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Organically pillared layer framework of [Eu(NH$_2$–BDC)(ox)(H$_3$O)]

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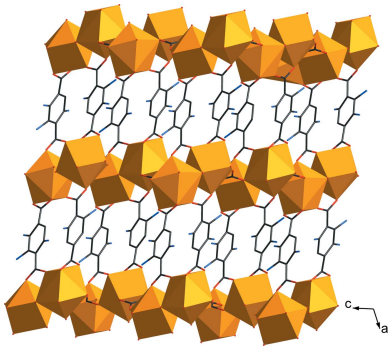
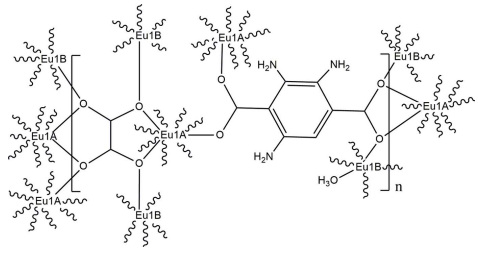
The non-porous three-dimensional structure of poly[(μ_5-2-aminobenzene-1,4-dicarboxylato)(μ_6-oxalato)(oxomium)europium(III)], [Eu($C_8H_5NO_4$)(C_2O_4)-(H_3O)]$_n$ or [Eu^{III}(NH$_2$–BDC)(ox)(H_3O)]$_n$ (NH$_2$–BDC^{2-} = 2-amino-terephthalate and ox^{2-} = oxalate) is constructed from two-dimensional layers of Eu^{III}–carboxylate–oxalate, which are connected by NH$_2$–BDC^{2-} pillars. The basic structural unit of the layer is an edge-sharing dimer of *TPRS*-{Eu^{III}O$_9$}, which is assembled through the ox^{2-} moiety. The intralayer void is partially occupied by *TPR*-{Eu^{III}O$_6$} motifs. Weak C—H···O and strong, classical intramolecular N—H···O and intermolecular O—H···O hydrogen-bonding interactions, as well as weak π–π stacking interactions, affix the organic pillars within the framework. The two-dimensional layer can be simplified to a uninodal 4-connected **sql/Shubnikov tetragonal plane** net with point symbol {4^4.6^2}.

1. Chemical context

Lanthanide coordination polymers (LnCPs) have emerged as authentic multifunctional materials finding potential in various applications, *e.g.* magnetism, optics, luminescence and in heterogeneous catalysis (Roy *et al.*, 2014). In the crystal engineering of LnCPs, the judicious choice of organic ligands is critical. Among the widely employed dicarboxylates, 1,4-benzenedicarboxylic acid (H_2BDC) tends to provide three-dimensional frameworks with permanent porosity. To enhance interactions with guest species, additional functional groups can be introduced onto the phenyl ring of BDC^{2-}, *e.g.* 2-amino-1,4-benzenediarboxylic acid (NH$_2$-H_2BDC) in NH$_2$-MIL-53(Al) enhanced the carbon dioxide capture capacity (Stavitski *et al.*, 2011; Flaig *et al.*, 2017; Wang *et al.*, 2012). The smallest dicarboxylic acid, *i.e.* oxalic acid (H_2ox), on the other hand, may not facilitate the porous framework (Zhang *et al.*, 2016; Xiahou *et al.*, 2013) and its presence as a secondary ligand in the fabrication may lead to diversity in the framework structures.





Herein, NH$_2$-H_2BDC and H_2ox were employed as mixed linkers in the synthesis of a new three-dimensional framework of europium, *i.e.* [Eu(NH$_2$-BDC)(ox)(H_3O)] (**I**). The crystal

structure of **I**, which exhibits site disorder at both the Eu^{III} ion and the amino group, is reported. Weak intermolecular interactions and the framework topology are also described.

2. Structural commentary

[Eu(NH_2–BDC)(ox)(H_3O)] crystallizes in the monoclinic space group $P2_1/c$. Its asymmetric unit comprises one Eu^{III} ion, which is disordered over two crystallographic sites with an occupying ratio of 0.86 (Eu1*A*): 0.14 (Eu1*B*) and whole molecules of NH_2–BDC^{2-}, ox^{2-} and H_3O^+ (Fig. 1). Eu1*A* is ninefold coordinated to nine O atoms from one chelating NH_2-–BDC^{2-}, two monodentate NH_2–BDC^{2-}, two chelating ox^{2-} and one monodentate ox^{2-} groups, all of which delineate into a distorted tricapped trigonal–prismatic geometry, *i.e.* *TPRS*-{$Eu^{III}O_9$}. Eu1*B*, on the other hand, adopts a sixfold coordination of trigonal anti-prismatic geometry, *i.e.* *TPR*-{$Eu^{III}O_6$}, which is completed by six O atoms from two monodentate NH_2–BDC^{2-}, three monodentate ox^{2-} and one H_3O^+ moieties. Noticeably, the three monodentate ox^{2-} moieties form one trigonal face whereas the two monodentate NH_2–BDC^{2-} and the ligated H_3O^+ moieties outline the other. The Eu^{III}—O bond distances ranging between 2.375 (2) and 2.562 (2) Å, are consistent with the values observed for other Eu^{III} coordination frameworks, *e.g.* $[(CH_3)_2NH_2]_2$-$[Eu_6(\mu_3\text{-}OH)_8(BDC\text{–}NH_2)_6(H_2O)_6]$ (Yi *et al.*, 2016) and $[Eu_2(ATPA)_3(DEF)_2]_n$ where $ATPA^{2-}$ = 2-aminoterephthalate and DEF = diethylformamide (Kariem *et al.*, 2016). In addition to the disorder at the Eu^{III} positions, there is an additional disorder at the amino group of NH_2–BDC^{2-}, which distributes over three crystallographic sites with site occupancies of 0.26 (N1), 0.44 (N2) and 0.31 (N3), respectively.

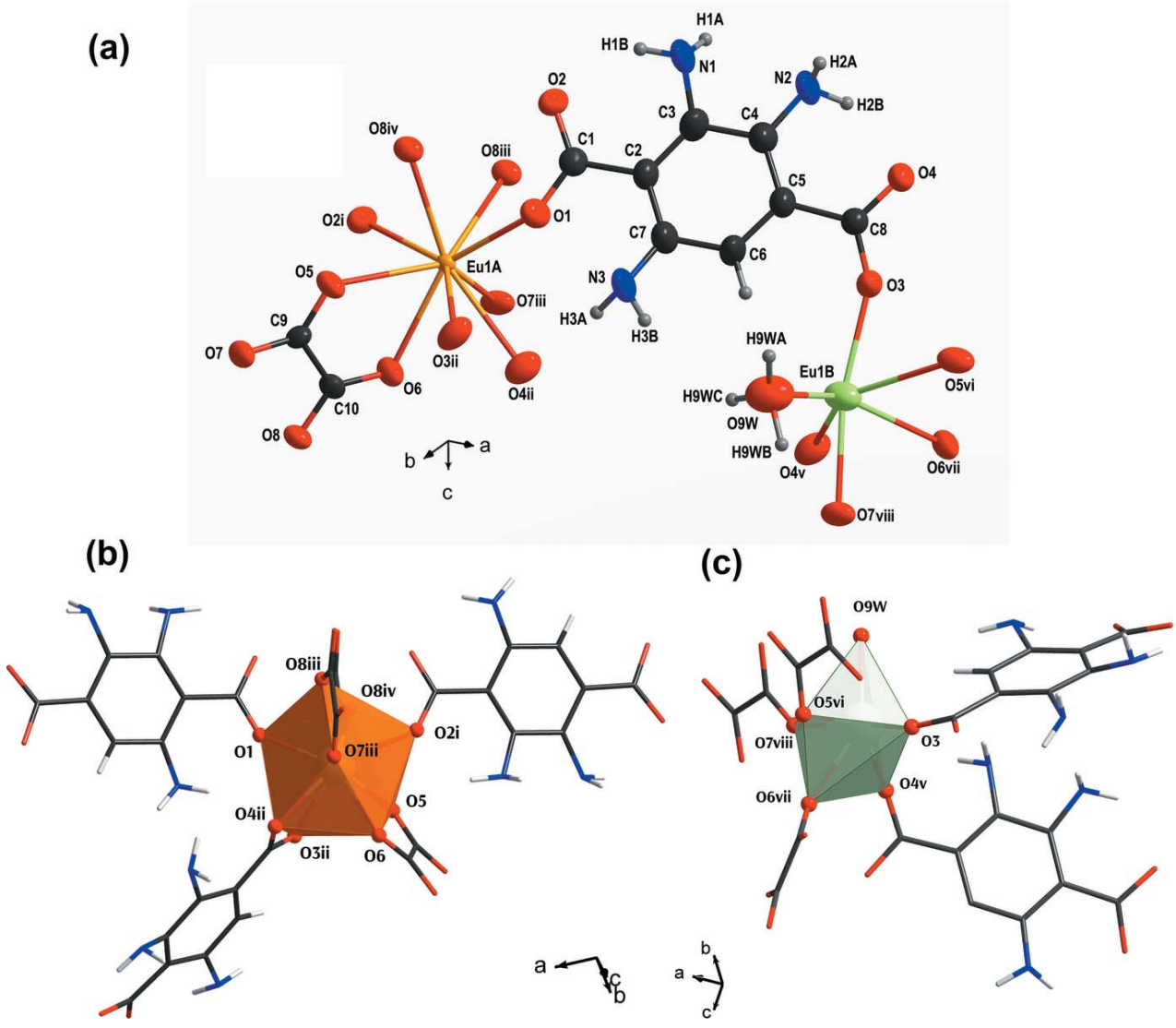


Figure 1
Views of (*a*) an extended asymmetric unit of **I** drawn using 60% probability ellipsoids and the coordination environments about (*b*) Eu1*A* and (*c*) Eu1*B*. [Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iv) $x, \frac{3}{2}-y, -\frac{1}{2}+z$; (v) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (vi) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vii) $1-x, 1-y, 1-z$; (viii) $1-x, \frac{3}{2}-y, \frac{1}{2}+z$.]

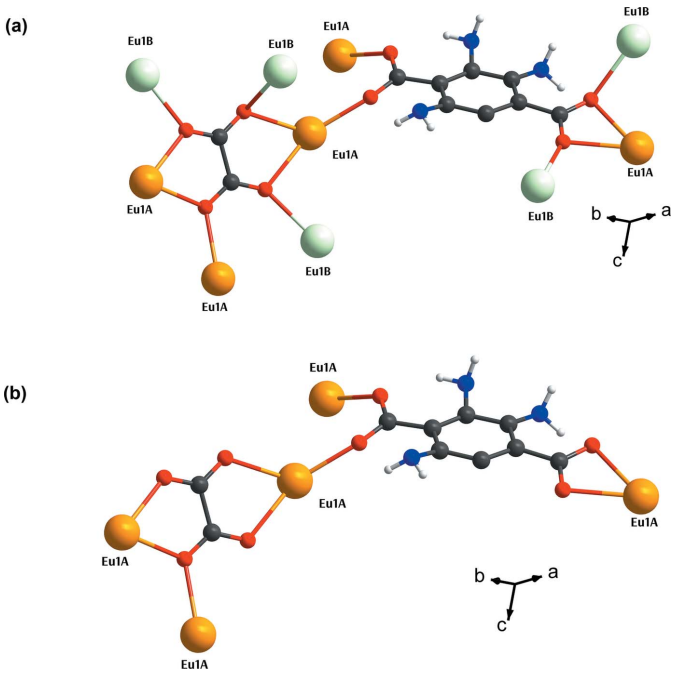


Figure 2
Depictions of coordination modes adopted by NH_2—BDC^{2-} and ox^{2-}; (*a*) with (*b*) without Eu1*B*.

As a result of the disorder of the Eu^{III} ion, the modes of coordinations for both NH_2–BDC^{2-} and ox^{2-} are diverse. If all of the possible sites of Eu^{III} are concurrently included, the μ_5-η^1:η^1:η^2:η^2 mode can be assigned to NH_2-BDC^{2-} as it connects three Eu1*A* and two Eu1*B* moieties together (Fig. 2). In a similar fashion, three Eu1*A* and three Eu1*B* moieties may be simultaneously linked by ox^{2-} using the μ_6-η^2:η^2:η^2:η^2 mode for coordination. It is worth noting that the μ_5-η^1:η^1:η^2:η^2 mode of NH_2-BDC^{2-} and the μ_6-η^2:η^2:η^2:η^2 mode of ox^{2-} are unprecedented. If only the dominating Eu1*A* is regarded, the adopted coordination modes would be μ_3-η^1:η^1:η^1:η^1 and μ_3-η^1:η^1:η^1:η^2 for NH_2–BDC^{2-} and ox^{2-}, respectively. Likewise, there are only sixteen structures containing ox^{2-} with a μ_3-η^1:η^1:η^1:η^2 mode and only two LnCPs comprising NH_2–BDC^{2-} with a μ_3-η^1:η^1:η^1:η^1 mode, *i.e.* $[Yb_2(OH)(atpt)_{2.5}(phen)_2]_n{\cdot}1.75nH_2O$ where $atpt^{2-}$ = 2-aminoterephthalate and phen = 1,10-phenanthroline (Liu *et al.*, 2004), and $\{[Ho_2(\mu_3\text{-}ATA)_2(\mu_4\text{-}ATA)(H_2O)_4]{\cdot}2DMF{\cdot}0.5H_2O\}_n$ where ATA^{2-} = 2-aminoterephthalate (Almáši *et al.*, 2014).

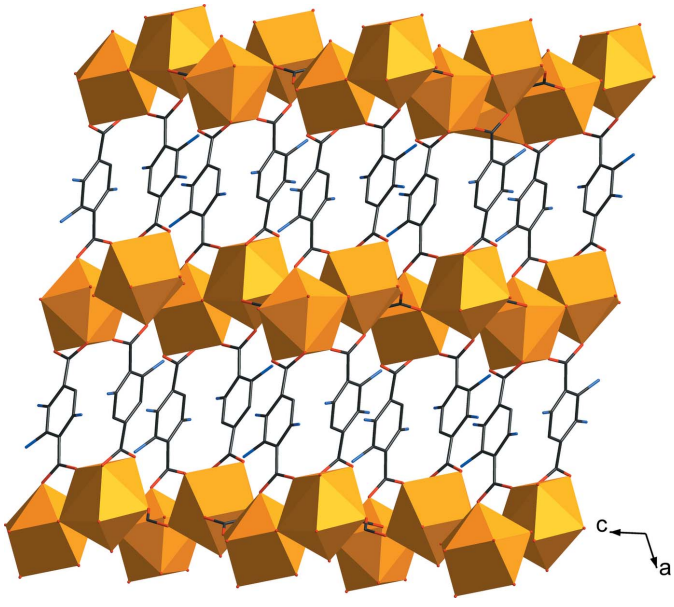


Figure 3
The three-dimensional framework structure of **I**.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O9W—H9WA···O2^{i}	1.11 (5)	1.81 (5)	2.904 (4)	171 (5)
O9W—H9WB···O5^{ii}	1.10 (5)	1.87 (5)	2.943 (4)	163 (4)
C6—H6···O3	0.93	2.47	2.781 (6)	100
N1—H1B···O2	0.86	2.03	2.736 (16)	139

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x+1, -y+\frac{3}{2}, z+\frac{1}{2}$.

3. Supramolecular features

The structure of **I** features a three-dimensional framework, which can be regarded as being built up of two-dimensional layers of Eu^{III}-carboxylate-oxalate connected by the NH_2–BDC^{2-} organic pillars (Fig. 3). The basic building motif of the layer is the edge-sharing dimer of *TPRS*-{$Eu^{III}O_9$} (Fig. 4), which is fused together through two O8 atoms from two ox^{2-} groups and two O1—C1—O2 bridges of two NH_2-BDC^{2-}.

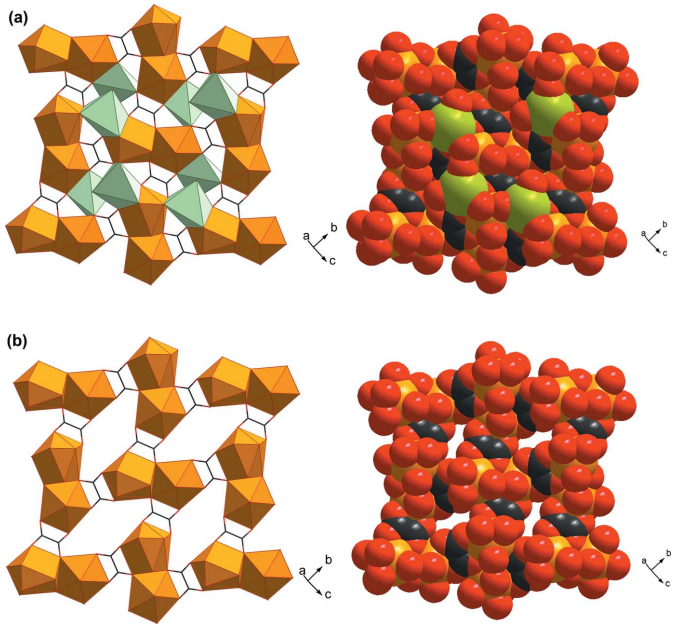


Figure 4
Polyhedral and space-filling representations of the Eu^{III}–oxalate–carboxylate layers (*a*) with *TPR*-{$Eu^{III}O_6$} motifs and (*b*) without *TPR*-{$Eu^{III}O_6$} motif.

Each $\{Eu_2^{III}O_{16}\}$ dimer of Eu1*A* is tied to the other four equivalent dimers through four ox^{2-} linkers in the *bc* plane. The as-described arrangement of these $\{Eu_2^{III}O_{16}\}$ dimers creates voids characterized as the twelve-membered rings, in which the partially occupied *TPR*-$\{Eu^{III}O_6\}$ motifs of Eu1*B* are situated. Each of the *TPR*-$\{Eu^{III}O_6\}$ motifs are affixed within the layer through four O atoms from four surrounding ox^{2-} groups and an O4 atom from NH_2–BDC^{2-}. These layers are further connected by the NH_2–BDC^{2-} organic pillars along the *a*-axis direction providing the non-porous three-dimensional framework. The roles of ox^{2-} and NH_2–BCD^{2-} in the framework of **I** are, therefore, to create the layer framework and to tether the layers, respectively.

The NH_2–BDC^{2-} pillar is apparently organized through intramolecular hydrogen-bonding interactions from both strong N—H···O and weak C—H···O interactions (Table 1), and through the face-to-face antiparallel displaced π–π interactions (Banerjee *et al.*, 2019) established between the phenyl rings of two adjacent NH_2–BDC^{2-} pillars (Fig. 5). In addition to the intramolecular hydrogen-bonding interactions, two H atoms from the H_3O^+ molecule are also involved in providing additional strong O—H···O intermolecular hydrogen-bonding interactions.

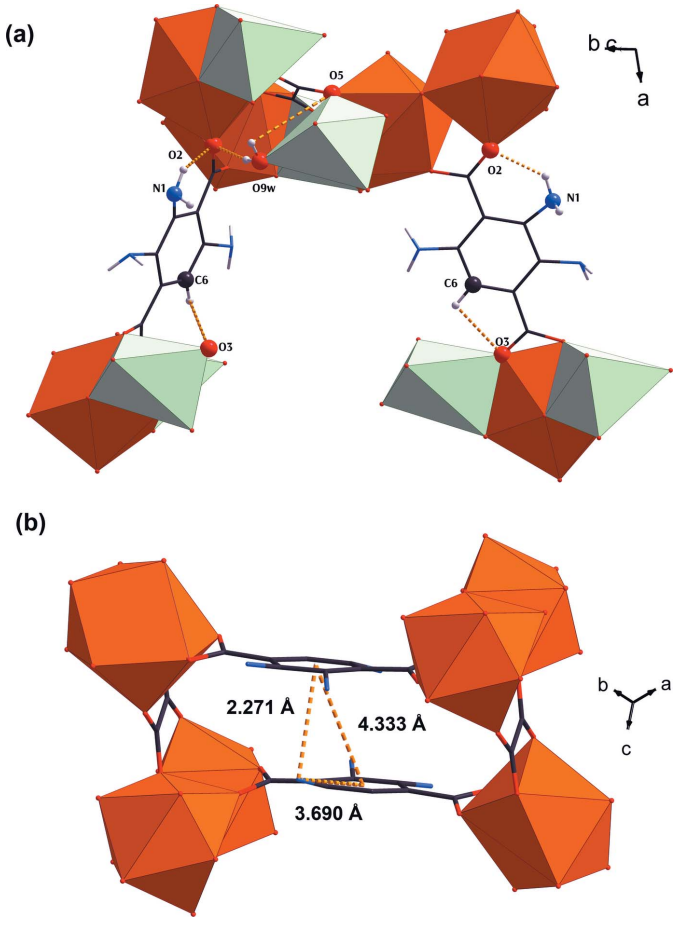


Figure 5
Views of (*a*) the hydrogen-bonding interactions and (*b*) the π–π interactions.

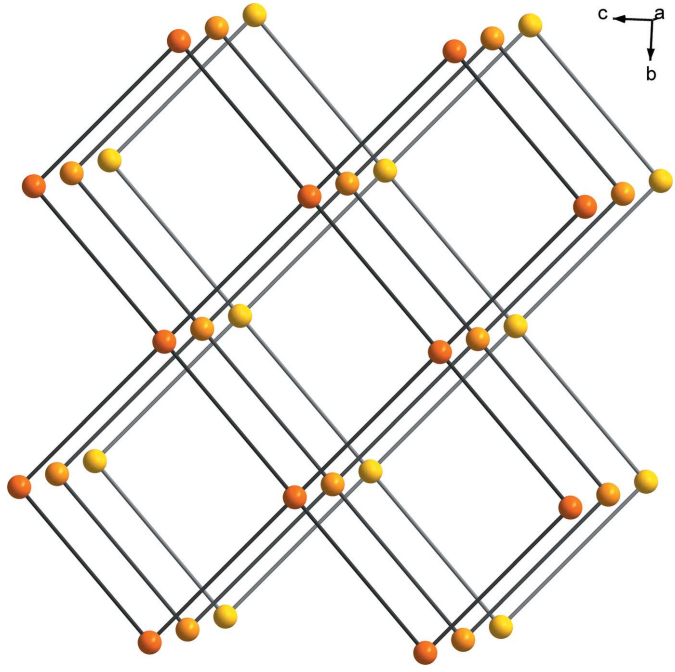


Figure 6
The simplified two- and three-dimensional topologies of **I.**

4. Topology

The topology of the two-dimensional layer of **I** was analysed using *TOPOS* software (Blatov, 2004). If only the dominating motif, *i.e.* the edge-sharing dimer of Eu1*A*, is taken as a node, which is connected to the other equivalent dimer *via* the ox^{2-} linker, the two-dimensional layer of Eu1 can be simplified to a uninodal 4-connected **sql/Shubnikov tetragonal plane** net with a point symbol $\{4^4.6^2\}$ (Blatov *et al.*, 2014) (Fig. 6). The inclusion of the partially occupied *TPR*-$\{Eu^{III}O_6\}$ motifs results in unknown topology. This is also the case for the three-dimensional framework with or without the *TPR*-$\{Eu^{III}O_6\}$ motifs.

5. Photoluminescent property

A room temperature photoluminescent spectrum of **I** was collected (Jasco FB-8500 spectrofluorometer, $\lambda_{excitation}$ = 337 nm). It exhibits none of the characteristic *f*–*f* emission of Eu^{III}. Even the broad emission characteristic of the ligand-centered π–π emission was not observed. This may be attributed to a proton-induced fluorescence-quenching mechanism facilitated by the presence of H_3O^+ in close proximity to the phenyl ring of NH_2-BDC^{2-} (Tobita & Shizuka, 1980; Shizuka & Tobita, 1982). The quenching consequently hinders the sensitization, which is important according to the antenna model (Einkauf *et al.*, 2017).

6. Database survey

Based on a survey of the Cambridge Structural Database (version 5.40, Nov 2018 with the update of May 2019; Groom *et al.*, 2016), no LnCP containing both NH_2-BDC^{2-} and ox^{2-}

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Eu(C_8H_5NO_4)(C_2O_4)(H_3O)]$
M_r	436.32
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	11.8348 (3), 11.3208 (3), 10.6531 (3)
β (°)	110.275 (3)
V (Å^3)	1338.86 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.73
Crystal size (mm)	0.2 × 0.05 × 0.05
Data collection	
Diffractometer	Rigaku OD SuperNova, single source at offset/far, HyPix3000
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)
T_{min}, T_{max}	0.753, 0.789
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15479, 2882, 2458
R_{int}	0.050
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.647
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.067, 1.09
No. of reflections	2882
No. of parameters	222
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.61, −0.54

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT* (Sheldrick, 2015*b*), *SHELXL* (Sheldrick, 2015*a*) and *OLEX2* (Dolomanov *et al.*, 2009).

has previously been reported. However, there are three closely relevant structures which have similar unit-cell parameters, *i.e.* *catena*-[(μ-tetracyanoborate)tetraaquabis(nitrato)lanthanum] (Zottnick *et al.*, 2017), *catena*-[hemikis(piperazinedium)(μ-benzene-1,2,4,5-tetracarboxylato)diaquapraseodymium(III)] (Liang *et al.*, 2017) and η^5-indenyl)dichlorotris(tetrahydrofuran-*O*)gadolinium tetrahydrofuran solvate (Fuxing *et al.*, 1992).

7. Synthesis and crystallization

To synthesize **I**, 2-aminoterephthalic acid (0.2 mmol, 0.0332 g), oxalic acid (0.2 mmol, 0.0180 g) and 1,4-diazabicyclo[2.2.2]-octane (0.4 mmol, 0.0448 g) were dissolved in 8.0 mL of DMF/H_2O (1 m:7 mL) to prepare solution **A**. Separately, solution **B** was prepared by dissolving Eu_2O_3 (0.1 mmol, 0.0180 g) in 1.0 mL of concentrated HNO_3 aqueous solution, which was then adjusted to pH 7 using a 10 *M* NaOH aqueous solution. Solution **B** was then gradually introduced into solution **A**, and the mixture was then transferred to a 22 mL Teflon-lined stainless-steel autoclave. The reaction was carried out under an autogenous pressure generated at 393 K for 7 days. Yellow crystals of **I** were then recovered by filtration. FT–IR of **I** (KBr; cm^{-1}): 3361, 2987, 1617, 1313, 1053, 798.

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The Eu^{III} ion was refined as being disordered over two crystallographic sites resulting in refined occupancies of 0.855 (Eu1*A*) and 0.145 (Eu1*B*). The disorder of the amino group over three crystallographic sites could be clearly seen in the electron-density map and was refined using the SUMP command providing occupancies of 0.259 (N1), 0.440 (N2) and 0.305 (N3). EADP constraints were necessary to make the anisotropic refinements of the disordered N atoms stable. The three H atoms on the ligated H_3O^+ (O9*W*) were evident in the electron-density map and therefore assigned as such. The SADI restraint was nonetheless applied on the refinements of the three O—H bonds. H atoms could be positioned from the electron-density maps and were refined as riding with U_{iso}(H) = 1.2U_{eq}(C, N) or 1.5U_{eq}(O). Bond restraints o N—H and O—H were applied in the refunements.

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supporting information

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: SHELXT (Sheldrick, 2015b); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015a); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Poly[(μ_6-oxalato)(oxomium)(μ_5-2-aminobenzene-1,4-dicarboxylato)europium(III)]

Crystal data

[Eu(C$_8$H$_5$NO$_4$)(C$_2$O$_4$)(H$_3$O)]
M_r = 436.32
Monoclinic, $P2_1/c$
a = 11.8348 (3) Å
b = 11.3208 (3) Å
c = 10.6531 (3) Å
β = 110.275 (3)°
V = 1338.86 (7) Å^3
Z = 4
$F(000)$ = 832
D_x = 2.165 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9488 reflections
θ = 1.8–27.3°
μ = 4.73 mm^{-1}
T = 293 K
Block, clear light yellow
0.2 × 0.05 × 0.05 mm

Data collection

Rigaku OD SuperNova, single source at offset/far, HyPix3000 diffractometer
Radiation source: micro-focus sealed X-ray tube
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2018)
T_{min} = 0.753, T_{max} = 0.789
15479 measured reflections
2882 independent reflections
2458 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 27.4°, θ_{min} = 1.8°
h = −14→15
k = −11→14
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.067
S = 1.09
2882 reflections
222 parameters
4 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2 + 0.0276P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Eu1A	0.07429 (2)	0.61284 (2)	0.15674 (2)	0.01311 (9)	0.8558 (8)
O6	0.0486 (2)	0.7311 (2)	0.3456 (2)	0.0298 (6)	
O8	−0.0221 (2)	0.89620 (19)	0.4069 (3)	0.0248 (6)	
O5	−0.0175 (2)	0.8135 (2)	0.0928 (2)	0.0314 (6)	
O2	0.1449 (2)	0.4078 (2)	−0.1090 (3)	0.0315 (7)	
O7	−0.0772 (2)	0.9814 (2)	0.1603 (2)	0.0298 (6)	
O4	0.7236 (2)	0.1331 (2)	0.1432 (3)	0.0356 (7)	
O1	0.2130 (2)	0.5301 (3)	0.0649 (3)	0.0385 (7)	
O3	0.7668 (2)	0.2640 (2)	0.3050 (3)	0.0366 (7)	
C10	0.0008 (3)	0.8307 (3)	0.3236 (4)	0.0212 (8)	
C1	0.2274 (3)	0.4463 (4)	−0.0068 (4)	0.0278 (9)	
C9	−0.0344 (3)	0.8795 (3)	0.1784 (4)	0.0229 (9)	
C8	0.6941 (3)	0.2224 (4)	0.1960 (4)	0.0290 (9)	
C2	0.3499 (3)	0.3911 (3)	0.0360 (4)	0.0319 (10)	
C5	0.5750 (3)	0.2802 (4)	0.1344 (4)	0.0353 (10)	
C6	0.5557 (4)	0.3900 (4)	0.1808 (5)	0.0502 (14)	
H6	0.619345	0.426877	0.246414	0.060*	
C3	0.3677 (4)	0.2839 (4)	−0.0150 (5)	0.0513 (13)	
C7	0.4454 (4)	0.4470 (4)	0.1332 (5)	0.0480 (12)	
C4	0.4805 (4)	0.2271 (4)	0.0321 (5)	0.0528 (13)	
N2	0.4834 (8)	0.1125 (8)	−0.0128 (12)	0.066 (3)	0.439 (6)
H2A	0.512716	0.113790	−0.078500	0.080*	0.439 (6)
H2B	0.531521	0.063870	0.047841	0.080*	0.439 (6)
N3	0.4511 (10)	0.5604 (13)	0.1717 (14)	0.066 (3)	0.312 (6)
H3A	0.407927	0.583997	0.230300	0.080*	0.312 (6)
H3B	0.527520	0.590092	0.221251	0.080*	0.312 (6)
N1	0.2993 (12)	0.2381 (15)	−0.1365 (15)	0.066 (3)	0.261 (6)
H1A	0.286630	0.164575	−0.125872	0.080*	0.261 (6)
H1B	0.231669	0.274954	−0.165662	0.080*	0.261 (6)
Eu1B	0.82330 (16)	0.39654 (13)	0.47691 (17)	0.0427 (7)	0.1442 (8)
O9W	0.8080 (3)	0.5707 (3)	0.3580 (3)	0.0593 (9)	
H9WA	0.816 (5)	0.581 (4)	0.258 (4)	0.089*	
H9WB	0.881 (4)	0.620 (4)	0.433 (5)	0.089*	
H9WC	0.725 (4)	0.578 (6)	0.383 (7)	0.15 (3)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Eu1A	0.01489 (13)	0.00998 (14)	0.01356 (13)	−0.00037 (7)	0.00379 (9)	−0.00035 (8)

O6	0.0446 (16)	0.0207 (15)	0.0244 (14)	0.0096 (12)	0.0121 (12)	0.0042 (12)
O8	0.0355 (15)	0.0197 (15)	0.0206 (15)	0.0018 (11)	0.0114 (13)	−0.0022 (11)
O5	0.0494 (17)	0.0224 (16)	0.0230 (14)	0.0099 (13)	0.0133 (13)	0.0000 (12)
O2	0.0215 (14)	0.0420 (19)	0.0291 (16)	−0.0002 (12)	0.0064 (12)	−0.0073 (13)
O7	0.0425 (16)	0.0182 (15)	0.0244 (14)	0.0085 (12)	0.0060 (12)	0.0020 (12)
O4	0.0320 (16)	0.0368 (18)	0.0329 (17)	0.0101 (12)	0.0045 (13)	−0.0070 (13)
O1	0.0243 (14)	0.048 (2)	0.0420 (17)	0.0037 (13)	0.0095 (13)	−0.0161 (15)
O3	0.0306 (15)	0.0333 (18)	0.0357 (17)	0.0088 (13)	−0.0014 (13)	−0.0089 (14)
C10	0.0242 (19)	0.014 (2)	0.026 (2)	−0.0034 (16)	0.0088 (16)	−0.0023 (17)
C1	0.025 (2)	0.030 (2)	0.029 (2)	−0.0008 (18)	0.0107 (18)	−0.0008 (19)
C9	0.026 (2)	0.021 (2)	0.017 (2)	0.0012 (16)	0.0008 (17)	0.0012 (16)
C8	0.028 (2)	0.027 (2)	0.028 (2)	0.0023 (18)	0.0054 (18)	−0.0028 (19)
C2	0.025 (2)	0.033 (3)	0.035 (2)	0.0063 (17)	0.0074 (19)	−0.0015 (19)
C5	0.030 (2)	0.035 (3)	0.036 (2)	0.0084 (18)	0.005 (2)	−0.004 (2)
C6	0.031 (3)	0.044 (3)	0.056 (3)	0.013 (2)	−0.010 (2)	−0.020 (2)
C3	0.031 (2)	0.048 (3)	0.058 (3)	0.009 (2)	−0.006 (2)	−0.017 (3)
C7	0.035 (2)	0.046 (3)	0.052 (3)	0.015 (2)	0.001 (2)	−0.016 (3)
C4	0.042 (3)	0.053 (3)	0.049 (3)	0.018 (2)	−0.003 (2)	−0.019 (3)
N2	0.033 (4)	0.064 (5)	0.081 (6)	0.026 (3)	−0.007 (4)	−0.040 (4)
N3	0.033 (4)	0.064 (5)	0.081 (6)	0.026 (3)	−0.007 (4)	−0.040 (4)
N1	0.033 (4)	0.064 (5)	0.081 (6)	0.026 (3)	−0.007 (4)	−0.040 (4)
Eu1B	0.0590 (12)	0.0319 (11)	0.0319 (10)	−0.0013 (7)	0.0090 (8)	−0.0028 (7)
O9W	0.076 (3)	0.056 (2)	0.044 (2)	−0.014 (2)	0.0174 (19)	0.0008 (19)

Geometric parameters (Å, º)

Eu1A—Eu1A^{i}	4.0868 (4)	O4—C8	1.264 (4)
Eu1A—O6	2.521 (2)	O4—Eu1B^{vii}	2.468 (3)
Eu1A—O8^{ii}	2.562 (2)	O1—C1	1.266 (4)
Eu1A—O8^{iii}	2.508 (3)	O3—C8	1.272 (4)
Eu1A—O5	2.508 (2)	O3—Eu1B	2.281 (3)
Eu1A—O2^{i}	2.476 (2)	C10—C9	1.558 (5)
Eu1A—O7^{ii}	2.444 (3)	C1—C2	1.497 (5)
Eu1A—O4^{iv}	2.604 (3)	C8—C5	1.484 (5)
Eu1A—O1	2.375 (2)	C2—C3	1.375 (5)
Eu1A—O3^{iv}	2.470 (3)	C2—C7	1.393 (6)
O6—C10	1.247 (4)	C5—C6	1.386 (6)
O6—Eu1B^{v}	2.445 (3)	C5—C4	1.398 (6)
O8—C10	1.256 (4)	C6—C7	1.386 (6)
O5—C9	1.247 (4)	C3—C4	1.408 (6)
O5—Eu1B^{iv}	2.811 (3)	C3—N1	1.368 (14)
O2—C1	1.261 (4)	C7—N3	1.343 (13)
O7—C9	1.247 (4)	C4—N2	1.387 (8)
O7—Eu1B^{vi}	2.349 (3)	Eu1B—O9W	2.317 (4)
O6—Eu1A—Eu1A^{i}	147.91 (6)	Eu1B^{vi}—O7—Eu1A^{ix}	99.74 (10)
O6—Eu1A—O8^{ii}	129.40 (8)	C8—O4—Eu1A^{x}	91.4 (2)
O6—Eu1A—O4^{iv}	68.33 (9)	C8—O4—Eu1B^{vii}	134.7 (3)

O8^{iii}—Eu1A—Eu1A^{i}	36.75 (5)	Eu1B^{vii}—O4—Eu1A^{x}	92.50 (9)
O8^{ii}—Eu1A—Eu1A^{i}	35.85 (6)	C1—O1—Eu1A	143.2 (2)
O8^{iii}—Eu1A—O6	137.05 (8)	C8—O3—Eu1A^{x}	97.5 (2)
O8^{iii}—Eu1A—O8^{ii}	72.60 (9)	C8—O3—Eu1B	153.3 (3)
O8^{ii}—Eu1A—O4^{iv}	111.70 (8)	Eu1B—O3—Eu1A^{x}	109.19 (11)
O8^{iii}—Eu1A—O4^{iv}	145.39 (9)	O6—C10—O8	126.6 (3)
O5—Eu1A—Eu1A^{i}	108.73 (6)	O6—C10—C9	117.1 (3)
O5—Eu1A—O6	64.84 (8)	O8—C10—C9	116.3 (3)
O5—Eu1A—O8^{iii}	75.76 (8)	O2—C1—O1	123.6 (3)
O5—Eu1A—O8^{ii}	138.85 (8)	O2—C1—C2	119.8 (4)
O5—Eu1A—O4^{iv}	109.32 (8)	O1—C1—C2	116.6 (3)
O2^{i}—Eu1A—Eu1A^{i}	69.48 (6)	O5—C9—C10	117.2 (3)
O2^{i}—Eu1A—O6	78.84 (8)	O7—C9—O5	126.9 (4)
O2^{i}—Eu1A—O8^{iii}	73.70 (9)	O7—C9—C10	115.9 (3)
O2^{i}—Eu1A—O8^{ii}	73.49 (8)	O4—C8—Eu1A^{x}	63.02 (19)
O2^{i}—Eu1A—O5	72.87 (8)	O4—C8—O3	119.9 (3)
O2^{i}—Eu1A—O4^{iv}	140.91 (9)	O4—C8—C5	121.5 (3)
O7^{ii}—Eu1A—Eu1A^{i}	98.87 (6)	O3—C8—Eu1A^{x}	56.94 (18)
O7^{ii}—Eu1A—O6	70.07 (9)	O3—C8—C5	118.6 (4)
O7^{ii}—Eu1A—O8^{ii}	64.12 (8)	C5—C8—Eu1A^{x}	174.2 (3)
O7^{ii}—Eu1A—O8^{iii}	134.20 (8)	C3—C2—C1	120.9 (4)
O7^{ii}—Eu1A—O5	130.79 (9)	C3—C2—C7	119.9 (4)
O7^{ii}—Eu1A—O2^{i}	80.22 (9)	C7—C2—C1	119.1 (4)
O7^{ii}—Eu1A—O4^{iv}	69.26 (8)	C6—C5—C8	119.1 (4)
O7^{ii}—Eu1A—O3^{iv}	119.41 (9)	C6—C5—C4	118.5 (4)
O4^{iv}—Eu1A—Eu1A^{i}	137.47 (6)	C4—C5—C8	122.4 (4)
O1—Eu1A—Eu1A^{i}	65.16 (6)	C5—C6—C7	122.5 (4)
O1—Eu1A—O6	146.09 (8)	C2—C3—C4	121.2 (4)
O1—Eu1A—O8^{ii}	69.59 (9)	N1—C3—C2	125.9 (7)
O1—Eu1A—O8^{iii}	70.84 (8)	N1—C3—C4	109.9 (7)
O1—Eu1A—O5	122.76 (9)	C6—C7—C2	118.6 (4)
O1—Eu1A—O2^{i}	134.63 (9)	N3—C7—C2	127.1 (6)
O1—Eu1A—O7^{ii}	105.55 (9)	N3—C7—C6	113.1 (6)
O1—Eu1A—O4^{iv}	78.60 (9)	C5—C4—C3	119.0 (4)
O1—Eu1A—O3^{iv}	75.28 (9)	N2—C4—C5	124.2 (5)
O3^{iv}—Eu1A—Eu1A^{i}	130.96 (7)	N2—C4—C3	116.0 (5)
O3^{iv}—Eu1A—O6	78.21 (9)	O6^{v}—Eu1B—O5^{x}	70.24 (9)
O3^{iv}—Eu1A—O8^{iii}	104.11 (8)	O6^{v}—Eu1B—O4^{xi}	71.76 (10)
O3^{iv}—Eu1A—O8^{ii}	143.79 (9)	O7^{xii}—Eu1B—O6^{v}	72.95 (10)
O3^{iv}—Eu1A—O5	69.54 (8)	O7^{xii}—Eu1B—O5^{x}	101.31 (10)
O3^{iv}—Eu1A—O2^{i}	141.55 (9)	O7^{xii}—Eu1B—O4^{xi}	73.14 (10)
O3^{iv}—Eu1A—O4^{iv}	51.17 (8)	O4^{xi}—Eu1B—O5^{x}	141.46 (10)
C10—O6—Eu1A	120.2 (2)	O3—Eu1B—O6^{v}	99.37 (11)
C10—O6—Eu1B^{v}	143.1 (2)	O3—Eu1B—O5^{x}	66.84 (9)
C10—O8—Eu1A^{viii}	126.6 (2)	O3—Eu1B—O7^{xii}	167.83 (13)
C10—O8—Eu1A^{ix}	118.0 (2)	O3—Eu1B—O4^{xi}	114.01 (12)
C9—O5—Eu1A	120.6 (2)	O3—Eu1B—O9W	100.09 (12)
C9—O5—Eu1B^{iv}	110.2 (2)	O9W—Eu1B—O6^{v}	146.74 (13)

C1—O2—Eu1A^{i}	130.7 (2)	O9W—Eu1B—O5^{x}	93.23 (12)
C9—O7—Eu1A^{ix}	123.2 (2)	O9W—Eu1B—O7^{xii}	82.84 (12)
C9—O7—Eu1B^{vi}	137.1 (2)	O9W—Eu1B—O4^{xi}	122.82 (13)

Symmetry codes: (i) −*x*, −*y*+1, −*z*; (ii) −*x*, *y*−1/2, −*z*+1/2; (iii) *x*, −*y*+3/2, *z*−1/2; (iv) −*x*+1, *y*+1/2, −*z*+1/2; (v) −*x*+1, −*y*+1, −*z*+1; (vi) *x*−1, −*y*+3/2, *z*−1/2; (vii) *x*, −*y*+1/2, *z*−1/2; (viii) *x*, −*y*+3/2, *z*+1/2; (ix) −*x*, *y*+1/2, −*z*+1/2; (x) −*x*+1, *y*−1/2, −*z*+1/2; (xi) *x*, −*y*+1/2, *z*+1/2; (xii) *x*+1, −*y*+3/2, *z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9*W*—H9*WA*···O2^{xiii}	1.11 (5)	1.81 (5)	2.904 (4)	171 (5)
O9*W*—H9*WB*···O5^{xii}	1.10 (5)	1.87 (5)	2.943 (4)	163 (4)
C6—H6···O3	0.93	2.47	2.781 (6)	100
N1—H1*B*···O2	0.86	2.03	2.736 (16)	139

Symmetry codes: (xii) *x*+1, −*y*+3/2, *z*+1/2; (xiii) −*x*+1, −*y*+1, −*z*.