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# Poly[[chloridodimethanol( $\mu_3$ -pyridine-2,3-dicarboxylato)europium(III)] methanol monosolvate]

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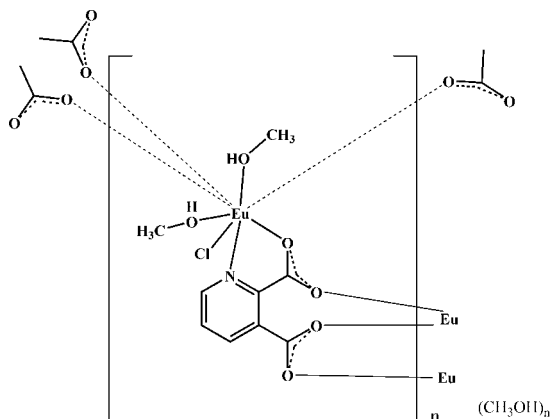
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Key indicators: single-crystal X-ray study;  $T = 150$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å;  $R$  factor = 0.026;  $wR$  factor = 0.057; data-to-parameter ratio = 13.9.

The asymmetric unit of the title compound,  $\{[\text{Eu}(\text{C}_7\text{H}_3\text{NO}_4)\text{-Cl}(\text{CH}_3\text{OH})_2]\cdot\text{CH}_3\text{OH}\}_n$ , contains one  $\text{Eu}^{\text{III}}$  ion, one pyridine 2,3-dicarboxylate dianion (PDC), two  $\text{CH}_3\text{OH}$  molecules coordinating to the metal atom, one coordinating chloride and one lattice occluded  $\text{CH}_3\text{OH}$  molecule. In the crystal, each PDC anion coordinates to three adjacent  $\text{Eu}^{\text{III}}$  ions by the pyridine N and O atoms of the carboxylate groups. The  $\text{Eu}^{\text{III}}$  cation is eightfold coordinated by four carboxylate O atoms, one pyridine N atom, two MeOH and one chloride anion in the form of a distorted polyhedron. Extended coordination of the PDC ligand lead to the formation of a two-dimensional coordination polymer parallel to  $(10\bar{1})$ .

## Related literature

For related work on pyridine-carboxylate transition-metal compounds, see: Swamy *et al.* (1998); Zhong *et al.* (1994); Zhang *et al.* (2003); Wu *et al.* (2003); Tong *et al.* (2000). For work on lanthanide compounds, see, for example: Zhao *et al.* (2004).



## Experimental

### Crystal data

$[\text{Eu}(\text{C}_7\text{H}_3\text{NO}_4)\text{Cl}(\text{CH}_3\text{O})_2]\cdot\text{CH}_3\text{O}$   
 $M_r = 448.64$   
 Monoclinic,  $P2_1/n$   
 $a = 10.4870$  (3) Å  
 $b = 10.9123$  (3) Å  
 $c = 12.9248$  (3) Å  
 $\beta = 99.694$  (2)°  
 $V = 1457.96$  (7) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 4.51$  mm<sup>-1</sup>  
 $T = 150$  K  
 $0.20 \times 0.15 \times 0.14$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 1997)  
 $T_{\text{min}} = 0.448$ ,  $T_{\text{max}} = 0.532$   
 7658 measured reflections  
 2550 independent reflections  
 2260 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.029$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.057$   
 $S = 1.02$   
 2550 reflections  
 184 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 1.34$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.56$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Eu1—O3 <sup>i</sup>	2.344 (3)	Eu1—O5	2.450 (3)
Eu1—O4	2.346 (3)	Eu1—O6	2.490 (3)
Eu1—O2	2.354 (3)	Eu1—N1 <sup>i</sup>	2.655 (3)
Eu1—O1 <sup>ii</sup>	2.373 (3)	Eu1—Cl1	2.7723 (11)

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DS2185).

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## supporting information

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## Poly[[chloridodimethanol( $\mu_3$ -pyridine-2,3-dicarboxylato)europium(III)] methanol monosolvate]

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### S1. Comment

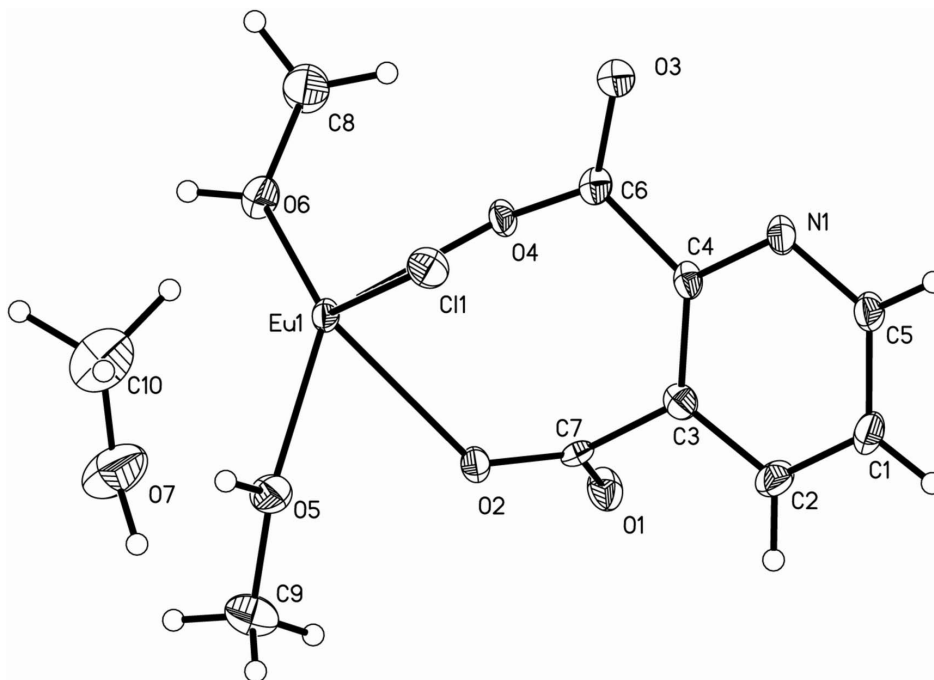
The pyridine dicarboxylic acid ( $H_2pydc$ ) is a diverse bridging ligand and has drawn some attention in photochemistry and crystal engineering. In case of pyridine-2,3-dicarboxylate functional groups,  $pydc$  exhibits bis(monodentate) (Swamy *et al.*, 1998), tridentate (Zhong *et al.*, 1994; Zhang *et al.*, 2003), bis(bidentate) (Wu *et al.*, 2003; Tong *et al.*, 2000) coordination modes to form a few transition metal coordination polymers. It should display high reactivity to the lanthanide, since the oxygen atom of carboxylate group has a strong affinity to  $Ln^{3+}$  ions (Zhao *et al.*, 2004). In this work, we selected pyridine-2,3-dicarboxylate and lanthanide ions to assemble coordination polymer under hydrothermal conditions, forming two-dimensional network structures. As depicted in Figure 1, the asymmetric unit contains one europium ion, one deprotonated pyridine 2,3-dicarboxylate ligand (PDC), two  $CH_3OH$  molecules coordinated to the metal center, one coordinated chloride and one lattice occluded  $CH_3OH$  molecule. In the crystal structure, each PDC ligand coordinates to three adjacent Eu ions by the pyridyl N and O atoms of the carboxylate moieties. Eu is coordinated by four O atoms of carboxylate, one pyridyl N, two MeOH and one chloride displaying eight-coordinated environment with average Eu—O bond length of being 2.3825 Å, obviously shorter than that of Eu—Cl 2.7724 Å (Table 1). Extended coordination of PDC ligand lead to the formation of a 2D coordination polymer (Figure 2).  $\pi\cdots\pi$  stacking interactions were found to stabilize two-dimensional structure with the shortest carbon $\cdots$ carbon distance of 3.487 Å in the plan.

### S2. Experimental

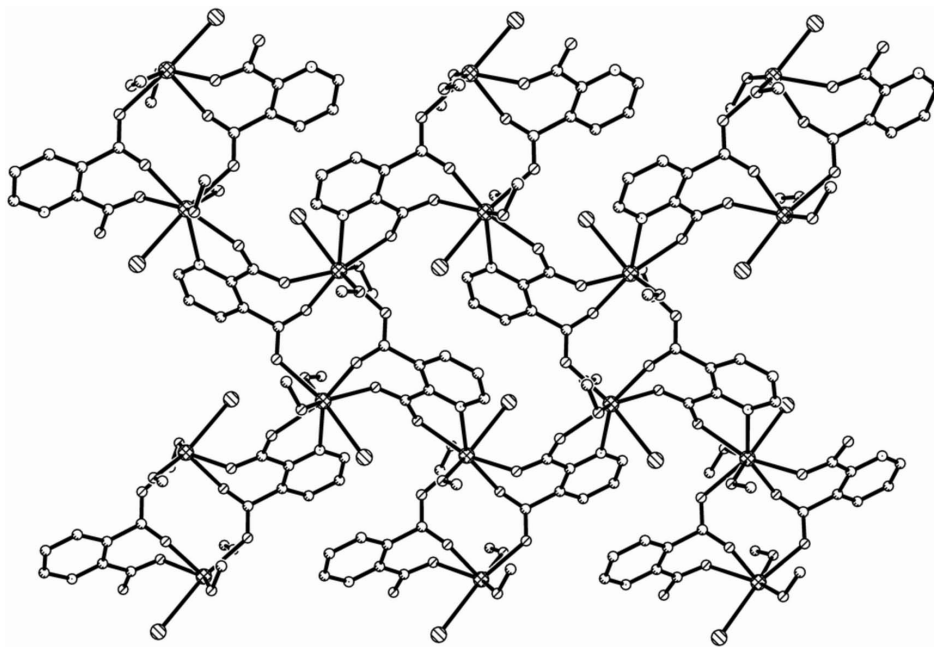
A mixture of  $EuCl_3 \cdot 6H_2O$  (0.037 g, 0.1 mmol),  $H_2pydc$  (0.017 g, 0.1 mmol) in 8 mL  $H_2O$  was stirred at room temperature for 30 min, the solution was put into a 25 mL Teflon-lined stainless-steel container, heated to 165 °C and maintained for 48 h, and then cooled to room temperature in 45 h. The colorless block crystal was obtained by filtration, washed with water and ethanol in 67% yield (based on Eu). Anal. Calc. for  $C_{10}H_{15}ClEuN_1O_7$ : C, 26.77; H, 3.37; N, 3.12. Found: C, 27.05; H, 3.47; N, 3.16%. IR (KBr pellet): 3407(m), 1698(m), 1594(s), 1565(s), 1442(m), 1381(s), 1254(m), 1095(m), 758(m)  $cm^{-1}$ .

### S3. Refinement

C-bound H atoms were placed geometrically and allowed to ride during refinement with C—H = 0.93–0.96 Å with  $U_{iso}(H) = 1.2 U_{eq}(C)$ . The hydroxy H atom of the methanol solvent molecule was located in a difference Fourier map and refined as riding with the parent atom with  $U_{iso}(H) = 1.5 U_{eq}(O)$ , O—H distances 0.82 and 0.85 Å.

**Figure 1**

The molecular structure of the title compound, the thermal ellipsoids were drawn at 50% probability level.

**Figure 2**

The 2-D packing structure of the title compound.

Poly[[chloridodimethanol( $\mu_3$ -pyridine-2,3-dicarboxylato)europium(III)] methanol monosolvate]

## Crystal data

[Eu(C<sub>7</sub>H<sub>3</sub>NO<sub>4</sub>)Cl(CH<sub>4</sub>O)<sub>2</sub>]-CH<sub>4</sub>O $M_r = 448.64$ Monoclinic,  $P2_1/n$ 

Hall symbol: -P 2yn

 $a = 10.4870$  (3) Å $b = 10.9123$  (3) Å $c = 12.9248$  (3) Å $\beta = 99.694$  (2)° $V = 1457.96$  (7) Å<sup>3</sup> $Z = 4$  $F(000) = 872$  $D_x = 2.044$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 5415 reflections

 $\theta = 3.0$ – $29.1$ ° $\mu = 4.51$  mm<sup>-1</sup> $T = 150$  K

Block, white

 $0.20 \times 0.15 \times 0.14$  mm

## Data collection

Bruker SMART CCD area-detector

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 $\phi$  and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 1997)

 $T_{\min} = 0.448$ ,  $T_{\max} = 0.532$ 

7658 measured reflections

2550 independent reflections

2260 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.029$  $\theta_{\max} = 25.0$ °,  $\theta_{\min} = 3.0$ ° $h = -12 \rightarrow 11$  $k = -12 \rightarrow 12$  $l = -14 \rightarrow 15$ 

## Refinement

Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.026$  $wR(F^2) = 0.057$  $S = 1.02$ 

2550 reflections

184 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 1.5721P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 1.34$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.56$  e Å<sup>-3</sup>

## 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.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional R-factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Eu1	0.19538 (2)	0.471828 (18)	0.142087 (15)	0.01375 (8)
C1	0.1686 (5)	1.0083 (4)	-0.0245 (4)	0.0217 (10)
H1A	0.1752	1.0679	-0.0747	0.026*
C2	0.1143 (4)	0.8967 (4)	-0.0540 (3)	0.0204 (10)

H2A	0.0830	0.8801	-0.1243	0.024*
C3	0.1066 (4)	0.8081 (4)	0.0227 (3)	0.0152 (9)
C4	0.1520 (4)	0.8388 (4)	0.1267 (3)	0.0141 (9)
C5	0.2135 (4)	1.0315 (4)	0.0803 (3)	0.0187 (9)
H5A	0.2508	1.1073	0.0992	0.022*
C6	0.1440 (4)	0.7542 (4)	0.2180 (3)	0.0142 (9)
C7	0.0458 (4)	0.6855 (4)	-0.0113 (3)	0.0149 (9)
C8	-0.0245 (5)	0.4395 (4)	0.3294 (4)	0.0309 (12)
H8A	-0.1158	0.4238	0.3164	0.046*
H8B	-0.0096	0.5262	0.3342	0.046*
H8C	0.0137	0.4012	0.3942	0.046*
C9	0.2592 (5)	0.3714 (5)	-0.1019 (4)	0.0298 (12)
H9A	0.3221	0.3790	-0.1476	0.045*
H9B	0.1840	0.4189	-0.1292	0.045*
H9C	0.2353	0.2869	-0.0974	0.045*
C10	0.6250 (6)	0.3148 (5)	0.1466 (4)	0.0437 (14)
H10A	0.7143	0.3136	0.1383	0.066*
H10B	0.6088	0.2489	0.1919	0.066*
H10C	0.6057	0.3915	0.1769	0.066*
Cl1	0.41214 (10)	0.62123 (9)	0.17815 (8)	0.0207 (2)
N1	0.2053 (3)	0.9493 (3)	0.1559 (3)	0.0161 (8)
O1	-0.0723 (3)	0.6882 (2)	-0.0493 (2)	0.0201 (7)
O2	0.1171 (3)	0.5928 (2)	-0.0058 (2)	0.0189 (7)
O3	0.1826 (3)	0.7950 (2)	0.3084 (2)	0.0180 (7)
O4	0.0993 (3)	0.6474 (2)	0.2001 (2)	0.0154 (6)
O5	0.3136 (3)	0.4156 (3)	0.0010 (2)	0.0222 (7)
O6	0.0332 (3)	0.3900 (3)	0.2445 (2)	0.0235 (7)
O7	0.5459 (4)	0.3005 (4)	0.0477 (3)	0.0470 (10)
H7A	0.5784	0.3203	-0.0159	0.056*
H5B	0.3905	0.3848	0.0202	0.056*
H6B	0.0268	0.3152	0.2582	0.056*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Eu1	0.01652 (13)	0.00914 (13)	0.01382 (12)	-0.00020 (9)	-0.00258 (8)	0.00020 (8)
C1	0.029 (3)	0.013 (2)	0.021 (2)	0.0009 (19)	0.001 (2)	0.0053 (18)
C2	0.024 (3)	0.019 (2)	0.015 (2)	-0.0010 (19)	-0.0036 (18)	0.0026 (18)
C3	0.012 (2)	0.016 (2)	0.017 (2)	0.0029 (18)	-0.0012 (16)	-0.0021 (17)
C4	0.011 (2)	0.011 (2)	0.018 (2)	0.0013 (17)	-0.0040 (17)	-0.0012 (17)
C5	0.024 (3)	0.011 (2)	0.019 (2)	-0.0006 (19)	-0.0025 (18)	-0.0003 (18)
C6	0.008 (2)	0.015 (2)	0.018 (2)	0.0021 (17)	-0.0011 (17)	0.0019 (17)
C7	0.021 (3)	0.015 (2)	0.007 (2)	0.0018 (19)	-0.0006 (17)	0.0021 (16)
C8	0.036 (3)	0.029 (3)	0.031 (3)	0.005 (2)	0.017 (2)	0.003 (2)
C9	0.031 (3)	0.033 (3)	0.024 (3)	-0.004 (2)	0.002 (2)	-0.008 (2)
C10	0.030 (3)	0.052 (4)	0.050 (4)	0.001 (3)	0.006 (3)	0.012 (3)
Cl1	0.0198 (6)	0.0199 (5)	0.0212 (6)	-0.0041 (4)	0.0000 (4)	-0.0028 (4)
N1	0.017 (2)	0.0103 (18)	0.0194 (19)	0.0012 (14)	-0.0013 (15)	-0.0002 (14)

O1	0.0193 (18)	0.0143 (15)	0.0243 (17)	-0.0021 (13)	-0.0027 (13)	-0.0026 (12)
O2	0.0263 (18)	0.0117 (15)	0.0163 (15)	0.0037 (14)	-0.0034 (13)	-0.0013 (12)
O3	0.0208 (18)	0.0147 (15)	0.0166 (16)	-0.0028 (13)	-0.0024 (13)	-0.0004 (12)
O4	0.0181 (17)	0.0090 (14)	0.0177 (15)	-0.0007 (12)	-0.0006 (12)	-0.0019 (12)
O5	0.0222 (18)	0.0244 (17)	0.0182 (16)	0.0044 (14)	-0.0019 (13)	-0.0003 (13)
O6	0.0294 (19)	0.0183 (16)	0.0224 (17)	-0.0005 (14)	0.0032 (14)	0.0033 (13)
O7	0.043 (3)	0.067 (3)	0.034 (2)	0.018 (2)	0.0145 (19)	0.0166 (19)

*Geometric parameters (Å, °)*

Eu1—O3 <sup>i</sup>	2.344 (3)	C7—O1	1.253 (5)
Eu1—O4	2.346 (3)	C7—O2	1.253 (5)
Eu1—O2	2.354 (3)	C8—O6	1.445 (5)
Eu1—O1 <sup>ii</sup>	2.373 (3)	C8—H8A	0.9600
Eu1—O5	2.450 (3)	C8—H8B	0.9600
Eu1—O6	2.490 (3)	C8—H8C	0.9600
Eu1—N1 <sup>i</sup>	2.655 (3)	C9—O5	1.438 (5)
Eu1—C11	2.7723 (11)	C9—H9A	0.9600
C1—C2	1.371 (6)	C9—H9B	0.9600
C1—C5	1.380 (6)	C9—H9C	0.9600
C1—H1A	0.9300	C10—O7	1.410 (7)
C2—C3	1.397 (6)	C10—H10A	0.9600
C2—H2A	0.9300	C10—H10B	0.9600
C3—C4	1.389 (6)	C10—H10C	0.9600
C3—C7	1.515 (6)	N1—Eu1 <sup>iii</sup>	2.655 (3)
C4—N1	1.355 (5)	O1—Eu1 <sup>ii</sup>	2.373 (3)
C4—C6	1.512 (6)	O3—Eu1 <sup>iii</sup>	2.344 (3)
C5—N1	1.340 (5)	O5—H5B	0.8701
C5—H5A	0.9300	O6—H6B	0.8404
C6—O3	1.253 (5)	O7—H7A	0.9656
C6—O4	1.262 (5)		
O3 <sup>i</sup> —Eu1—O4	146.02 (10)	N1—C5—H5A	118.7
O3 <sup>i</sup> —Eu1—O2	141.52 (10)	C1—C5—H5A	118.7
O4—Eu1—O2	72.05 (9)	O3—C6—O4	123.4 (4)
O3 <sup>i</sup> —Eu1—O1 <sup>ii</sup>	75.98 (10)	O3—C6—C4	117.3 (3)
O4—Eu1—O1 <sup>ii</sup>	122.41 (10)	O4—C6—C4	119.2 (3)
O2—Eu1—O1 <sup>ii</sup>	85.21 (10)	O1—C7—O2	125.6 (4)
O3 <sup>i</sup> —Eu1—O5	71.06 (10)	O1—C7—C3	115.6 (4)
O4—Eu1—O5	137.83 (10)	O2—C7—C3	118.6 (4)
O2—Eu1—O5	71.76 (10)	O6—C8—H8A	109.5
O1 <sup>ii</sup> —Eu1—O5	74.93 (10)	O6—C8—H8B	109.5
O3 <sup>i</sup> —Eu1—O6	87.13 (10)	H8A—C8—H8B	109.5
O4—Eu1—O6	75.79 (10)	O6—C8—H8C	109.5
O2—Eu1—O6	117.19 (10)	H8A—C8—H8C	109.5
O1 <sup>ii</sup> —Eu1—O6	69.05 (10)	H8B—C8—H8C	109.5
O5—Eu1—O6	141.48 (10)	O5—C9—H9A	109.5
O3 <sup>i</sup> —Eu1—N1 <sup>i</sup>	63.22 (10)	O5—C9—H9B	109.5

O4—Eu1—N1 <sup>i</sup>	83.10 (10)	H9A—C9—H9B	109.5
O2—Eu1—N1 <sup>i</sup>	151.18 (10)	O5—C9—H9C	109.5
O1 <sup>ii</sup> —Eu1—N1 <sup>i</sup>	121.25 (10)	H9A—C9—H9C	109.5
O5—Eu1—N1 <sup>i</sup>	123.02 (10)	H9B—C9—H9C	109.5
O6—Eu1—N1 <sup>i</sup>	68.52 (10)	O7—C10—H10A	109.5
O3 <sup>i</sup> —Eu1—C11	92.51 (7)	O7—C10—H10B	109.5
O4—Eu1—C11	81.38 (7)	H10A—C10—H10B	109.5
O2—Eu1—C11	88.32 (8)	O7—C10—H10C	109.5
O1 <sup>ii</sup> —Eu1—C11	151.46 (8)	H10A—C10—H10C	109.5
O5—Eu1—C11	76.64 (7)	H10B—C10—H10C	109.5
O6—Eu1—C11	137.37 (7)	C5—N1—C4	117.8 (4)
N1 <sup>i</sup> —Eu1—C11	73.41 (8)	C5—N1—Eu1 <sup>iii</sup>	126.3 (3)
C2—C1—C5	119.5 (4)	C4—N1—Eu1 <sup>iii</sup>	115.6 (2)
C2—C1—H1A	120.2	C7—O1—Eu1 <sup>ii</sup>	126.7 (3)
C5—C1—H1A	120.2	C7—O2—Eu1	128.4 (2)
C1—C2—C3	119.2 (4)	C6—O3—Eu1 <sup>iii</sup>	128.6 (3)
C1—C2—H2A	120.4	C6—O4—Eu1	130.2 (3)
C3—C2—H2A	120.4	C9—O5—Eu1	126.9 (3)
C4—C3—C2	117.9 (4)	C9—O5—H5B	109.8
C4—C3—C7	123.5 (4)	Eu1—O5—H5B	116.4
C2—C3—C7	118.5 (4)	C8—O6—Eu1	132.9 (3)
N1—C4—C3	122.8 (4)	C8—O6—H6B	98.2
N1—C4—C6	113.6 (3)	Eu1—O6—H6B	123.2
C3—C4—C6	123.6 (4)	C10—O7—H7A	120.6
N1—C5—C1	122.6 (4)		

Symmetry codes: (i)  $-x+1/2, y-1/2, -z+1/2$ ; (ii)  $-x, -y+1, -z$ ; (iii)  $-x+1/2, y+1/2, -z+1/2$ .