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Poly[hexaaquahexakis(μ-pyridine-2,4-dicarboxylato)tricopper(II)-dieuropium(III)]

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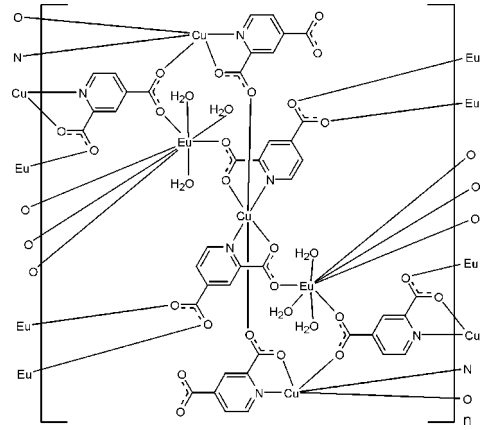
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.005 Å; R factor = 0.028; wR factor = 0.066; data-to-parameter ratio = 15.4.

The asymmetric unit of the title heterometallic coordination polymer, $[Cu_3Eu_2(C_7H_3NO_4)_6(H_2O)_6]_n$, contains one Eu^{III} and two Cu^{II} atoms, three pyridine-2,4-dicarboxylate $(pdc)^{2-}$ anions and three water molecules. One Cu^{II} atom is located on an inversion center and is *N*,*O*-chelated by two pdc^{2-} anions in the equatorial plane and further coordinated by two carboxylate O atoms from another two pdc anions in the axial positions, with an elongated octahedral geometry [Cu—O = 2.409 (3) Å in the axial direction]; the other Cu atom is *N*,*O*-chelated by two pdc anions in the coordination basal plane and coordinated by a carboxyl O atom at the apical position with a distorted square-pyramidal geometry [Cu—O = 2.359 (3) Å in the apical direction]. The Eu atom is eight-coordinated with a distorted square-antiprismatic geometry formed by five carboxylate O atoms from five pdc anions and three water molecules. The carboxylate anions bridge adjacent Eu and Cu atoms, forming the coordination polymer. Inter- and intramolecular O—H···O hydrogen bonding occurs in the structure. π–π stacking further consolidates the crystal structure, the centroid–centroid distance between parallel pyridine rings being 3.367 (2) Å.

Related literature

For structures and applications of related heterometallic lanthanide-transition metal coordination polymers, see: Huang *et al.* (2008*a*,*b*). For the coordination modes of the pyridine-2,6-dicarboxylate ligand, see: Ma *et al.* (2010); Zhao *et al.* (2007); Wang *et al.* (2007). For the coordination modes of the pyridine-2,5-dicarboxylate ligand, see: Song *et al.* (2006); Wang *et al.* (2009). For the coordination modes of the pyridine-2,3-dicarboxylate ligand, see: Wang *et al.* (2010).



Experimental

Crystal data

$[Cu_3Eu_2(C_7H_3NO_4)_6(H_2O)_6]$
M_r = 1593.29
Triclinic, $P\overline{1}$
a = 9.4296 (10) Å
b = 10.7002 (11) Å
c = 12.2874 (13) Å
α = 86.186 (2)°
β = 81.556 (2)°
γ = 86.561 (2)°
V = 1222.0 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 3.92 mm^{-1}
T = 294 K
0.24 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.659, T_{max} = 0.977
12982 measured reflections
5780 independent reflections
4828 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.066
S = 0.98
5780 reflections
376 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.69 e Å^{-3}
$\Delta\rho_{min}$ = −0.94 e Å^{-3}

Table 1
Selected bond lengths (Å).

Eu1—O6^{i}	2.485 (2)	Cu1—O1	1.932 (3)
Eu1—O8	2.386 (3)	Cu1—O5^{iv}	1.944 (2)
Eu1—O10^{ii}	2.404 (2)	Cu1—O7	2.359 (3)
Eu1—O11^{iii}	2.385 (2)	Cu1—N1	1.975 (3)
Eu1—O12^{i}	2.328 (2)	Cu1—N2^{iv}	1.975 (3)
Eu1—O13	2.454 (3)	Cu2—O2	2.409 (3)
Eu1—O14	2.442 (3)	Cu2—O9	1.968 (2)
Eu1—O15	2.510 (3)	Cu2—N3	1.969 (3)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O13—H13A···O5^{i}	0.82	2.00	2.769 (3)	155
O13—H13B···O15^{v}	0.82	2.02	2.822 (4)	164
O14—H14A···O7	0.82	1.89	2.690 (4)	164
O14—H14B···O4^{vi}	0.82	1.88	2.667 (4)	161
O15—H15A···O3^{vii}	0.82	1.83	2.630 (4)	164
O15—H15B···O4^{vi}	0.82	2.06	2.814 (4)	153

Symmetry codes: (i) $-x+1, -y+1, -z$; (v) $-x+1, -y+1, -z+1$; (vi) $-x, -y+2, -z+1$; (vii) $x, y-1, z$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5066).

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supporting information

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Poly[hexaaquahexakis(*μ*-pyridine-2,4-dicarboxylato)tricopper(II)dieuropium(III)]

Shie Fu Lush and Fwu Ming Shen

S1. Comment

In recent years, many research groups have devoted their work to the design and synthesis of lanthanide–transition(3 d-4f) heterometallic coordination frameworks with bridging multifunctional organic ligands, such as pyridinedicarboxylic acid (Ma *et al.*, 2010; Song *et al.*, 2006; Wang *et al.*,2007; Wang *et al.*, 2009; Wang *et al.*, 2010; Zhao *et al.*,2007). Pyridine-2,4-dicarboxylic acid ($pdaH_2$) ligand is a good candidate due to its flexible and various coordination donors containing either N– or O–atom donors. Some examples of coordination with $pdaH_2$ have been reported (Huang *et al.*, 2008*a*; Huang *et al.*, 2008*b*.).

Herein we report a new 3 d-4f heterometallic coordination polymer based on $pdaH_2$ ligand, formulated as $[Eu_2Cu_3(C_7H_3NO_4)_6(H_2O)_6]_n$. The symmetric unit of the title compound contains one octa-coordinated Eu^{III} atom and two types of environments of Cu^{II} center, the penta-coordinate Cu^{II} atom is in a square- pyramidal geometry, the other Cu^{II} atom is in a slightly distorted octahedral geometry. The Eu^{III} ion presents a EuO_8 square antiprismatic coordination geometry, formed by five mono-dentate pda O atoms and three coordinate water molecules, the $Cu1^{II}$ion presents a CuN_2O_3 square- pyramidal coordination geometry, formed by two bidentate pda (–NO–) ligand (2-carboxy) in the equatorial plane, and one O atom from monodentate pda (4-carboxy) ligand at the axial sites, the other $Cu2^{II}$ ion presents a slightly distorted (CuN_2O_4) octahedral coordination geometry, formed by two bidentate pda (–NO–) ligand (2-carboxy) in the equatorial plane, and two monodentate pda(2-carboxy) ligands at the axial sites (Table 1, Fig 1). The pda One carboxyl group bridges the neighboring Eu or Cu cations, forming the 3-D polymeric architecture.

In the title crystal structure, a three-dimensional network is formed *via* intra- intermolecular O—H···O hydrogen bonds (Table 2, Fig. 2). In addition, C—H···O hydrogen bonds (full details and symmetry codes are given in Table 2), C7—O3···*Cg*8 (N3/C15—C19) interactions are also present. The *π*···*π*, *π*···Metal stacking interactions are also observed, the centroid-centroid distance between the pyridine rings being 3.367 (2)Å [$Cg7^{iv}$···*Cg*7 (N2/C8—C12)] [symmetry codes: -*x*, 1 - *y*, -*z*]. The *Cg*1 (Cu1/O1—N1—C1—C6)···Cu1 interaction is 3.905Å [symmetry codes: -*x*, 2 - *y*, -*z*].

S2. Experimental

A mixture of europium chloride hexahydrate (0.25 mmol, 0.0916 g), copper acetate hydrate (0.25 mmol, 0.050 g), pyridine-2,4-dicarboxylic acid (0.25 mmol, 0.0418 g) and 10 ml H_2O were put in a 23-ml Teflon liner reactor and heated at 418 K in oven for 48 h. The resulting solution was slowly cooled to room temperature. The blue transparent single crystals of the title complex were obtained in 43.21% yield (based on Eu).

S3. Refinement

Water H atoms wre located in a difference Fourier map and refined with the distances constraints of O—H = 0.82 Å, U_{iso}(H) = 1.5U_{eq}(O). Other H atoms were positioned geometrically with C—H = 0.93 Å (aromatic), and refined using a

riding model with $U_{iso}(H) = 1.2U_{eq}(C)$.

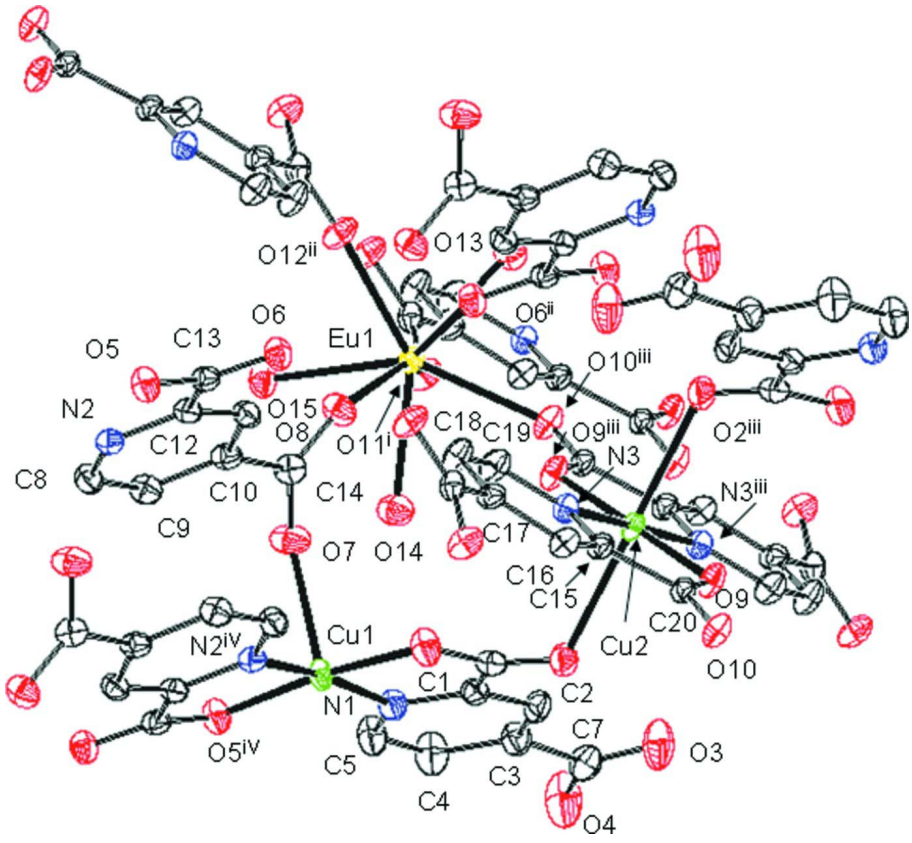

Figure 1

View of the title compound with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) *x*, *y*, *z* + 1; (ii) -*x* + 1, -*y* + 1, -*z*; (iii) -*x* + 1, -*y* + 2, -*z*; (iv) -*x*, -*y* + 1, -*z*].

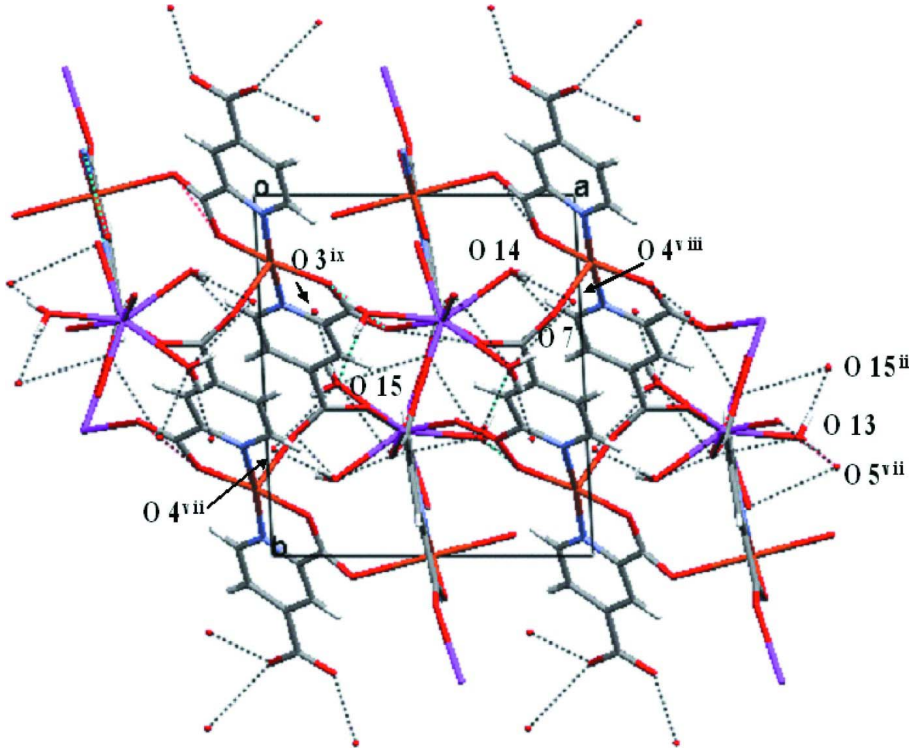

Figure 2

The molecular packing for the title compound, viewed along the *c* axis. Hydrogen bonds are shown as dashed lines.

Poly[hexaaquahexakis(*μ*-pyridine-2,4-dicarboxylato)tricopper(II)dieuropium(III)]

Crystal data

$[Cu_3Eu_2(C_7H_3NO_4)_6(H_2O)_6]$
M_r = 1593.29
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 9.4296 (10) Å
b = 10.7002 (11) Å
c = 12.2874 (13) Å
α = 86.186 (2)°
β = 81.556 (2)°
γ = 86.561 (2)°
V = 1222.0 (2) Å^3
Z = 1
F(000) = 777
D_x = 2.165 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 6583 reflections
θ = 2.5–25.0°
μ = 3.92 mm^{-1}
T = 294 K
Equant, blue
0.24 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 9 pixels mm^{-1}
φ and *ω* scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.659, T_{max} = 0.977
12982 measured reflections
5780 independent reflections
4828 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 28.3°, θ_{min} = 1.7°
h = −12→12
k = −13→13
l = −15→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.066$
$S = 0.98$
5780 reflections
376 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
$w = 1/[\sigma^2(F_o^2) + (0.0323P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.69$ e Å^{-3}
$\Delta\rho_{min} = -0.94$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Eu1	0.42924 (2)	0.65169 (1)	0.35169 (1)	0.0161 (1)
Cu1	−0.04296 (4)	0.81387 (4)	0.11987 (3)	0.0220 (1)
Cu2	0.50000	1.00000	0.00000	0.0188 (2)
O1	0.1188 (3)	0.8879 (2)	0.0288 (2)	0.0274 (8)
O2	0.2474 (3)	1.0583 (2)	0.0150 (2)	0.0272 (8)
O3	0.1716 (3)	1.3256 (3)	0.3467 (2)	0.0406 (10)
O4	−0.0222 (3)	1.2972 (3)	0.4696 (3)	0.0524 (11)
O5	0.2216 (2)	0.2480 (2)	−0.19845 (19)	0.0238 (7)
O6	0.3969 (2)	0.3742 (2)	−0.18098 (19)	0.0236 (8)
O7	0.0882 (3)	0.6635 (2)	0.2196 (2)	0.0313 (8)
O8	0.3149 (3)	0.5865 (2)	0.2057 (2)	0.0258 (8)
O9	0.5336 (3)	1.1177 (2)	−0.13010 (19)	0.0230 (7)
O10	0.5037 (3)	1.1358 (2)	−0.30699 (19)	0.0235 (7)
O11	0.3895 (3)	0.7209 (2)	−0.46529 (19)	0.0254 (8)
O12	0.4790 (3)	0.5533 (2)	−0.3775 (2)	0.0269 (8)
O13	0.6647 (3)	0.6702 (3)	0.4101 (2)	0.0318 (9)
O14	0.2105 (3)	0.7873 (2)	0.3621 (2)	0.0285 (8)
O15	0.2311 (3)	0.5207 (2)	0.4481 (2)	0.0262 (8)
N1	−0.0265 (3)	0.9489 (3)	0.2186 (2)	0.0222 (9)
N2	0.0738 (3)	0.3055 (3)	−0.0108 (2)	0.0190 (8)
N3	0.4749 (3)	0.8802 (3)	−0.1097 (2)	0.0179 (8)
C1	0.0834 (3)	1.0218 (3)	0.1776 (3)	0.0193 (10)
C2	0.1182 (4)	1.1211 (3)	0.2322 (3)	0.0232 (10)
C3	0.0356 (4)	1.1510 (3)	0.3314 (3)	0.0260 (11)
C4	−0.0795 (4)	1.0771 (4)	0.3712 (3)	0.0344 (12)

C5	−0.1064 (4)	0.9764 (4)	0.3138 (3)	0.0314 (12)
C6	0.1590 (4)	0.9878 (3)	0.0650 (3)	0.0213 (10)
C7	0.0646 (4)	1.2678 (4)	0.3881 (3)	0.0282 (12)
C8	−0.0144 (4)	0.3380 (3)	0.0799 (3)	0.0214 (10)
C9	0.0190 (4)	0.4295 (3)	0.1443 (3)	0.0225 (10)
C10	0.1511 (4)	0.4835 (3)	0.1200 (3)	0.0200 (10)
C11	0.2450 (3)	0.4447 (3)	0.0287 (3)	0.0199 (10)
C12	0.2009 (3)	0.3591 (3)	−0.0364 (3)	0.0177 (9)
C13	0.2824 (3)	0.3236 (3)	−0.1467 (3)	0.0187 (10)
C14	0.1878 (4)	0.5861 (3)	0.1875 (3)	0.0209 (10)
C15	0.4789 (3)	0.9361 (3)	−0.2116 (3)	0.0177 (9)
C16	0.4629 (4)	0.8712 (3)	−0.3016 (3)	0.0195 (10)
C17	0.4471 (4)	0.7427 (3)	−0.2868 (3)	0.0193 (10)
C18	0.4458 (4)	0.6855 (3)	−0.1819 (3)	0.0248 (10)
C19	0.4564 (4)	0.7580 (3)	−0.0948 (3)	0.0233 (10)
C20	0.5063 (3)	1.0751 (3)	−0.2176 (3)	0.0178 (9)
C21	0.4380 (4)	0.6657 (3)	−0.3837 (3)	0.0195 (10)
H2A	0.19630	1.16800	0.20320	0.0280*
H4A	−0.13820	1.09550	0.43650	0.0410*
H5A	−0.18220	0.92660	0.34220	0.0380*
H8A	−0.10000	0.29790	0.09970	0.0260*
H9A	−0.04660	0.45500	0.20380	0.0270*
H11A	0.33600	0.47600	0.01220	0.0240*
H13A	0.71830	0.70010	0.35740	0.0480*
H13B	0.70360	0.60960	0.44030	0.0480*
H14A	0.16690	0.76300	0.31500	0.0430*
H14B	0.15520	0.77690	0.41960	0.0430*
H15A	0.19680	0.46590	0.41800	0.0390*
H15B	0.15630	0.55220	0.48000	0.0390*
H16A	0.46260	0.91230	−0.37070	0.0230*
H18A	0.43800	0.59920	−0.17040	0.0300*
H19A	0.45030	0.72020	−0.02400	0.0280*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Eu1	0.0202 (1)	0.0122 (1)	0.0166 (1)	−0.0010 (1)	−0.0040 (1)	−0.0033 (1)
Cu1	0.0214 (2)	0.0212 (2)	0.0238 (2)	−0.0061 (2)	0.0003 (2)	−0.0088 (2)
Cu2	0.0269 (3)	0.0140 (3)	0.0167 (3)	−0.0032 (2)	−0.0048 (2)	−0.0041 (2)
O1	0.0258 (13)	0.0283 (15)	0.0280 (14)	−0.0073 (11)	0.0036 (11)	−0.0125 (11)
O2	0.0224 (13)	0.0206 (14)	0.0364 (15)	−0.0039 (10)	0.0047 (11)	−0.0022 (11)
O3	0.0470 (18)	0.0376 (17)	0.0378 (16)	−0.0199 (14)	0.0054 (14)	−0.0160 (13)
O4	0.0512 (19)	0.046 (2)	0.057 (2)	−0.0178 (15)	0.0228 (16)	−0.0343 (16)
O5	0.0226 (12)	0.0271 (14)	0.0222 (12)	−0.0056 (10)	−0.0001 (10)	−0.0089 (10)
O6	0.0211 (12)	0.0235 (14)	0.0258 (13)	−0.0055 (10)	0.0027 (10)	−0.0073 (10)
O7	0.0308 (14)	0.0296 (15)	0.0369 (15)	0.0100 (12)	−0.0139 (12)	−0.0169 (12)
O8	0.0222 (13)	0.0320 (15)	0.0250 (13)	−0.0017 (11)	−0.0061 (11)	−0.0095 (11)
O9	0.0349 (14)	0.0140 (12)	0.0215 (12)	−0.0062 (10)	−0.0067 (11)	−0.0016 (10)

O10	0.0352 (14)	0.0145 (12)	0.0207 (12)	−0.0031 (10)	−0.0032 (11)	−0.0002 (10)
O11	0.0367 (14)	0.0211 (13)	0.0190 (12)	0.0028 (11)	−0.0064 (11)	−0.0042 (10)
O12	0.0392 (15)	0.0133 (13)	0.0285 (14)	0.0033 (11)	−0.0062 (12)	−0.0056 (10)
O13	0.0287 (14)	0.0401 (17)	0.0280 (14)	−0.0078 (12)	−0.0103 (11)	0.0068 (12)
O14	0.0282 (14)	0.0287 (15)	0.0301 (14)	0.0032 (11)	−0.0076 (11)	−0.0084 (11)
O15	0.0264 (13)	0.0219 (13)	0.0304 (14)	−0.0060 (10)	0.0002 (11)	−0.0076 (11)
N1	0.0215 (15)	0.0211 (16)	0.0239 (15)	−0.0018 (12)	0.0000 (12)	−0.0070 (12)
N2	0.0182 (14)	0.0165 (14)	0.0220 (15)	0.0014 (11)	−0.0025 (12)	−0.0018 (11)
N3	0.0223 (14)	0.0156 (14)	0.0159 (14)	−0.0019 (11)	−0.0018 (11)	−0.0034 (11)
C1	0.0178 (16)	0.0178 (17)	0.0229 (17)	0.0008 (13)	−0.0037 (14)	−0.0049 (13)
C2	0.0240 (18)	0.0167 (17)	0.0295 (19)	−0.0045 (14)	−0.0036 (15)	−0.0030 (14)
C3	0.0252 (19)	0.024 (2)	0.029 (2)	−0.0025 (15)	−0.0016 (16)	−0.0078 (16)
C4	0.037 (2)	0.034 (2)	0.031 (2)	−0.0092 (18)	0.0076 (17)	−0.0137 (17)
C5	0.029 (2)	0.032 (2)	0.032 (2)	−0.0102 (17)	0.0068 (17)	−0.0101 (17)
C6	0.0179 (17)	0.0220 (18)	0.0242 (18)	0.0047 (14)	−0.0054 (14)	−0.0030 (14)
C7	0.035 (2)	0.022 (2)	0.029 (2)	−0.0021 (16)	−0.0053 (17)	−0.0090 (16)
C8	0.0175 (16)	0.0229 (19)	0.0233 (17)	−0.0030 (13)	−0.0005 (14)	−0.0022 (14)
C9	0.0218 (17)	0.0253 (19)	0.0202 (17)	0.0024 (14)	−0.0017 (14)	−0.0061 (14)
C10	0.0215 (17)	0.0199 (18)	0.0197 (17)	0.0032 (14)	−0.0074 (14)	−0.0040 (13)
C11	0.0157 (16)	0.0218 (18)	0.0229 (17)	−0.0012 (13)	−0.0040 (14)	−0.0040 (14)
C12	0.0167 (16)	0.0178 (17)	0.0187 (16)	0.0004 (13)	−0.0027 (13)	−0.0021 (13)
C13	0.0188 (16)	0.0173 (17)	0.0207 (17)	0.0024 (13)	−0.0050 (14)	−0.0037 (13)
C14	0.0253 (18)	0.0232 (18)	0.0147 (16)	0.0010 (14)	−0.0046 (14)	−0.0036 (13)
C15	0.0205 (16)	0.0133 (16)	0.0195 (16)	−0.0003 (13)	−0.0030 (13)	−0.0026 (13)
C16	0.0272 (18)	0.0164 (17)	0.0154 (16)	0.0005 (13)	−0.0056 (14)	−0.0010 (13)
C17	0.0216 (17)	0.0158 (17)	0.0208 (17)	0.0016 (13)	−0.0033 (14)	−0.0048 (13)
C18	0.040 (2)	0.0151 (17)	0.0200 (17)	−0.0041 (15)	−0.0046 (16)	−0.0028 (13)
C19	0.036 (2)	0.0182 (18)	0.0160 (16)	−0.0015 (15)	−0.0051 (15)	0.0006 (13)
C20	0.0169 (16)	0.0136 (16)	0.0220 (17)	−0.0005 (12)	0.0009 (13)	−0.0031 (13)
C21	0.0209 (17)	0.0193 (18)	0.0184 (16)	−0.0049 (13)	−0.0001 (14)	−0.0043 (13)

Geometric parameters (Å, º)

Eu1—O6^{i}	2.485 (2)	O15—H15B	0.8200
Eu1—O8	2.386 (3)	O15—H15A	0.8200
Eu1—O10^{ii}	2.404 (2)	N1—C5	1.335 (5)
Eu1—O11^{iii}	2.385 (2)	N1—C1	1.352 (4)
Eu1—O12^{i}	2.328 (2)	N2—C8	1.341 (4)
Eu1—O13	2.454 (3)	N2—C12	1.346 (4)
Eu1—O14	2.442 (3)	N3—C15	1.348 (4)
Eu1—O15	2.510 (3)	N3—C19	1.327 (5)
Cu1—O1	1.932 (3)	C1—C6	1.517 (5)
Cu1—O5^{iv}	1.944 (2)	C1—C2	1.374 (5)
Cu1—O7	2.359 (3)	C2—C3	1.392 (5)
Cu1—N1	1.975 (3)	C3—C7	1.528 (5)
Cu1—N2^{iv}	1.975 (3)	C3—C4	1.392 (5)
Cu2—O2	2.409 (3)	C4—C5	1.382 (6)
Cu2—O9	1.968 (2)	C8—C9	1.377 (5)

Cu2—N3	1.969 (3)	C9—C10	1.389 (5)
Cu2—O2^{ii}	2.409 (3)	C10—C11	1.393 (5)
Cu2—O9^{ii}	1.968 (2)	C10—C14	1.505 (5)
Cu2—N3^{ii}	1.969 (3)	C11—C12	1.376 (5)
O1—C6	1.283 (4)	C12—C13	1.516 (5)
O2—C6	1.227 (4)	C15—C20	1.520 (5)
O3—C7	1.242 (5)	C15—C16	1.375 (5)
O4—C7	1.242 (5)	C16—C17	1.389 (5)
O5—C13	1.272 (4)	C17—C21	1.508 (5)
O6—C13	1.242 (4)	C17—C18	1.388 (5)
O7—C14	1.251 (4)	C18—C19	1.381 (5)
O8—C14	1.251 (5)	C2—H2A	0.9300
O9—C20	1.261 (4)	C4—H4A	0.9300
O10—C20	1.241 (4)	C5—H5A	0.9300
O11—C21	1.260 (4)	C8—H8A	0.9300
O12—C21	1.242 (4)	C9—H9A	0.9300
O13—H13B	0.8200	C11—H11A	0.9300
O13—H13A	0.8200	C16—H16A	0.9300
O14—H14A	0.8200	C18—H18A	0.9300
O14—H14B	0.8200	C19—H19A	0.9300

O8—Eu1—O13	143.07 (9)	H15A—O15—H15B	99.00
O8—Eu1—O14	76.92 (8)	Eu1—O15—H15A	123.00
O8—Eu1—O15	75.96 (8)	Eu1—O15—H15B	122.00
O8—Eu1—O11^{iii}	144.45 (9)	C1—N1—C5	118.9 (3)
O6^{i}—Eu1—O8	68.55 (8)	Cu1—N1—C1	111.1 (2)
O8—Eu1—O12^{i}	88.94 (8)	Cu1—N1—C5	130.0 (3)
O8—Eu1—O10^{ii}	108.10 (8)	Cu1^{iv}—N2—C8	128.5 (2)
O13—Eu1—O14	133.64 (9)	C8—N2—C12	119.2 (3)
O13—Eu1—O15	126.29 (9)	Cu1^{iv}—N2—C12	112.3 (2)
O11^{iii}—Eu1—O13	72.28 (9)	Cu2—N3—C19	128.7 (2)
O6^{i}—Eu1—O13	75.67 (8)	Cu2—N3—C15	111.9 (2)
O12^{i}—Eu1—O13	74.51 (10)	C15—N3—C19	119.4 (3)
O10^{ii}—Eu1—O13	72.65 (10)	N1—C1—C6	114.2 (3)
O14—Eu1—O15	73.99 (8)	C2—C1—C6	123.6 (3)
O11^{iii}—Eu1—O14	74.60 (9)	N1—C1—C2	122.2 (3)
O6^{i}—Eu1—O14	124.22 (8)	C1—C2—C3	119.5 (3)
O12^{i}—Eu1—O14	144.83 (9)	C2—C3—C4	117.7 (3)
O10^{ii}—Eu1—O14	71.70 (9)	C2—C3—C7	120.2 (3)
O11^{iii}—Eu1—O15	76.07 (8)	C4—C3—C7	122.0 (3)
O6^{i}—Eu1—O15	132.71 (7)	C3—C4—C5	120.0 (3)
O12^{i}—Eu1—O15	71.37 (9)	N1—C5—C4	121.7 (4)
O10^{ii}—Eu1—O15	143.28 (8)	O1—C6—C1	115.5 (3)
O6^{i}—Eu1—O11^{iii}	146.55 (8)	O1—C6—O2	125.7 (3)
O11^{iii}—Eu1—O12^{i}	102.40 (8)	O2—C6—C1	118.8 (3)
O10^{ii}—Eu1—O11^{iii}	82.57 (8)	O3—C7—C3	116.6 (3)
O6^{i}—Eu1—O12^{i}	77.62 (8)	O3—C7—O4	126.3 (4)
O6^{i}—Eu1—O10^{ii}	79.02 (8)	O4—C7—C3	117.1 (3)

O10^{ii}—Eu1—O12^{i}	143.40 (10)	N2—C8—C9	121.5 (3)
O1—Cu1—O7	97.47 (10)	C8—C9—C10	119.7 (3)
O1—Cu1—N1	84.50 (11)	C9—C10—C11	118.4 (3)
O1—Cu1—O5^{iv}	172.30 (10)	C9—C10—C14	120.4 (3)
O1—Cu1—N2^{iv}	94.73 (11)	C11—C10—C14	121.1 (3)
O1—Cu1—O2^{v}	92.14 (9)	C10—C11—C12	118.9 (3)
O7—Cu1—N1	93.91 (10)	C11—C12—C13	124.3 (3)
O5^{iv}—Cu1—O7	90.08 (9)	N2—C12—C13	113.4 (3)
O7—Cu1—N2^{iv}	93.32 (10)	N2—C12—C11	122.1 (3)
O2^{v}—Cu1—O7	164.52 (8)	O5—C13—C12	115.7 (3)
O5^{iv}—Cu1—N1	96.55 (10)	O6—C13—C12	118.4 (3)
N1—Cu1—N2^{iv}	172.76 (12)	O5—C13—O6	125.9 (3)
O2^{v}—Cu1—N1	99.09 (10)	O8—C14—C10	117.1 (3)
O5^{iv}—Cu1—N2^{iv}	83.28 (10)	O7—C14—O8	126.2 (3)
O2^{v}—Cu1—O5^{iv}	80.16 (8)	O7—C14—C10	116.7 (3)
O2^{v}—Cu1—N2^{iv}	73.73 (10)	N3—C15—C20	113.9 (3)
O2—Cu2—O9	88.97 (10)	C16—C15—C20	123.7 (3)
O2—Cu2—N3	88.99 (10)	N3—C15—C16	122.4 (3)
O2—Cu2—O2^{ii}	180.00	C15—C16—C17	118.4 (3)
O2—Cu2—O9^{ii}	91.03 (10)	C16—C17—C21	120.6 (3)
O2—Cu2—N3^{ii}	91.01 (10)	C18—C17—C21	120.5 (3)
O9—Cu2—N3	83.49 (11)	C16—C17—C18	118.9 (3)
O2^{ii}—Cu2—O9	91.03 (10)	C17—C18—C19	119.3 (3)
O9—Cu2—O9^{ii}	180.00	N3—C19—C18	121.6 (3)
O9—Cu2—N3^{ii}	96.51 (10)	O9—C20—C15	115.9 (3)
O2^{ii}—Cu2—N3	91.01 (10)	O10—C20—C15	118.3 (3)
O9^{ii}—Cu2—N3	96.51 (11)	O9—C20—O10	125.7 (3)
N3—Cu2—N3^{ii}	180.00	O12—C21—C17	117.9 (3)
O2^{ii}—Cu2—O9^{ii}	88.97 (10)	O11—C21—O12	124.9 (3)
O2^{ii}—Cu2—N3^{ii}	88.99 (10)	O11—C21—C17	117.2 (3)
O9^{ii}—Cu2—N3^{ii}	83.49 (10)	C1—C2—H2A	120.00
Cu1—O1—C6	114.4 (2)	C3—C2—H2A	120.00
Cu2—O2—C6	120.1 (2)	C3—C4—H4A	120.00
Cu1^{v}—O2—Cu2	138.98 (10)	C5—C4—H4A	120.00
Cu1^{v}—O2—C6	94.1 (2)	N1—C5—H5A	119.00
Cu1^{iv}—O5—C13	115.0 (2)	C4—C5—H5A	119.00
Eu1^{i}—O6—C13	131.3 (2)	N2—C8—H8A	119.00
Cu1—O7—C14	130.9 (2)	C9—C8—H8A	119.00
Eu1—O8—C14	134.9 (2)	C8—C9—H9A	120.00
Cu2—O9—C20	113.9 (2)	C10—C9—H9A	120.00
Eu1^{ii}—O10—C20	127.0 (2)	C10—C11—H11A	121.00
Eu1^{vi}—O11—C21	125.3 (2)	C12—C11—H11A	121.00
Eu1^{i}—O12—C21	173.8 (3)	C15—C16—H16A	121.00
H13A—O13—H13B	112.00	C17—C16—H16A	121.00
Eu1—O13—H13A	108.00	C17—C18—H18A	120.00
Eu1—O13—H13B	120.00	C19—C18—H18A	120.00
H14A—O14—H14B	104.00	N3—C19—H19A	119.00
Eu1—O14—H14A	105.00	C18—C19—H19A	119.00

Eu1—O14—H14B	114.00

O13—Eu1—O8—C14	−178.0 (3)	Cu1—O7—C14—C10	−65.8 (4)
O14—Eu1—O8—C14	−27.5 (3)	Eu1—O8—C14—O7	31.0 (5)
O15—Eu1—O8—C14	49.0 (3)	Eu1—O8—C14—C10	−149.5 (2)
O11^{iii}—Eu1—O8—C14	9.9 (4)	Cu2—O9—C20—O10	171.5 (3)
O6^{i}—Eu1—O8—C14	−162.9 (3)	Cu2—O9—C20—C15	−10.4 (3)
O12^{i}—Eu1—O8—C14	120.0 (3)	Eu1^{ii}—O10—C20—O9	6.3 (5)
O10^{ii}—Eu1—O8—C14	−93.0 (3)	Eu1^{ii}—O10—C20—C15	−171.72 (19)
O8—Eu1—O11^{iii}—C21^{iii}	119.5 (3)	Eu1^{vi}—O11—C21—O12	−20.8 (5)
O13—Eu1—O11^{iii}—C21^{iii}	−55.5 (3)	Eu1^{vi}—O11—C21—C17	159.0 (2)
O14—Eu1—O11^{iii}—C21^{iii}	157.4 (3)	Cu1—N1—C1—C2	−179.0 (3)
O15—Eu1—O11^{iii}—C21^{iii}	80.5 (3)	Cu1—N1—C1—C6	3.7 (3)
O8—Eu1—O6^{i}—C13^{i}	152.9 (3)	C5—N1—C1—C2	1.9 (5)
O13—Eu1—O6^{i}—C13^{i}	−36.4 (3)	C5—N1—C1—C6	−175.5 (3)
O14—Eu1—O6^{i}—C13^{i}	97.0 (3)	Cu1—N1—C5—C4	−179.0 (3)
O15—Eu1—O6^{i}—C13^{i}	−163.0 (3)	C1—N1—C5—C4	0.0 (5)
O8—Eu1—O10^{ii}—C20^{ii}	−10.3 (3)	C12—N2—C8—C9	3.3 (5)
O13—Eu1—O10^{ii}—C20^{ii}	130.9 (3)	Cu1^{iv}—N2—C8—C9	−175.7 (3)
O14—Eu1—O10^{ii}—C20^{ii}	−79.3 (3)	C8—N2—C12—C11	1.3 (5)
O15—Eu1—O10^{ii}—C20^{ii}	−100.9 (3)	C8—N2—C12—C13	−174.1 (3)
O7—Cu1—O1—C6	−96.6 (2)	Cu1^{iv}—N2—C12—C11	−179.6 (3)
N1—Cu1—O1—C6	−3.3 (2)	Cu1^{iv}—N2—C12—C13	5.0 (3)
N2^{iv}—Cu1—O1—C6	169.5 (3)	Cu2—N3—C15—C16	−179.6 (3)
O2^{v}—Cu1—O1—C6	95.6 (2)	Cu2—N3—C15—C20	1.9 (3)
O1—Cu1—O7—C14	−48.9 (3)	C19—N3—C15—C16	0.7 (5)
N1—Cu1—O7—C14	−133.9 (3)	C19—N3—C15—C20	−177.8 (3)
O5^{iv}—Cu1—O7—C14	129.6 (3)	Cu2—N3—C19—C18	−177.5 (3)
N2^{iv}—Cu1—O7—C14	46.3 (3)	C15—N3—C19—C18	2.2 (5)
O1—Cu1—N1—C1	−0.5 (2)	N1—C1—C2—C3	−2.1 (5)
O1—Cu1—N1—C5	178.5 (3)	C6—C1—C2—C3	175.1 (3)
O7—Cu1—N1—C1	96.6 (2)	N1—C1—C6—O1	−6.7 (4)
O7—Cu1—N1—C5	−84.4 (3)	N1—C1—C6—O2	170.7 (3)
O5^{iv}—Cu1—N1—C1	−172.9 (2)	C2—C1—C6—O1	176.0 (3)
O5^{iv}—Cu1—N1—C5	6.2 (3)	C2—C1—C6—O2	−6.7 (5)
O2^{v}—Cu1—N1—C1	−91.8 (2)	C1—C2—C3—C4	0.4 (5)
O2^{v}—Cu1—N1—C5	87.2 (3)	C1—C2—C3—C7	−174.7 (3)
O7—Cu1—O5^{iv}—C13^{iv}	−98.6 (2)	C2—C3—C4—C5	1.4 (6)
N1—Cu1—O5^{iv}—C13^{iv}	167.5 (2)	C7—C3—C4—C5	176.3 (4)
O1—Cu1—N2^{iv}—C8^{iv}	14.0 (3)	C2—C3—C7—O3	−6.4 (5)
O1—Cu1—N2^{iv}—C12^{iv}	−166.9 (2)	C2—C3—C7—O4	172.3 (4)
O7—Cu1—N2^{iv}—C8^{iv}	−83.8 (3)	C4—C3—C7—O3	178.8 (4)
O7—Cu1—N2^{iv}—C12^{iv}	95.3 (2)	C4—C3—C7—O4	−2.5 (6)
O1—Cu1—O2^{v}—C6^{v}	−12.3 (2)	C3—C4—C5—N1	−1.6 (6)
N1—Cu1—O2^{v}—C6^{v}	72.5 (2)	N2—C8—C9—C10	−4.7 (5)
O9—Cu2—O2—C6	158.3 (3)	C8—C9—C10—C11	1.4 (5)
O9—Cu2—O2—Cu1^{v}	15.88 (14)	C8—C9—C10—C14	178.3 (3)
N3—Cu2—O2—C6	74.8 (3)	C9—C10—C11—C12	2.9 (5)

N3—Cu2—O2—Cu1^{v}	−67.63 (15)	C14—C10—C11—C12	−173.9 (3)
O9^{ii}—Cu2—O2—C6	−21.7 (3)	C9—C10—C14—O7	−37.3 (5)
N3^{ii}—Cu2—O2—C6	−105.2 (3)	C9—C10—C14—O8	143.1 (3)
O2—Cu2—O9—C20	−80.0 (2)	C11—C10—C14—O7	139.4 (3)
N3—Cu2—O9—C20	9.1 (2)	C11—C10—C14—O8	−40.2 (5)
O2^{ii}—Cu2—O9—C20	100.0 (2)	C10—C11—C12—N2	−4.4 (5)
N3^{ii}—Cu2—O9—C20	−170.9 (2)	C10—C11—C12—C13	170.5 (3)
O2—Cu2—N3—C15	83.5 (2)	N2—C12—C13—O5	−0.9 (4)
O2—Cu2—N3—C19	−96.9 (3)	N2—C12—C13—O6	175.6 (3)
O9—Cu2—N3—C15	−5.6 (2)	C11—C12—C13—O5	−176.2 (3)
O9—Cu2—N3—C19	174.1 (3)	C11—C12—C13—O6	0.3 (5)
O2^{ii}—Cu2—N3—C15	−96.5 (2)	N3—C15—C16—C17	−2.3 (5)
O2^{ii}—Cu2—N3—C19	83.1 (3)	C20—C15—C16—C17	176.1 (3)
O9^{ii}—Cu2—N3—C15	174.4 (2)	N3—C15—C20—O9	5.8 (4)
O9^{ii}—Cu2—N3—C19	−6.0 (3)	N3—C15—C20—O10	−176.0 (3)
Cu1—O1—C6—O2	−171.0 (3)	C16—C15—C20—O9	−172.7 (3)
Cu1—O1—C6—C1	6.1 (4)	C16—C15—C20—O10	5.5 (5)
Cu2—O2—C6—O1	−76.7 (4)	C15—C16—C17—C18	1.0 (5)
Cu2—O2—C6—C1	106.3 (3)	C15—C16—C17—C21	−176.4 (3)
Cu1^{v}—O2—C6—O1	79.6 (4)	C16—C17—C18—C19	1.7 (6)
Cu1^{v}—O2—C6—C1	−97.4 (3)	C21—C17—C18—C19	179.1 (3)
Cu1^{iv}—O5—C13—O6	179.9 (3)	C16—C17—C21—O11	−27.2 (5)
Cu1^{iv}—O5—C13—C12	−3.9 (3)	C16—C17—C21—O12	152.6 (4)
Eu1^{i}—O6—C13—O5	−4.7 (5)	C18—C17—C21—O11	155.5 (4)
Eu1^{i}—O6—C13—C12	179.13 (19)	C18—C17—C21—O12	−24.7 (5)
Cu1—O7—C14—O8	113.8 (4)	C17—C18—C19—N3	−3.4 (6)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) −*x*+1, −*y*+2, −*z*; (iii) *x*, *y*, *z*+1; (iv) −*x*, −*y*+1, −*z*; (v) −*x*, −*y*+2, −*z*; (vi) *x*, *y*, *z*−1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O13—H13*A*···O5^{i}	0.82	2.00	2.769 (3)	155
O13—H13*B*···O15^{vii}	0.82	2.02	2.822 (4)	164
O14—H14*A*···O7	0.82	1.89	2.690 (4)	164
O14—H14*B*···O4^{viii}	0.82	1.88	2.667 (4)	161
O15—H15*A*···O3^{ix}	0.82	1.83	2.630 (4)	164
O15—H15*B*···O4^{viii}	0.82	2.06	2.814 (4)	153
C18—H18*A*···O6	0.93	2.48	3.389 (4)	167

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (vii) −*x*+1, −*y*+1, −*z*+1; (viii) −*x*, −*y*+2, −*z*+1; (ix) *x*, *y*−1, *z*.