crystal engineering

Three new europium(III) methanetriacetate metal-organic frameworks: the influence of synthesis on the product topology

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Three new metal-organic framework structures containing Eu^{III} and the little explored methanetriacetate ($C_7H_7O_6^{3-}$, mta^{3-}) ligand have been synthesized. Gel synthesis yields a two-dimensional framework with the formula $[Eu(mta)(H_2O)_3]_n \cdot 2nH_2O$, (I), while two polymorphs of the three-dimensional framework material $[Eu(mta)(H_2O)]_n \cdot nH_2O$, (II) and (III), are obtained through hydrothermal synthesis at either 423 or 443 K. Compounds (I) and (II) are isomorphous with previously reported Gd^{III} compounds, but compound (III) constitutes a new phase. Compound (I) can be described in terms of dinuclear $[Eu_2(H_2O)_4]^{6+}$ units bonded through mta^{3-} ligands to form a two-dimensional framework with topology corresponding to a (6,3)-connected binodal $(4^3)(4^6 6^8 3^3)$-**kgd** net, where the dinuclear $[Eu_2(H_2O)_4]^{6+}$ units are considered as a single node. Compounds (II) and (III) have distinct three-dimensional topologies, namely a $(4^{12}6^3)(4^9 6^6)$-**nia** net for (II) and a $(4^{10}6^5)(4^{11}6^4)$-**K₂O₂; 36641** net for (III). The crystal density of (III) is greater than that of (II), consistent with the increase of temperature, and thereby autogeneous pressure, in the hydrothermal synthesis.

1. Introduction

The construction of metal-organic frameworks (MOFs) based on different self-assembly synthetic routes is a fruitful strategy to obtain new polymorphic systems (Furukawa *et al.*, 2013; Kitagawa *et al.*, 2004; Tian *et al.*, 2007; Yaghi *et al.*, 2003). Three important aspects should be taken into account in the self-assembly strategy: (*a*) utilization of organic ligands with well characterized coordination modes, which act as linkers; (*b*) selection of metal ions with a desirable coordination geometry, acting as nodes in the framework; (*c*) control of the various interactions between the linkers and nodes (covalent, hydrogen bonds, van der Waals *etc.*), in order to generate a particular topology in the MOF product. Assembly of organic linkers with inorganic nodes opens a huge number of possibilities in crystal engineering, where the resulting MOFs show interesting properties that are strongly influenced by their topology. These compounds have attracted the attention of researchers for many different applications, such as gas storage, catalysis or magnetism (for example Li *et al.*, 2011; Wang, Zhang, Liu *et al.*, 2007; Sumida *et al.*, 2012; Zhang *et al.*, 2011; Lee *et al.*, 2009; Farha *et al.*, 2010; Cañadillas-Delgado *et al.*, 2012).

The appropriate selection of the organic linker together with a rational synthetic route can be used to modulate structural diversity. Among the different organic ligands, those containing carboxylate groups are often selected due to their abundant coordination modes, which allow the occurrence of

Table 1
Experimental details.

Experiments were carried out at 293 K with Mo $K\alpha$ radiation using a Nonius Kappa CCD diffractometer. H-atom parameters were constrained.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_7H_{13}EuO_9 \cdot 2H_2O$	$C_7H_9EuO_7 \cdot H_2O$	$C_7H_9EuO_7 \cdot H_2O$
M_r	429.17	375.12	375.12
Crystal system, space group	Triclinic, $P\bar{1}$	Orthorhombic, $Pca2_1$	Orthorhombic, $Pbcn$
a, b, c (Å)	8.0917 (13), 8.8680 (12), 10.115 (2)	17.4543 (19), 7.8087 (6), 14.9761 (18)	14.1085 (3), 7.7825 (2), 18.0083 (4)
α, β, γ (°)	86.994 (17), 73.002 (16), 68.172 (15)	90, 90, 90	90, 90, 90
V (Å^3)	643.06 (19)	2041.2 (4)	1977.30 (8)
Z	2	8	8
μ (mm^{-1})	4.93	6.17	6.37
Crystal size (mm)	$0.80 \times 0.40 \times 0.20$	$0.70 \times 0.26 \times 0.24$	$0.32 \times 0.30 \times 0.24$
Data collection			
Absorption correction	For a sphere Dwiggins (1975)	For a cylinder mounted on the φ axis Dwiggins (1975)	For a sphere Dwiggins (1975)
T_{min}, T_{max}	0.110, 0.439	0.370, 0.383	0.235, 0.310
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10 427, 2943, 2743	8250, 3215, 3040	15 892, 3133, 2860
R_{int}	0.042	0.076	0.041
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649	0.667	0.726
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.059, 1.10	0.063, 0.167, 1.14	0.029, 0.074, 1.13
No. of reflections	2943	3215	3133
No. of parameters	172	291	145
No. of restraints	0	1	0
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.28, −0.56	1.39, −1.82	0.96, −1.16
Absolute structure	–	Refined as an inversion twin	–
Absolute structure parameter	–	0.38 (3)	–

Computer programs: *COLLECT* (Nonius, 1998), *EVALCCD* (Duisenberg *et al.*, 2003), *HKL2000* (Otwinowski & Minor, 1997), *SHELXS97*, *SHELXL97* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 1999), *WinGX* (Farrugia, 1999), *PARST95* (Nardelli, 1995) and *PLATON* (Spek, 2009).

different structural topologies, together with the ability of the carboxylate group to act as a hydrogen-bond acceptor and/or donor, which can help to stabilize the crystal structure. Moreover, carboxylate groups are hard Lewis bases with a remarkable ability to bind strongly to lanthanide ions. In order to tune the topology of new MOFs, it would be useful to exploit organic building blocks with a desirable symmetry, in order to attempt to reproduce that symmetry in the generated framework structure. We have explored the use of tripodal carboxylate ligands, of which the rigid 1,3,5-benzenetricarboxylic acid (btc) is one of the most highly represented in the literature (Chen *et al.*, 2007; Gao *et al.*, 2006; Gustafsson *et al.*, 2008). Among btc-lanthanide complexes, one of the better characterized corresponds to MOF-76, where Ln^{III} binds to six different btc ligands, and each btc ligand binds to six different Ln^{III} ions, giving rise to a chiral three-dimensional framework with square-shaped channels (Rosi *et al.*, 2005). The conformational freedom of flexible ligands may provide an extra possibility for the construction of unprecedented topologies, as in the case of propane-1,2,3-tricarboxylic acid (tricarballylic acid, H$_3$tca; Cañadillas-Delgado *et al.*, 2008), where the ligand adopts a T-shaped conformation that promotes (6,3)-type networks with 'brickwall' or 'herringbone' morphologies. In an effort to obtain systems with higher symmetry, we have explored methanetriacetic acid (hereafter denoted H$_3$mta),

which represents a C_3-symmetric scaffold that can promote hexagonal topologies in the final framework structure.

Our selection of lanthanide ions as nodes for the preparation of new framework structures is based on their relatively large ionic radii, which give rise to large coordination numbers. In the particular case of Eu^{III}, the most common coordination number is nine, mostly with distorted tricapped trigonal prismatic or monocapped square antiprismatic geometry. Coordination numbers of eight or ten are less common, although they are quite well represented in the literature, in contrast to coordination numbers of six or seven, which are scarce. Therefore, the selection of Eu^{III} to act as a framework node promotes the occurrence of high-dimensional systems with unusual network topologies.

In this paper we report three new metal-organic frameworks containing Eu^{III} and the mta^{3-} ligand. Two of them, [Eu(mta)(H$_2$O)$_3$]$_n \cdot 2n$H$_2$O (I) and [Eu(mta)(H$_2$O)]$_n \cdot n$H$_2$O (II), are isomorphous with known Gd^{III} compounds (Cañadillas-Delgado *et al.*, 2010), while the third, [Eu(mta)(H$_2$O)]$_n \cdot n$H$_2$O (III), is a polymorph of (II) and is a new phase. The three compounds have been obtained using either gel synthesis [for (I)] or hydrothermal methods [for (II) and (III)]. Polymorphs (II) and (III) are obtained by varying the temperature, and consequently the autogenous pressure, of the hydrothermal synthesis.

Table 2
Selected distances (Å) and angles (°) for (I), (II) and (III).

(I)		(III)	
Eu1—O1	2.565 (2)	Eu1—O1	2.521 (2)
Eu1—O2	2.530 (2)	Eu1—O1^v	2.485 (2)
Eu1—O1^{ii}	2.386 (2)	Eu1—O2	2.449 (2)
Eu1—O3^i	2.314 (2)	Eu1—O3^{ii}	2.411 (3)
Eu1—O5^{iii}	2.415 (2)	Eu1—O4^i	2.382 (2)
Eu1—O6^{iv}	2.442 (2)	Eu1—O5^{iii}	2.413 (2)
Eu1—O1W	2.541 (2)	Eu1—O5^{iv}	2.525 (2)
Eu1—O2W	2.455 (3)	Eu1—O6^{iv}	2.480 (2)
Eu1—O3W	2.450 (3)	Eu1—O1W	2.486 (3)
Eu1···Eu1^{ii}	4.0363 (8)	Eu1···Eu1^{vi}	4.0897 (1)
Eu1—O1—Eu1^{ii}	109.18 (9)	Eu1—O1—Eu1^{vi}	109.53 (9)
		Eu1—O5^{iii}—Eu1^{vi}	111.80 (9)

(II)			
Eu1—O1	2.431 (7)	Eu2—O1	2.502 (7)
Eu1—O3^i	2.307 (6)	Eu2—O2	2.445 (7)
Eu1—O5^{ii}	2.445 (6)	Eu2—O4^i	2.435 (9)
Eu1—O7	2.480 (6)	Eu2—O5^{ii}	2.499 (7)
Eu1—O8	2.520 (6)	Eu2—O6^{ii}	2.480 (7)
Eu1—O10^{iii}	2.462 (8)	Eu2—O8^{vi}	2.472 (6)
Eu1—O11^i	2.521 (7)	Eu2—O9^{iv}	2.319 (6)
Eu1—O12^i	2.488 (6)	Eu2—O12^v	2.443 (7)
Eu1—O1W	2.526 (7)	Eu2—O2W	2.495 (7)
Eu1···Eu2	4.0767 (5)	Eu2···Eu1^{vi}	4.0767 (5)
Eu1—O1—Eu2	111.5 (3)	Eu2—O8^{vi}—Eu1^{vi}	109.5 (2)
Eu1—O5^{ii}—Eu2	111.2 (2)	Eu2—O12^v—Eu1^{vi}	111.5 (3)

Symmetry codes for (I): (i) $-x, -y + 2, -z$; (ii) $-x, -y + 1, -z$; (iii) $x - 1, y, z$; (iv) $-x + 1, -y + 1, -z$. Symmetry codes for (II): (i) $-x + \frac{1}{2}, y, z - \frac{1}{2}$; (ii) $-x, -y, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + 1, z$; (iv) $x - \frac{1}{2}, -y, z$; (v) $-x + \frac{1}{2}, y - 1, z - \frac{1}{2}$; (vi) $x, y - 1, z$. Symmetry codes for (III): (i) $-x + 1, y, -z - \frac{1}{2}$; (ii) $x + \frac{1}{2}, y - \frac{1}{2}, -z - \frac{1}{2}$; (iii) $-x + \frac{3}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (iv) $x, -y + 1, z - \frac{1}{2}$; (v) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (vi) $-x + \frac{3}{2}, y + \frac{1}{2}, z$.

Table 3
Hydrogen-bond geometry (Å, °) for (I), (II) and (III).

D—H···A	D—H	H···A	D···A	D—H···A
(I)				
O1W—H1W···O2^i	0.85	1.87	2.714 (4)	172
O1W—H2W···O4	0.85	2.30	3.024 (4)	141
O2W—H3W···O1W^v	0.85	2.17	2.901 (4)	144
O2W—H4W···O4W^{ii}	0.85	1.99	2.824 (4)	168
O3W—H5W···O5W^{vi}	0.85	1.91	2.747 (4)	166
O3W—H6W···O5W^{ii}	0.85	1.96	2.797 (4)	169
O4W—H7W···O6	0.85	2.04	2.877 (4)	169
O4W—H8W···O4W^{vii}	0.85	2.02	2.869 (4)	177
O5W—H9W···O4	0.85	1.88	2.717 (4)	170
O5W—H10W···O4W^{viii}	0.85	1.93	2.765 (4)	166
(II)				
O1W—H1W···O4^{vii}	0.85	1.98	2.833 (10)	177
O1W—H2W···O3W^{viii}	0.85	1.89	2.740 (12)	172
O2W—H3W···O10^{iii}	0.85	1.95	2.800 (9)	180
O2W—H4W···O4W^{ix}	0.85	1.90	2.749 (9)	179
O3W—H5W···O6^{ii}	0.85	1.93	2.781 (12)	179
O4W—H7W···O7^x	0.85	2.03	2.832 (9)	157
O4W—H8W···O11^x	0.85	2.03	2.869 (10)	169
(III)				
O1W—H1W···O3^{vii}	0.85	2.06	2.913 (4)	180
O1W—H2W···O2W	0.85	1.98	2.807 (7)	165
O2W—H3W···O6^i	0.85	1.94	2.794 (7)	180

Symmetry codes are as listed in Table 1. Additional symmetry codes for (I): (v) $-x - 1, -y + 2, -z$; (vi) $x, y, z - 1$; (vii) $x + 1, y - 1, z$; (viii) $-x, -y + 1, -z + 1$. Additional symmetry codes for (II): (vii) $-x + \frac{1}{2}, y + 1, z - \frac{1}{2}$; (viii) $x + \frac{1}{2}, -y, z$; (ix) $x - 1, y - 1, z$; (x) $x + \frac{1}{2}, -y + 1, z$. Additional symmetry code for (III): (vii) $-x + 1, y - 1, -z - \frac{1}{2}$.

2. Experimental

2.1. Synthesis

Methanetriacetic acid (H$_3$mta) was prepared and characterized following reported methods (Baumeister *et al.*, 2002; Gupta *et al.*, 1987; Cañadillas-Delgado *et al.*, 2010). The other reagents and solvents were purchased from commercial sources and used as received. X-ray quality crystals of (I) were grown by slow diffusion within a gel medium following the technique described by Henisch (1970), whereas those of (II) and (III) were obtained through hydrothermal synthesis (Byrappa & Yoshimura, 2001). Elemental analyses (C, H) were performed on an EA1108 CHNS-O microanalytical instrument.

2.1.1. [Eu(mta)(H$_2$O)$_3$]$_n$·2nH$_2$O (I). The pH of an 0.07 *M* aqueous solution of methanetriacetic acid (3 ml H$_2$O and 4 ml of ethanol) was adjusted to 4.5 by adding an aqueous solution of NaOH. Afterwards, 0.7 ml of tetramethoxysilane was added to the resulting solution. The mixture was introduced into a test tube, covered and stored for 1 d at room temperature to allow the formation of a gel. Finally, an aqueous solution of Eu(NO$_3$)$_3$·6H$_2$O (0.1 *M*, 2.5 ml) was placed on the gel, with care being taken to avoid damaging the gel surface, and the tubes were stored at 303 K. Colourless needle-like crystals of (I) appeared after a few days. The yield at that moment was *ca* 40%. Anal.: calc. for C$_7$H$_{17}$EuO$_{11}$: C 19.58, H 3.99%; found: C 19.32, H 3.92%.

2.1.2. [Eu(mta)(H$_2$O)]$_n$·nH$_2$O (II) and (III). An aqueous solution of methanetriacetic acid (0.1 *M*, 10 ml) was poured into an 0.05 *M* (20 ml) aqueous solution of Eu(NO$_3$)$_3$·6H$_2$O. The resulting mixture was sealed into a 45 ml stainless-steel reactor with teflon liner, and heated at either 423 (II) or 443 K (III) for 48 h. After cooling, yellow cube-shaped crystals suitable for X-ray analysis were collected from the teflon liners and air dried. Yield *ca* 60% for both compounds. Anal.: calc. for C$_7$H$_{11}$EuO$_8$: C 22.40, H 2.96%; found: C 22.33, H 2.86% for (II); C 22.28, H 2.89% for (III).

2.2. X-ray data collection and refinement

Single crystals of (I), (II) and (III) were mounted on a Nonius Kappa CCD diffractometer and diffraction data were collected at 293 K using graphite-monochromated Mo *Kα* radiation (λ = 0.7107 Å). Crystal data, data collection and structure refinement details are summarized in Table 1.[1] Selected bond lengths and angles are listed in Table 2. The H atoms of the mta^{3-} ligands were placed geometrically and refined as riding atoms. H atoms of the water molecules were introduced so as to create a reasonable hydrogen-bonding network (Table 3), then refined as riding on their parent O atoms. The positions of these H atoms were generally quite clear, except for one H atom on O3W in (II) and one H atom on O2W in (III), which are not listed as forming hydrogen bonds in Table 3, and whose positions are uncertain. Compound (II) crystallizes in the non-centrosymmetric space group *Pca*2$_1$, with a refined Flack parameter [0.38 (3)] signif-

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[1] Supporting information for this paper is available from the IUCr electronic archives (Reference: BI5013).

icantly different from zero, indicating inversion twinning. Different crystals of (II) were studied by single-crystal X-ray diffraction, but all tested samples presented a non-zero Flack parameter, pointing to an intrinsic twinning problem.

3. Results and discussion

3.1. [Eu(mta)(H$_2$O)$_3$]$_n$·2nH$_2$O (I)

Compound (I) (Fig. 1) is isomorphous with a previously published Gd^{III} compound (Cañadillas-Delgado *et al.*, 2010). It presents a two-dimensional framework structure, where dinuclear [Eu$_2$(H$_2$O)$_4$]$^{6+}$ units are bonded through mta^{3-} ligands to form layers parallel to (001), and these layers are stacked along the *c* axis in an *AA* sequence. From a topological point of view, considering the Eu^{III} ions as single nodes, a 5-*c* uninodal net is formed, designated (4^{8}6^2) in Schläfi notation (Blatov, 2006). The minimum interlayer Eu^{III}···Eu^{III}

distance is 8.673 (2) Å, which does not differ significantly from that reported for the isomorphous Gd^{III} compound [8.6750 (8) Å]. Each [Eu$_2$(H$_2$O)$_4$]$^{6+}$ dinuclear unit is connected to its six nearest neighbors with a shortest inter-dimer Eu^{III}···Eu^{III} distance of 8.0917 (13) Å (along the *a* axis; Fig. 2). The structure includes three coordinated water molecules (O1*W*, O2*W* and O3*W*) and two waters of crystal-
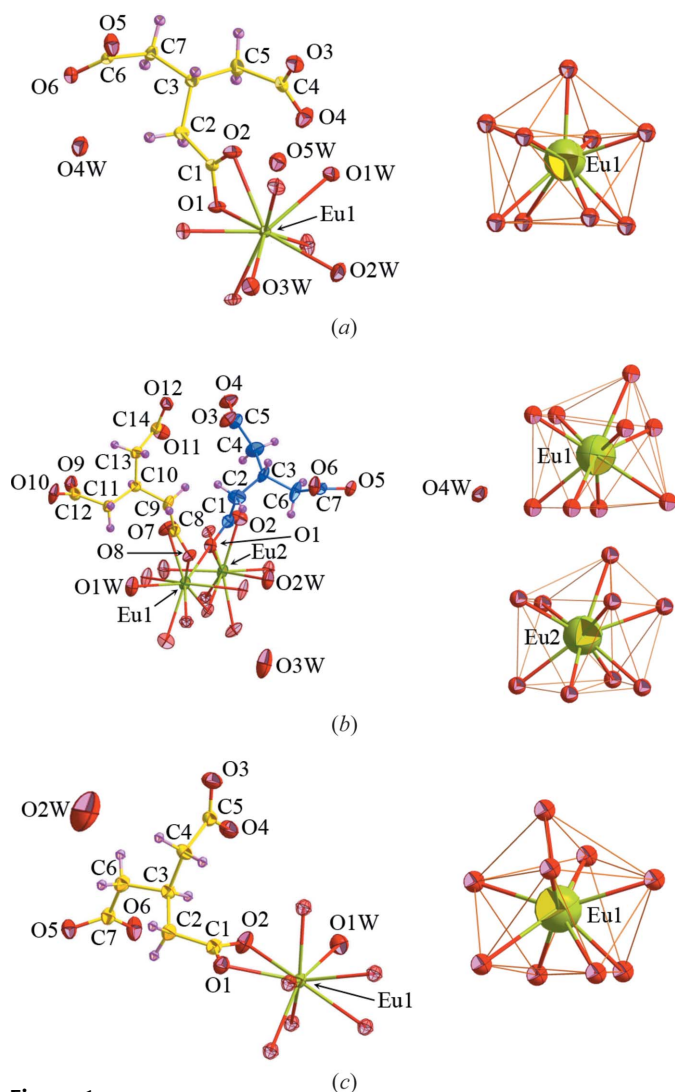

(a)

(b)

(c)

Figure 1
Asymmetric units of (I), (II) and (III) together with the coordination polyhedra for the crystallographically independent Eu^{III} atoms (displacement ellipsoids at 50% probability). Unlabelled atoms are generated by symmetry operations.
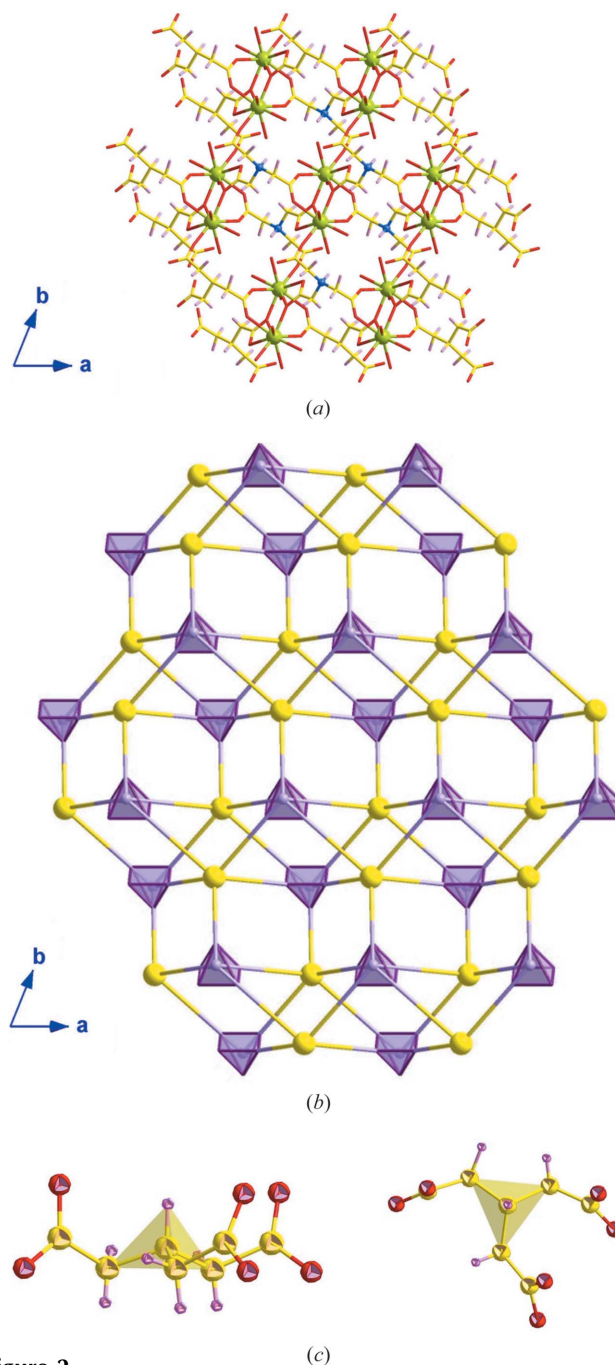

(a)

(b)

(c)

Figure 2
(a) View of the two-dimensional structure of (I) along the *c* axis, highlighting the [Eu$_2$(H$_2$O)$_4$]$^{6+}$ dinuclear unit connected to six neighbours through six mta^{3-} ligands (central C atom in blue); (b) topological representation of the fivefold connected (4^{8}6^2) uninodal network of (I), where the mta^{3-} ligands and Eu^{III} atoms are represented in violet and yellow colours, respectively; (c) detail of the conformation of the mta^{3-} ligand.

lization (O4W and O5W), which are involved in hydrogen bonds (Table 3) that link the two-dimensional frameworks into the full three-dimensional crystal structure. If the unco-ordinated water molecules are removed from the structure, there is a solvent-accessible void space of about 190 Å^3 per unit cell, which constitutes 28.5% of the total volume (Spek, 2009).

The Eu^{III} atom is nine-coordinated, surrounded by six O atoms from five different mta^{3-} ligands (O1, O2, O1^{ii}, O3^{i}, O5^{iii}, O6^{iv}; symmetry codes as listed in Table 2), and three water molecules (O1W, O2W and O3W), which build a distorted monocapped square antiprism geometry with Eu—O distances varying from 2.314 (2) to 2.565 (2) Å (Fig. 1 and Table 2). The mta^{3-} ligand presents bidentate (through O1 and O2 towards Eu1) and tetrakis-monodentate coordination modes [through O1, O3, O6 and O5 towards Eu1^{i}, Eu1^{ii}, Eu1^{iv} and Eu1^{ix}, respectively; symmetry code: (ix) $x + 1$, y, z], linking three [Eu$_2$(H$_2$O)$_4$]$^{6+}$ units within the (001) plane (Fig. 2). Each [Eu$_2$(H$_2$O)$_4$]$^{6+}$ dinuclear unit occupies an inversion centre. The separation Eu1···Eu1^{ii} and the angle at the oxo-bridge, Eu1—O1—Eu1^{ii}, are as indicated in Table 2.

3.2. [Eu(mta)(H$_2$O)]$_n$·nH$_2$O (II)

Compound (II) is also isomorphous with a previously reported Gd^{III} compound (Cañadillas-Delgado *et al.*, 2010). Its structure consists of [Eu(H$_2$O)]$^{3+}$ units and six-connecting mta^{3-} ligands acting as octahedral and trigonal prismatic nodes, respectively, which result in a three-dimensional network showing the NiAs topology [a (6,6)-connected binodal **nia**-net (Blatov, 2006), with a $(4^{12}6^3)(4^96^6)$ Schläfli symbol], which is quite rare among MOF architectures (Figs. 3 and 4; Delgado-Friedrichs *et al.*, 2006; Wang *et al.*, 2007; Chen *et al.*, 2012; Bai *et al.*, 2008; Cañadillas-Delgado *et al.*, 2010; Chae *et al.*, 2001; Jia *et al.*, 2012). The structure contains chains of oxo- and *syn–syn* carboxylate-bridged Eu^{III} ions running along the *b* axis, which are interconnected through the mta^{3-} ligands to yield the full three-dimensional framework. Each Eu^{III} chain is linked to its six nearest neighbours within the (010) plane with a shortest interchain separation of 7.7373 (11) Å (Eu1···Eu2^{vii}: symmetry code as listed in Table 3) (Fig. 3). Four water molecules are also present in the structure, two coordinated to Eu^{III} (O1W and O2W) and two crystallization water molecules (O3W and O4W), which form hydrogen bonds to the carboxylate O atoms (Table 3). The O3W and O4W water molecules are located between the central C atoms of the mta^{3-} ligands along the *b* axis in such a way that they fill the void space. In this case, removal of both uncoordinated water molecules leaves voids of about 160 Å^3 per unit cell, which accounts for 7.8% of the total cell volume (Spek, 2009).

Two crystallographically independent Eu^{III} atoms are present in (II) (Fig. 1), both being nine-coordinated with distorted monocapped square-antiprismatic environments. Eu1 is surrounded by eight O atoms from six mta^{3-} ligands (O1, O3^{i}, O5^{ii}, O7, O8, O10^{iii}, O11^{i}, O12^{i}; symmetry codes as listed in Table 2), and one water molecule (O1W). Atoms O1, O7, O8 and O10^{iii} form the base of the poly-hedron, while O3^{i}, O5^{ii}, O12^{i} and O1W build the upper plane, and O11^{i} caps the antiprism. The mean value of the Eu1—O bond distance is 2.464 Å (Table 2) and the dihedral angle between the upper and basal planes is 10.0 (2)°. Eu2 is also surrounded by eight O atoms from six mta^{3-} ligands (O1, O2, O4^{i}, O5^{ii}, O6^{ii}, O8^{vi}, O9^{iv}, O12^{v}) and one
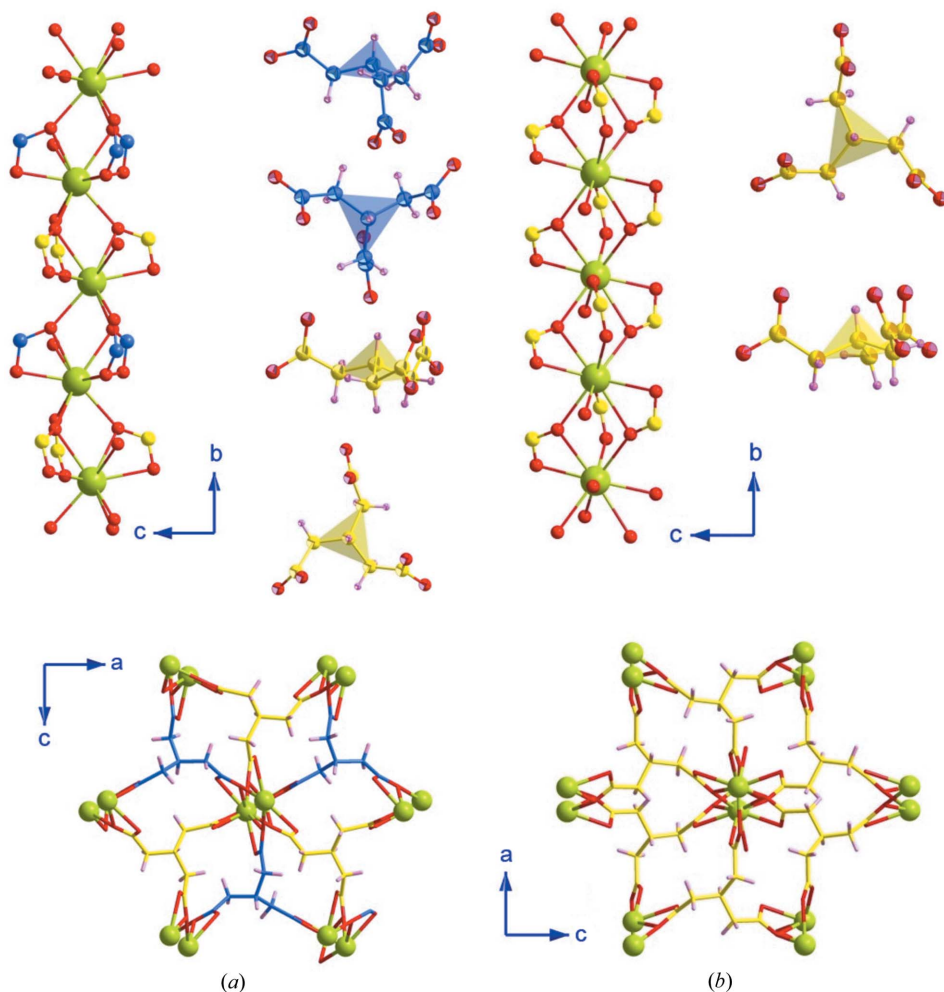

Figure 3
Crystal structures of (II) and (III), with details of the ligand conformation: (*a*) compound (II), with mta(1) coloured blue and mta(2) yellow; (*b*) compound (III).

water molecule (O2W). The basal and upper planes around Eu2 are built by atoms O1, O2, O4[1], O8[vi], and atoms O5[ii], O9[iv], O12[v], O2W, respectively, while atom O6[ii] caps the antiprism. The mean Eu2—O distance is 2.454 Å and the dihedral angle between the basal and upper mean planes is 9.4 (2)°.

The two crystallographically independent mta^{3-} ligands in (II) present both bis-bidentate/tetrakis-monodentate coordination modes. The ligand containing atom C3 [denoted mta(1), see Fig. 1] chelates Eu2 through O1 and O2 and Eu2[xi] through O5 and O6. It also connects Eu1 to Eu2 by means of O1, Eu1[xi] to Eu2[xi] by means of O5, and Eu1[xii] to Eu2[xii] through the carboxylate group O3—C5—O4 [symmetry codes: (xi) $-x, -y, z + \frac{1}{2}$, (xii) $-x + \frac{1}{2}, y, z + \frac{1}{2}$]. On the other side, the ligand containing atom C10 [denoted mta(2), see Fig. 1] presents a bidentate coordination mode towards Eu1 by means of O7 and O8, and to Eu1[xii] through O11 and O12, and a monodentate coordination mode towards Eu2[xiii], Eu2[viii], Eu1[x] and Eu2[xiv] through O8, O9, O10 and O12, respectively [symmetry codes: (xiii) $x, y + 1, z$; (xiv) $-x + \frac{1}{2}, y + 1, z + \frac{1}{2}$]. Both mta^{3-} ligands link three Eu^{III} chains within the (010) plane as shown in Fig. 3. The acetate arms of the mta^{3-} ligands present similar dihedral angles compared with those encountered in the isomorphous Gd^{III} compound (Cañadillas-Delgado et al., 2010). In the case of mta(1), these angles are 62.3 (4)° for ac(1)/ac(2) [ac(1) = O1, O2, C1, C2; ac(2) = O3, O4, C4, C5], 54.5 (3)° for ac(1)/ac(3) [ac(3) = O5, O6, C6, C7] and 63.2 (4)° for ac(2)/ac(3). For mta(2) these values are 56.1 (4)° for ac(4)/ac(5) [ac(4) = O7, O8, C8, C9; ac(5) = O9, O10, C11, C12], 60.4 (3)° for ac(4)/ac(6) [ac(6) = O11, O12, C13, C14] and 80.3 (3)° for ac(5)/ac(6).

Within the chains of Eu^{III} ions that run along the b axis, Eu1 and Eu2 alternate and are linked through two μ-oxo and one carboxylate bridge. Eu1 and Eu2 are linked through μ-O1; κ-O1O2, μ-O5[ii]; κ-O5[ii]O6[ii] and the carboxylate group O3[i]—C5[i]—O4[i] in a syn–syn conformation with an Eu1⋯Eu2 distance of 4.0767 (5) Å. At the same time, Eu2 and Eu1[vi] are linked by μ-O8[vi]; κ-O8[vi]O7[vi], μ-O12[v]; κ-O12[v]O11[v] and the carboxylate group O9[iv]-C12[iv]-O10[iv] in a syn–syn conformation with an Eu2⋯Eu1[vi] distance of 4.0767 (5) Å (Table 2).

3.3. [Eu(mta)(H₂O)]ₙ·nH₂O (III)

Compound (III) is a new polymorph of [Eu(mta)(H₂O)]$_n$·nH₂O. Although it presents a similar structure to that of (II), it crystallizes in a different space group, Pbcn, which is a minimal non-isomorphic supergroup of Pca2₁. Although there exists a group–subgroup relationship between the two structures, they are apparently not related by any structural phase transition.
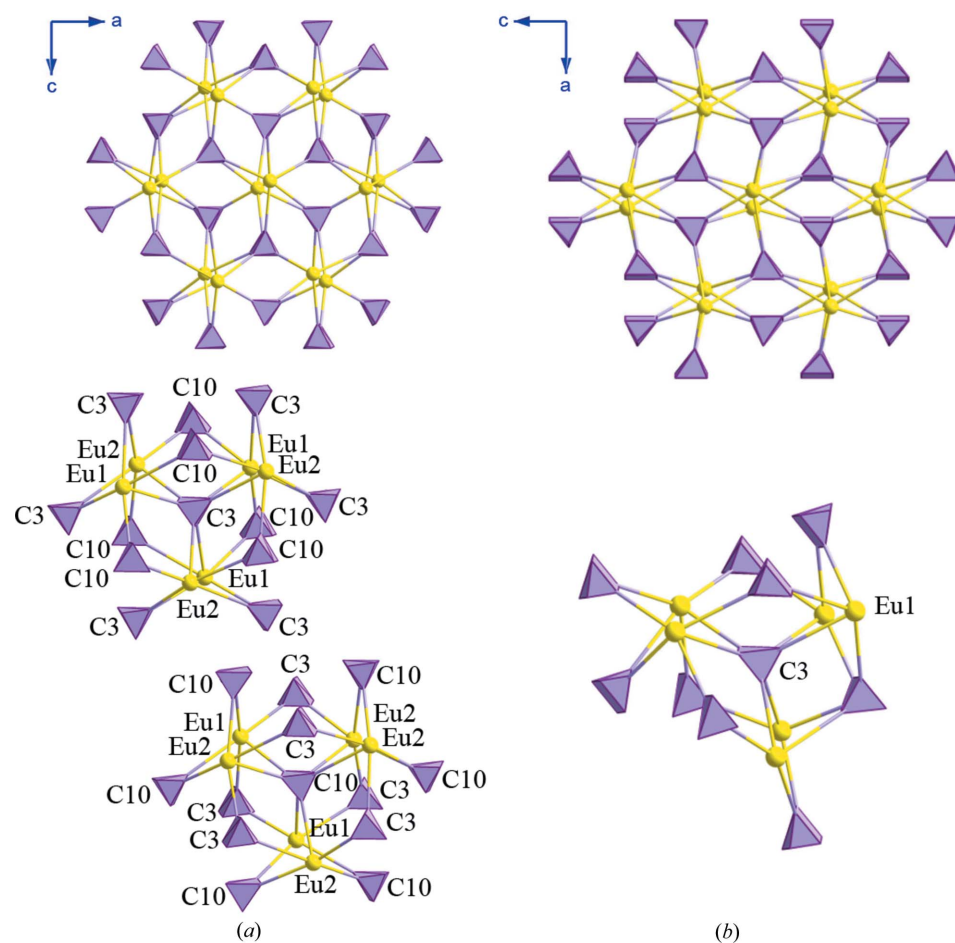
The structure of (III) consists of [Eu(H₂O)]$^{3+}$ units connected through six mta^{3-} ligands acting as octahedral and trigonal prismatic nodes, respectively, which result in a three-dimensional network that is different from (II). For (III) the network is a (6,6)-connected binodal **K₂O₂; 36641**-net (Blatov, 2006) with a $(4^{10}6^5)(4^{11}6^4)$ Schläfli symbol (Figs. 3 and 4). The three-dimensional structure can be described as chains of oxo- and syn–syn carboxylate-bridged Eu^{III} ions running along the b axis, connected along the a and c directions through the mta^{3-} ligands, with a shortest interchain separation notably shorter than that in (II) [Eu1⋯Eu1[viii] = 6.7524 (1) Å; symmetry code: (viii) $x, -y + 1, -z + \frac{1}{2}$]. There is one coordinated (O1W) and one crystallization water molecule (O2W) that together with the carboxylate O atoms form hydrogen bonds (Table 3). The O2W water molecule is located

Figure 4
Topological views of the crystal structures of (a) compound (II) and (b) compound (III), with the Eu^{III} atoms and mta^{3-} ligands represented in yellow and magenta colours, respectively. The main differences in topology are enlarged.

between two adjacent mta^{3-} ligands along the *b* direction, near to the central C atoms, in such a way that it fills the void space. Removal of the uncoordinated water molecule leaves voids of 159.7 Å^3 per unit cell, which accounts for 7.8% of the total cell volume (Spek, 2009), noticeably less than that in (II). This reduction in the potential void space (and increase in crystal density; Table 1) is consistent with the increase of temperature in the hydrothermal synthesis, which increases the autogenous pressure inside the reactor.

Only one crystallographically independent Eu^{III} atom is present in (III) (Fig. 1), which is nine-coordinated with a distorted monocapped square antiprismatic environment. It is surrounded by eight O atoms from six mta^{3-} ligands (O1, O1^v, O2, O3^{ii}, O4^i, O5^{iii}, O5^{iv} and O6^{iv}; symmetry codes as in Table 2) and one water molecule (O1W). Atoms O1, O1^v, O2 and O3^{ii} form the base of the polyhedron, while O4^i, O5^{iii}, O5^{iv} and O1W build the upper plane, and O6^{iv} caps the antiprism. The mean value of the Eu1—O bond distance is 2.461 Å, and the dihedral angle between the upper and basal planes is 6.0 (7)° (Table 2).

One crystallographically independent mta^{3-} ligand is present in (III) (Fig. 1), with the bis-bidentate/tetrakis-monodentate coordination mode, which links three Eu^{III} chains within the *ac* plane, as in (II). The ligand chelates Eu1 (through O1 and O2) and Eu1^{ix} (through O5 and O6), and connects Eu1^x to Eu1 (by means of O1), Eu1^{ix} to Eu1^{iii} (by means of O5), and Eu1^{xi} to Eu1^{viii} [through the carboxylate link O3—C5—O4; symmetry codes: (ix) $-x + 1, y, z - \frac{1}{2}$; (x) $x + \frac{1}{2}, -y + \frac{3}{2}, z$; (xi) $x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$]. The acetate arms of the mta^{3-} ligand present dihedral angles of 81.8 (1)° [ac(1)/ac(2)] [ac(1): O1,O2,C1,C2; ac(2): O3,O4,C4,C5], 66.3 (1)° [ac(1)/ac(3)] [ac(3): O5,O6,C6,C7] and 45.5 (1)° [ac(2)/ac(3)].

The Eu^{III} chain runs along the *b* axis with the Eu^{III} ions linked through two μ-oxo and one carboxylate bridge. Atoms Eu1 and Eu1^x are linked through μ-O1; κ-O1O2, μ-O5^{xii}; κ-O5^{xii}O6^{xii} [symmetry code: (xii) $-x + \frac{3}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$] and the carboxylate group O3^{viii}—C5^{viii}—O4^{viii} in *syn–syn* conformation with a Eu1$\cdots$Eu1^x distance of 4.0897 (1) Å (see Table 2).

3.4. Comparison of the structures

There are several features in the crystal structure of (III) that are quite similar to that of (II), including the topological description, although the Schläfli notation reveals differences between the two structures. That is, each ligand in (II) is connected to six Eu^{III} ions that also are bonded among them through 13 mta^{3-} ligands. In (III), however, each ligand is connected to six Eu^{III} ions which are connected among them through only 10 mta^{3-} ligands (see Fig. 4).

The mta^{3-} ligand adopts different coordination modes in (I) (bidentate/tetrakis-monodentate), (II) and (III) (bis-bidentate/tetrakis-monodentate), but also the ligand conformation differs in all of them (Fig. 5). There are three different conformations of the ligand where the carboxylate branches (CH$_2$—COO) rotate around the single bond with the central C atom (see Figs. 2 and 3). The first one, present in (I), disposes the three carboxylate branches out of the plane formed by the three C atoms bonded to the central one [distances from plane 0.595 (4), 0.632 (4) and 0.680 (5) Å for C1, C4 and C6, respectively], pointing to the same direction as the central H atom. Moreover, looking along the centre C—H bond, two of these branches rotate in a counter-clockwise sense while the third one rotates in a clockwise sense. It should be noted that the rotation senses change under the application of the inversion centre present in (I) [torsion angles: −48.6 (2)° for H3—C3—C2—C1; 49.9 (2)° for H3—C3—C5—C4 and −51.3 (2)° for H3—C3—C7—C6]. The second ligand conformation, observed in (II) and (III), again places all three branches out of the plane formed by the three C atoms bonded to the central one, with all carboxylate branches pointing to the same direction as the central H atom [distances from the plane 0.783 (7), 0.630 (6) and 0.709 (8) Å for C8, C12 and C14, in (II), respectively, and 0.634 (4), 0.941 (3) and 0.696 (3) Å for C1, C5 and C7, in (III), respectively]. Looking along the central C—H bond, all three branches rotate in the same sense [torsion angles: −40.8 (8)° for H10—C10—C9—C8; −51.4 (8)° for H10—C10—C11—C12 and −45.3 (8)° for H10—C10—C13—C14, in compound (II); and 50.9 (3)° for H3—C3—C2—C1; 26.7 (4)° for H3—C3—C4—C5 and 47.2 (4)° for H3—C3—C6—C7, in compound (III)]. Even though (II) crystallizes in a non-centrosymmetric space group, the application of the mirror symmetry contained in the *ac* and *bc* planes gives rise to the occurrence of both ligand rotation senses within the crystal structure. The same feature occurs in (III), where mta^{3-} ligands with the carboxylate arms rotated in both senses are present due to the occurrence of an inversion centre. The third conformation is present only in (II), where two of the carboxylate branches point towards the central H atom [distances from plane 0.838 (8) and 1.137 (7) Å for C5 and C7, respectively], one of them rotating in a clockwise sense and the other one in a counter-clockwise sense [torsion angles: −37.1 (10)° for H3—C3—C4—C5 and 7.4 (9)° for H3—C3—C6—C7]. The third carboxylate branch points in the opposite direction [distance from plane 1.485 (8) Å for C1] and stays almost parallel to the central C—H bond [torsion angle: −172.9 (7)° for H3—C3—C2—C1].
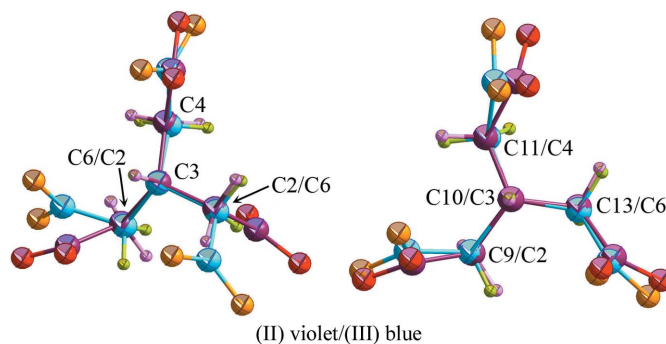

Figure 5
View of the superposition of the mta^{3-} ligands present in (II) and (III), where the mta^{3-} in (II) is represented with C, O and H atoms in violet, red and pink, respectively, while the mta^{3-} ligand in (III) is depicted with C, O and H atoms in blue, orange and green, respectively.

4. Conclusions

The first Eu^{III}-containing methanetriacetate compounds have been synthesized, through gel [for (I)] and hydrothermal methods [for (II) and (III)]. Two of them, (I) and (II), are isomorphous with two Gd^{III} compounds reported previously (Cañadillas-Delgado *et al.*, 2010), where the main differences arise from the lanthanide contraction. Compound (III) represents a new polymorph. Compounds (II) and (III) crystallize in space groups *Pbcn* and *Pca*2$_1$, respectively. Although there exists a group–subgroup relation between them, the compounds are not related by a phase transition, although their crystal structures show significant similarities. Both polymorphs were obtained through hydrothermal conditions, although at different synthetic temperatures, and consequently autogenous pressures. An increase in temperature produced not only the different topology [**nia**-net in (II) and **K$_2$O$_2$; 36641**-net in (III)], but also a reduction in the unit-cell volume (an increase in density) and in the available space for solvent molecules [7.8 and 5% of the total unit-cell volume for (II) and (III), respectively]. Additionally, it can be seen that hydrothermal synthesis in general favours high-dimensional compact architectures, since compound (I) presents a two-dimensional arrangement, while compounds (II) and (III) are three-dimensional framework structures with small solvent-accessible space.

The mta^{3-} ligand adopts two different coordination modes in (I) (bidentate/tetrakis-monodentate), (II) and (III) (bis-bidentate/tetrakis-monodentate), but also its conformation differs in all of them. There are three different conformations of the ligand, where the acetate branches rotate around the single bond with the central C atom. These different conformations and coordination modes adopted by the mta^{3-} anion demonstrate the flexibility of the ligand.

In summary, the combination of flexible tripodal ligands with lanthanide ions opens a huge number of possibilities for construction of MOFs, within the crystal engineering field. For that reason, full understanding of the different coordination modes and conformations of a given ligand is mandatory to obtain smart materials with tailored properties. The construction of further novel architectures based on lanthanide ions with different ionic radii is in progress, together with investigations of the applications of these materials in luminescent systems.

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