

An Eu-based metal–organic framework: poly[[tris-(μ_4 -benzene-1,4-dicarboxylato)bis(μ_2 -*N,N*-diethylformamide)dieuropium(III)] 0.7-hydrate]Henrik F. Clausen,^a Jacob Overgaard,^a Rasmus D. Poulsen,^a Wolfgang Morgenroth^b and Bo B. Iversen^{a*}^aDepartment of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark, and ^bDeutsches Elektronen-Synchrotron, D3 beamline, Hasylab, Notkestrasse 85, Hamburg D-22603, Germany

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Key indicators

Single-crystal synchrotron study

T = 100 K

Mean σ (C–C) = 0.002 Å

H-atom completeness 97%

Disorder in main residue

R factor = 0.037

wR factor = 0.090

Data-to-parameter ratio = 76.9

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

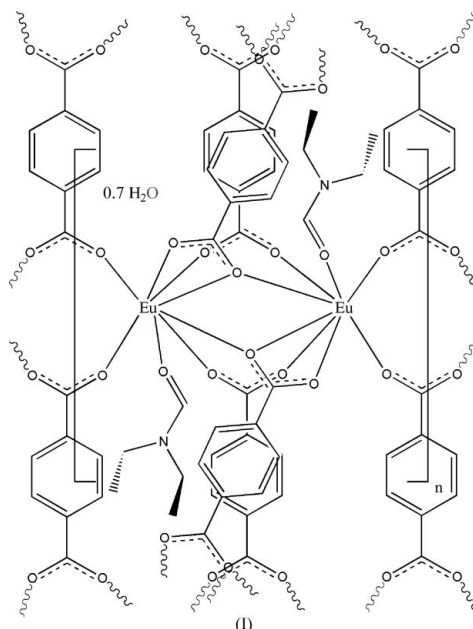
The crystal structure of the title compound, $\{[\text{Eu}_2(\text{C}_8\text{H}_4\text{O}_4)_3(\text{C}_5\text{H}_{11}\text{NO})_2] \cdot 0.7\text{H}_2\text{O}\}_n$, consists of chains formed by Eu atoms connected by the carboxylate groups of the benzene-1,4-dicarboxylate (BDC) linker. The chains are interconnected by BDC linkers, generating a three-dimensional framework with large voids. The Eu atoms are coordinated by seven carboxylate O atoms and one solvent O atom in a sterically constrained manner due to the carboxylate group rigidity, and this causes the coordination to be distorted dodecahedral. The ethyl groups of the solvent ligand are disordered in the void. The elongated Eu–O bond to the solvent indicates that it is loosely bound to the framework, and hence solvent exchange may be possible. In the void there is additionally one partly occupied disordered water molecule.

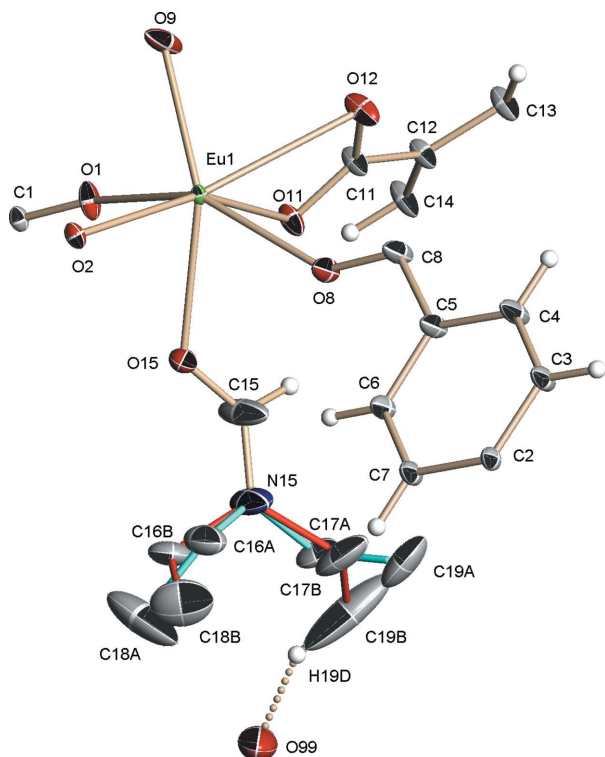
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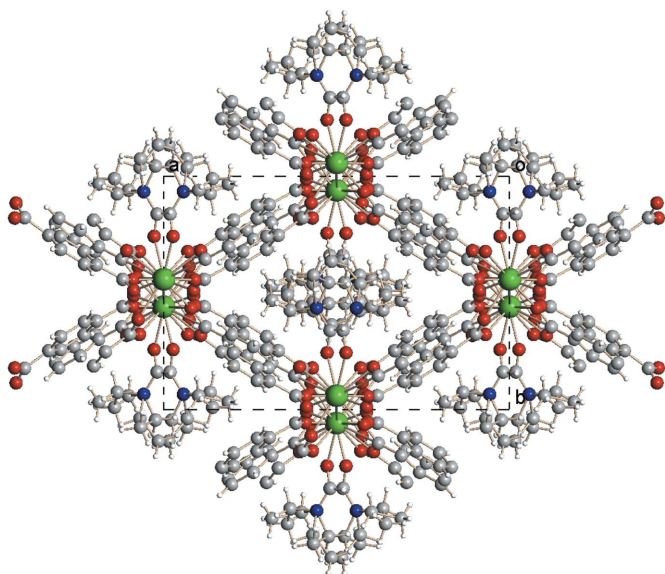
Comment

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 attracted enormous attention worldwide. The main research activity in our group has focused on the magnetic properties of these compounds (Poulsen, Bentien *et al.*, 2005). The present structure, (I), is one in a series of MOFs which may combine interesting magnetic effects and potential gas storage due to the electron-rich metal centers. An isostructural Gd-based compound was reported by Poulsen, Overgaard *et al.* (2005).




Figure 1

The asymmetric unit of the title compound. The disorder of the ethyl groups is shown with turquoise and red bonds (47%/53%). All ethyl H atoms except H19D have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.


Figure 2

The packing of the structure, viewed along the *c* axis of the unit cell.

Eu atoms are connected by carboxylate groups of the deprotonated terephthalate ligands, generating chains of metal atoms. These chains are interconnected by the terephthalate ligands, resulting in a three-dimensional network. The intra-chain Eu···Eu distance is alternately 4.034 (2) and 5.572 (4) Å, whereas the inter-chain distance is much larger (> 9.6 Å). This could lead to a unique magnetic direction along the *c* axis of the unit cell.

The short intra-chain distance has four bridging carboxylate groups and two direct μ -bridging O atoms (O12). The bridging atom has one short [Eu—O = 2.4007 (15) Å] and one long [Eu—O = 2.7884 (18) Å] bond to the Eu atoms. Excluding the longer bridging bond, the bond length average from the carboxylate O atoms to the Eu atom, $\langle \text{Eu—O}(\text{carboxylate}) \rangle$, is 2.353 (2) Å. This average is smaller than the bond length to the diethyl formamide molecule, $\langle \text{Eu—O}(\text{DEF}) \rangle = 2.436 (6)$ Å, hence this molecule is more weakly bonded and could be subject to solvent exchange. Because of the sterically constrained carboxylate groups, the coordination of the Eu atoms is distorted dodecahedral.

A slight degree of electron localization is observed in the carboxylate group bridging the long Eu···Eu distance, while the others are delocalized. A carboxylate group has a net charge of $-1e^-$, and a formal electron count suggests that the Eu atom has a charge of +3, which is in agreement with the synthesis conditions.

The voids of the network are occupied by disordered solvent molecules [0.525 (3):0.475 (3)], which are directly bonded to the Eu atoms. The bonding of solvent to the framework metal center was previously reported in Mn-based systems (Poulsen *et al.*, 2004; Poulsen, Bentien *et al.*, 2005).

A partially occupied water molecule [0.350 (8)], which is disordered over two equivalent crystallographic positions, also occupies the void. The large displacement parameter observed for atom C19B could mask disorder related to hydrogen bonding to the partly occupied water molecule, O99.

Experimental

The title compound was prepared by adding a mixture of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (1.0 mmol, 0.366 g) and DEF (3 ml) to a mixture of benzene-1,4-dicarboxylic acid, H_2BDC (1 mmol, 0.166 g), and DEF (7 ml) in an autoclave. After heating at 393 K for 72 h, white crystals suitable for single-crystal X-ray diffraction experiments were formed.

Crystal data

$[\text{Eu}_2(\text{C}_8\text{H}_4\text{O}_4)_3(\text{C}_5\text{H}_{11}\text{NO})_2] \cdot 0.7\text{H}_2\text{O}$
 $M_r = 505.08$
 Monoclinic, $C2/c$
 $a = 18.010 (7)$ Å
 $b = 11.478 (7)$ Å
 $c = 18.743 (12)$ Å
 $\beta = 108.91 (3)^\circ$
 $V = 3665 (4)$ Å³

$Z = 8$
 $D_x = 1.831$ Mg m⁻³
 Synchrotron radiation
 $\lambda = 0.550 (1)$ Å
 $\mu = 1.63$ mm⁻¹
 $T = 100 (2)$ K
 Rectangular block, white
 0.10 × 0.10 × 0.08 mm

Data collection

Huber four-circle diffractometer
 φ scans
 Absorption correction: none
 424451 measured reflections

22159 independent reflections
 19344 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.126$
 $\theta_{\text{max}} = 38.8^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.090$
 $S = 1.05$
 22159 reflections
 288 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 7.3908P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.011$
 $\Delta\rho_{\text{max}} = 3.47$ e Å⁻³
 $\Delta\rho_{\text{min}} = -3.26$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00453 (17)

H atoms were included in calculated positions ($C-H = 0.93-0.97 \text{ \AA}$) and refined in a riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$ for all H atoms besides the methyl groups, where the value was $1.5U_{eq}(C)$. The disorder in the DEF molecule has no overlapping positions, and the sum of two disordered occupancies was fixed at unity. Bonding to the framework limits the disorder in the DEF molecule and enabled refinement of the anisotropic displacement parameters of all non-H atoms. The occupancy of the water molecule was refined to 0.350 (8), and because of disorder the two H atoms could not be located, but they are included in the formula. A correction for the oblique incidence of the X-ray beam through the detector has been made using a transmission factor of 0.37 for the MarCCD detector measured at a wavelength of 0.55 &.

Data collection: *MarFID3* (Paulmann & Morgenroth, 2005); cell refinement: *XDS2004* (Kabsch, 1993); data reduction: *XDS2004*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XSELL* (Version 4.02); software used to prepare material for publication: *enCIFer* (Version 1.2; Allen *et al.*, 2004).

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References

- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Kabsch, W. (1993). *J. Appl. Cryst.* **26**, 795–800.
- Kitahawa, S., Kitaura, R. & Noro, S. (2004). *Angew. Chem. Int. Ed.* **43**, 2334–2375.
- Lu, J. Y. (2003). *Coord. Chem. Rev.* **246**, 327–347.
- O’Keeffe, M., Eddaoudi, M., Li, H., Reineke, T. & Yaghi, O. M. (2000). *J. Solid State Chem.* **152**, 1, 3–20.
- Paulmann, C. & Morgenroth, W. (2005). *MarFID3*. CCD Data Collection Software at Crystallographic Beamlines D3 and F1, Hasylab Jahresbericht, pp. 1121–1122.
- Poulsen, R. D., Bentien, A., Chevalier, M. & Iversen, B. B. (2005). *J. Am. Chem. Soc.* **127**, 9156–9166.
- Poulsen, R. D., Bentien, A., Graber, T. & Iversen, B. B. (2004). *Acta Cryst. A* **60**, 382–389.
- Poulsen, R. D., Overgaard, J., Chevallier, M.-A., Clausen, H. F. & Iversen, B. B. (2005). *Acta Cryst. E* **61**, m1337–m1339.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.