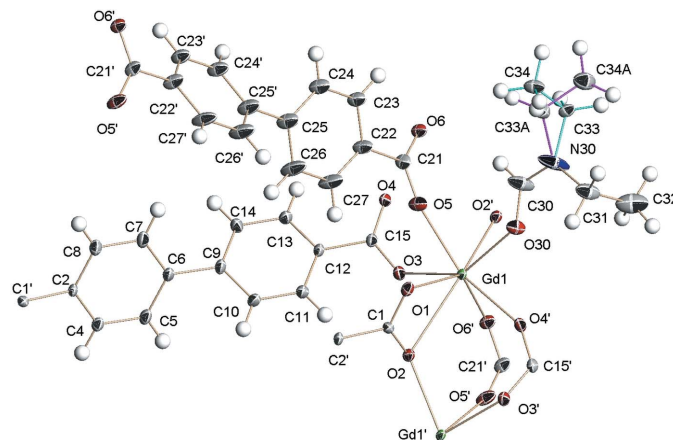
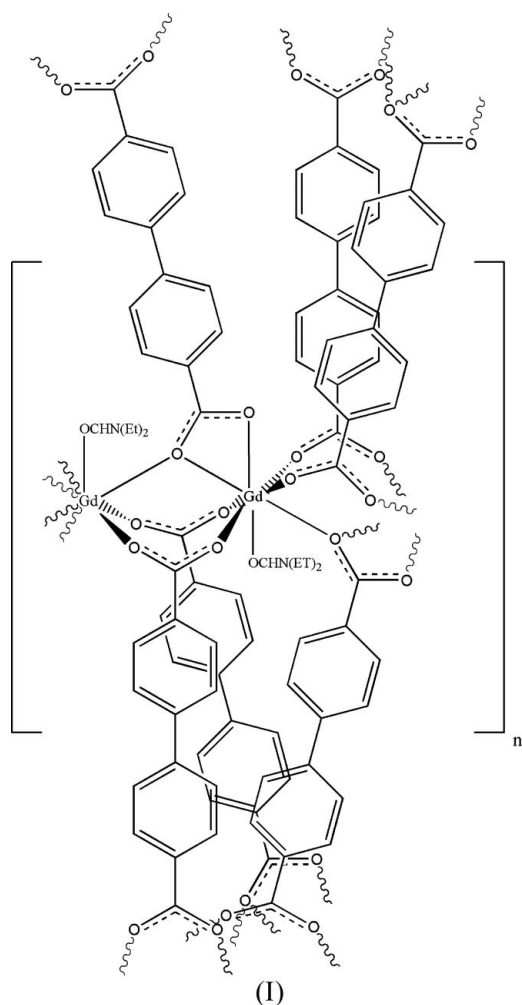


Figure 1
Part of the structure of (I), showing the atomic numbering scheme. The disorder of the ethyl groups is shown with purple and turquoise bonds, and displacement ellipsoids are drawn at the 50% probability level.



The Gd ion is coordinated by seven O atoms from the carboxylate groups and one O atom from the DEF molecule. There is one bridging carboxylate atom, O2, which bridges two neighbouring Gd atoms with long [Gd–O = 2.766 (2) Å] and short [Gd–O = 2.396 (2) Å] bonds. Not taking the long bond into account, the average length of the remaining bonds to carboxylate O atoms is 2.356 (2) Å, while Gd–O(DEF) is 2.382 (2) Å. The connection of the Gd atoms by bridging carboxylate groups and only one bridging atom, O2, gives rise to a continuous Gd–O–Gd coupling. The carboxylate groups are all delocalized, with an average C–O bond length of 1.260 (3) Å. This gives a net negative 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 an earlier study, a Gd MOF based on the benzene-1,4-dicarboxylate linker (BDC) has been characterized, [Gd₂(C₈H₄O₄)₃(C₅H₁₁NO)₂·H₂O], (II) (Poulsen, Overgaard *et al.*, 2005). The goal of the present study of (I) was to achieve a similar framework, using a somewhat elongated organic linker that would give longer interchain distances. Despite the observation that the coordination of eight O atoms around the

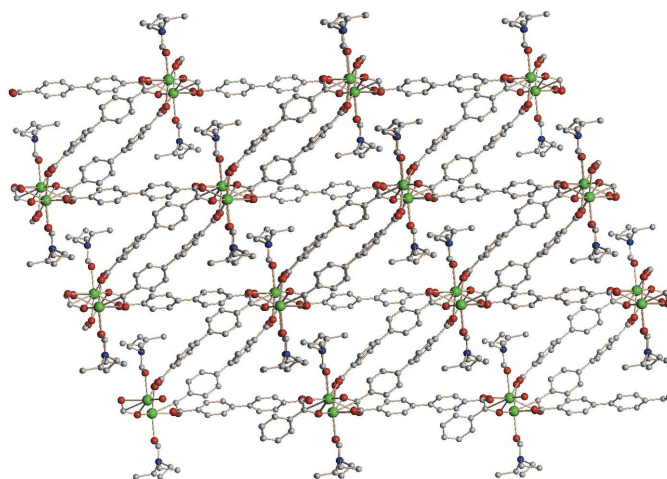


Figure 2
A packing diagram for (I).

Gd centres in (I) and (II) is similar, the framework structures are not identical. Additionally, contrary to what is observed in (II), the bridging atom O2 in (I) forms a continuous Gd–O–Gd coupling throughout the Gd chain, which may result in a better magnetic coupling of the Gd atoms within the metal-atom chains. Furthermore, contrary to the coplanar BDC linkers of the structure of (II), the π systems of the two benzene rings of the BPDC linker of (I) are twisted with respect to each other and with respect to the two carboxylate groups, hence creating unaligned π systems. For one of the two unique BPDC ligands, the twist occurs only along the main axis of the BPDC linker, while the two benzene rings of the other BPDC ligand are also bent with respect to each other, resulting in a banana-shaped ligand.

The BPDC linkers of (I) span voids, which then are occupied by the coordinated diethylformamide (DEF) solvent molecules, bonded directly to the Gd atoms. This has previously been reported in other MOF systems (Poulsen, Bonten *et al.*, 2005; Poulsen, Overgaard *et al.*, 2005), where DEF is bound directly to the metal centres.

Experimental

The title compound was prepared in an autoclave by adding a mixture of biphenyldicarboxylic acid (1 mmol, 0.243 g) and diethylformamide (DEF, 7 ml) to a solution of Gd(NO₃)₃·5H₂O (1 mmol, 0.434 g) dissolved in DEF (3 ml). This was kept at 403 K for 48 h. White crystals of (I) suitable for single-crystal X-ray analysis were formed.

Crystal data

[Gd(C₁₄H₈O₄)_{1.5}(C₅H₁₁NO)₂]
 M_r = 618.70
 Monoclinic, C2/c
 a = 29.9380 (6) Å
 b = 8.8060 (2) Å
 c = 19.6782 (4) Å
 β = 116.252 (1)°
 V = 4652.75 (17) Å³
 Z = 8

D_x = 1.766 Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5090 reflections
 θ = 2.3–28.8°
 μ = 2.90 mm⁻¹
 T = 120 (2) K
 Block, white
 0.08 × 0.03 × 0.03 mm

Data collection

Bruker SMART APEXII CCD diffractometer	7882 independent reflections
φ and ω scans	5967 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	$R_{\text{int}} = 0.068$
$T_{\text{min}} = 0.884$, $T_{\text{max}} = 0.930$	$\theta_{\text{max}} = 31.8^\circ$
53683 measured reflections	$h = -44 \rightarrow 44$
	$k = -12 \rightarrow 13$
	$l = -28 \rightarrow 29$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.028$	$w = 1/[\sigma^2(F_o^2) + (0.024P)^2]$
$wR(F^2) = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{\text{max}} = 0.002$
7882 reflections	$\Delta\rho_{\text{max}} = 1.19 \text{ e } \text{\AA}^{-3}$
338 parameters	$\Delta\rho_{\text{min}} = -1.01 \text{ e } \text{\AA}^{-3}$

The H atoms of the biphenyldicarboxylate linker and the diethylformamide molecule were placed in calculated positions, with C–H = 0.95 (aromatic), 0.98 (methyl) or 0.99 Å (methylene), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic and methylene C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. Disorder in the DEF molecule was noted and resolved into two sites (anisotropic refinement) with no overlapping positions; the major component has a site occupancy factor of 0.533 (8). The maximum and minimum residuals were distributed around the Gd atom, at distances of 0.80 and 0.77 Å, respectively.

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

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

Financial support of this work by the Carlsberg Foundation is gratefully acknowledged.

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