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# Synthesis and crystal structure of a new polymorph of potassium europium(III) bis(sulfate) mono-hydrate, $KEu(SO_4)_2 \cdot H_2O$

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The mixed-metal sulfate,  $KEu(SO_4)_2 \cdot H_2O$ , has been obtained as a new polymorph using hydrothermal conditions. The crystal structure is isotypic with  $NaCe(SO_4)_2 \cdot H_2O$  and shows a three-dimensional connectivity of the tetrahedral sulfate units with  $Eu^{III}$  and  $K^I$  ions. Tricapped trigonal–prismatic  $EuO_9$  units and square-antiprismatic  $KO_8$  units link the  $SO_4$  tetrahedra, building the three-dimensional structure. Topological analysis reveals the existence of two nodes with 6- and 10-connected nets. The compound was previously reported [Kazmierczak & Höppe (2010). *J. Solid State Chem.* **183**, 2087–2094] in the monoclinic space group  $P2_1/c$  with a similar structural connectivity and coordination environments to the present compound.

#### 1. Chemical context

The design of new solids including rare earth metal ions is an emerging field because of their potential applications in catalysis, luminescence and optoelectronics (Ramva et al., 2012; Höppe, 2009; Mahata et al., 2008; Shehee et al., 2003). In general, the discovery of new solids is a major thrust in the field of solid-state research because of their diverse topological architectures and properties. In particular for rare earth metal compounds, the connectivity within the crystal structure becomes novel and complex as the coordination numbers are higher than for transition metals. In this regard, crystal engineering becomes challenging with non-centrosymmetric solids as it can lead to many chiral-related applications such as enantioselective separation, heterogeneous chiral catalysis or non-linear optical (NLO) effects (Ramya et al., 2012; Höppe, 2009; Mahata et al., 2008; Shehee et al., 2003; Halasyamani & Poeppelmeier, 1998; Sweeting & Rheingold, 1987). Obtaining new structures with various anions such as silicates, phosphates, phosphites, carboxylates, sulfates, arsenates, selenates, selenites, germanates, borates or thiosulfates is a long-standing research area (Sweeting et al., 1992; Paul, 2016; Paul & Natarajan, 2010; Paul et al., 2009, 2010; Natarajan & Mandal, 2008; Natarajan et al., 2006; Feng et al., 2005; Hathwar et al., 2011; Held, 2014). A rare earth metal can be a better choice than a transition metal as it provides many variations arising from coordination preferences, ligand geometry and valence states. The presence of two metals in a crystal structure can introduce more structural variation along with specific properties. From earlier reports, it is obvious that the design of chiral frameworks mostly require chiral fragments or chiral ligands. The synthesis of sulfate compounds with a chiral



**Figure 1** Three-dimensional framework observed by connectivity between the  $Eu^{III}$  ions and the  $SO_4^{2-}$  units. Green, yellow and red spheres represent Eu, S and O sites, respectively.

framework is a challenging task that requires a particular strategy. Hence, the synthetic strategy was modified (piperazine was used, which is not in the product but supports the crystallization of the sulfate compound) and the resultant compound is a new polymorph of  $\text{KEu}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  that is isotypic with trigonal NaCe(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (Blackburn & Gerkin, 1995).



Figure 2

Three-dimensional framework observed by connectivity between the  $K^{I}$  ions and the  $SO_4^{2-}$  units. Cyan, yellow and red spheres represent K, S and O sites, respectively.



Figure 3 Overall three-dimensional connectivity between the  $Eu^{III}$  ions, the  $K^{I}$  ions and the  $SO_4^{2-}$  units. Green, cyan, yellow and red spheres represent Eu, K, S and O sites, respectively

#### 2. Structural commentary

The asymmetric unit of trigonal  $KEu(SO_4)_2 \cdot H_2O$  contains eight non-hydrogen atoms, of which one Eu, one K and one O site (defining the water molecule) are located on a twofold rotation axis, and one complete sulfate unit. The Eu<sup>III</sup> ion is coordinated by the O atoms of six sulfate tetrahedra (two chelating, four in a monodentate way) and one water molecule in a tricapped-trigonal-prismatic environment. The Eu-O bond lengths range from 2.425 (4) to 2.518 (4) Å with an average of 2.469 Å. The resulting three-dimensional Eu/SO<sub>4</sub> framework is displayed in Fig. 1. The K<sup>I</sup> ion is eightcoordinated by six sulfate units, again two chelating and four in a monodentate way, leading to a square-antiprismatic  $KO_8$ coordination polyhedron with K-O distances ranging from 2.374 (5) to 2.830 (4) Å and an average of 2.556 Å. The  $K^{I}$  ions form a similar three-dimensional potassium sulfate framework (Fig. 2). The sulfate ion is an almost regular tetrahedron with S-O distances ranging from 1.456 (4) to 1.484 (4) Å and O-S-O angles of 105.2 (2)-112.4 (3)°. The overall threedimensional connectivity between the two metal cations and the sulfate anions is given in Fig. 3. The present framework structure crystallizes isotypically with NaCe(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (Blackburn & Gerkin, 1995). It should be noted that the reported structure of NaEu(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (Wu & Liu, 2006) shows the same space-group type, very similar lattice parameters, and unexpectedly also very similar Na-O distances in comparison with the K–O distances of the title compound. The previously reported KEu $(SO_4)_2$ ·H<sub>2</sub>O polymorph crystallizes in space group  $P2_1/c$  (Kazmierczak & Höppe, 2010) and in comparison shows a similar connectivity and respective coordination polyhedra.

## research communications



Figure 4

Three-dimensional node connectivity of the title compound. Green, cyan and yellow spheres represent the Eu and K sites and the  $SO_4$  unit, respectively.

#### 3. Supramolecular features

As the hydrogen-atom positions could not be located during the present study, hydrogen-bonding interactions are not discussed here. An interesting structural feature arises due to the formation of three kinds of helices along the  $3_1$  screw axes. A detailed structural analysis of the topology of the framework was performed using TOPOS (Blatov et al., 2014). The EuO<sub>9</sub>, KO<sub>8</sub> and SO<sub>4</sub> polyhedra are considered as different nodes and represented in different colors (Fig. 4). Although the potassium and europium cations have different coordination environments, both have similar coordination behaviors, with terminal water only extra for europium. In topological terms, both form similar 10-connected nets with three-, four-, five- and six-membered rings, point symbol 3<sup>12</sup>.4<sup>14</sup>.5<sup>12</sup>.6<sup>7</sup>. The sulfate unit is associated with three-, fourand five-membered rings and forms a 6-connected net with point symbol  $3^{6}.4^{6}.5^{3}$ . The topological approach thus allows the present complex structure to be visualized in a different way by considering the node-connectivity.

#### 4. Synthesis and crystallization

The title compound was synthesized under hydrothermal conditions. All chemicals were purchased from Aldrich and used without further purification.  $Eu(COOCH_3)_3 \cdot xH_2O$  (0.329 g, 1 mmol) was dissolved in 10 ml water. Then K<sub>2</sub>SO<sub>4</sub> (0.348 g, 2 mmol) was added to the solution, which was stirred for 30 mins. Finally, piperazine (0.043 g, 0.5 mmol) was added to the reaction mixture and the pH was observed to be 8. The entire mixture was stirred for another 30 mins and poured into a 23 ml Teflon-lined autoclave. The autoclave was kept at 426 K for 5 d. The product was then filtered off and washed with water. The product contained some block-like single crystals accompanied with a light-yellow powder. The yield was approximately 75% based on Eu metal.

Table 1	
Experimental details.	
Crystal data	
Chemical formula	KEu(SO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O
Mr	399.18
Crystal system, space group	Trigonal, P3 <sub>1</sub> 21
Temperature (K)	293
<i>a</i> , <i>c</i> (Å)	6.9065 (2), 12.7802 (5)
$V(Å^3)$	527.94 (3)
Ζ	3
Radiation type	Μο Κα
$\mu (\text{mm}^{-1})$	10.12
Crystal size (mm)	$0.14 \times 0.12 \times 0.08$
Data collection	
Diffractometer	Bruker SMART CCD area detector
Absorption correction	Multi-scan ( <i>SADABS</i> ; Sheldrick, 1996)
Tmin Tmar	0.332, 0.498
No. of measured, independent and	3856, 848, 823
observed $[I > 2\sigma(I)]$ reflections	, ,
R <sub>int</sub>	0.032
$(\sin \theta / \lambda)_{\rm max} ({\rm \AA}^{-1})$	0.674
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.024, 0.058, 1.07
No. of reflections	848
No. of parameters	56
$\Delta \rho_{\rm max},  \Delta \rho_{\rm min}  ({\rm e}  {\rm \AA}^{-3})$	1.16, -0.86
Absolute structure	Flack (1983)
Absolute structure parameter	-0.02 (3)

Computer programs: *SMART* and *SAINT* (Bruker, 2000), *SIR92* (Altomare *et al.*, 1993), *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *CAMERON* (Watkin *et al.*, 1993) and *PLATON* (Spek, 2009).

#### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The correctness of all atom types was checked by free refinement of the occupancy. Hydrogen atoms of the lattice water molecule could not be located in difference-Fourier maps. If the hydrogen atoms were included in calculated positions and refined with a riding model, the structure did not refine with suitable parameters, and therefore the hydrogen atoms were omitted in the final refinement. Except for atom O2 that was refined with an isotropic displacement parameter, all other atoms were refined with anisotropic displacement parameters.

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# supporting information

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Synthesis and crystal structure of a new polymorph of potassium europium(III) bis(sulfate) monohydrate, KEu(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O

### **Avijit Kumar Paul**

**Computing details** 

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *PLATON* (Spek, 2009).

Potassium europium(III) bis(sulfate) monohydrate

Crystal data	
KEu(SO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O $M_r = 399.18$ Trigonal, $P3_121$ Hall symbol: P 31 2" a = 6.9065 (2) Å c = 12.7802 (5) Å V = 527.94 (3) Å <sup>3</sup> Z = 3 F(000) = 558	$D_x = 3.767 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ Å}$ Cell parameters from 848 reflections $\theta = 3.4-28.6^{\circ}$ $\mu = 10.12 \text{ mm}^{-1}$ T = 293  K Block like, light yellow $0.14 \times 0.12 \times 0.08 \text{ mm}$
Data collection	
Bruker SMART CCD area detector diffractometer Radiation source: fine-focus sealed tube Graphite monochromator $\varphi$ and $\omega$ scans Absorption correction: multi-scan (SADABS; Sheldrick, 1996) $T_{\min} = 0.332, T_{\max} = 0.498$	3856 measured reflections 848 independent reflections 823 reflections with $I > 2\sigma(I)$ $R_{int} = 0.032$ $\theta_{max} = 28.6^{\circ}, \ \theta_{min} = 3.4^{\circ}$ $h = -9 \rightarrow 9$ $k = -8 \rightarrow 9$ $l = -16 \rightarrow 17$
Refinement	
Refinement on $F^2$ Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.024$ $wR(F^2) = 0.058$ S = 1.07 848 reflections 56 parameters 0 restraints Primary atom site location: structure-invariant	Secondary atom site location: difference map H-atom parameters not defined $w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 3.0791P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{max} < 0.001$ $\Delta\rho_{max} = 1.16$ e Å <sup>-3</sup> $\Delta\rho_{min} = -0.86$ e Å <sup>-3</sup> Absolute structure: Flack (1983)
direct methods	Absolute structure parameter: $-0.02$ (3)

Fourier

#### Special details

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

**Refinement**. Refinement of F<sup>2</sup> against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F<sup>2</sup>, conventional R-factors R are based on F, with F set to zero for negative F<sup>2</sup>. The threshold expression of F<sup>2</sup> >  $2\sigma(F^2)$  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<sup>2</sup> are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

	x	У	Ζ	$U_{ m iso}$ */ $U_{ m eq}$	
Eu1	0.56354 (7)	0.56354 (7)	0.5000	0.00972 (12)	
<b>S</b> 1	0.5565 (2)	0.5452 (2)	0.25595 (8)	0.0068 (2)	
K1	0.5398 (3)	0.5398 (3)	0.0000	0.0196 (4)	
O4	0.3795 (8)	0.5049 (8)	0.1823 (3)	0.0156 (11)	
O3	0.6104 (7)	0.7411 (7)	0.3231 (3)	0.0142 (9)	
O5	0.4906 (8)	0.3578 (8)	0.3288 (3)	0.0155 (10)	
01	0.9181 (15)	0.9181 (15)	0.5000	0.068 (4)	
O2	0.7533 (7)	0.5868 (7)	0.1949 (3)	0.0165 (10)*	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters  $(Å^2)$ 

Atomic displacement parameters  $(Å^2)$ 

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Eu1	0.01111 (18)	0.01111 (18)	0.00863 (18)	0.0068 (2)	-0.00007 (9)	0.00007 (9)
S1	0.0073 (6)	0.0090 (6)	0.0053 (5)	0.0049 (6)	0.0001 (5)	-0.0008(4)
K1	0.0254 (8)	0.0254 (8)	0.0167 (8)	0.0191 (10)	0.0004 (4)	-0.0004 (4)
O4	0.013 (2)	0.025 (3)	0.0128 (18)	0.012 (2)	-0.0075 (17)	-0.0030 (18)
03	0.020 (2)	0.010 (2)	0.0136 (18)	0.008 (2)	-0.0018 (16)	-0.0061 (15)
O5	0.022 (3)	0.016 (2)	0.014 (2)	0.013 (2)	0.0000 (17)	0.0023 (16)
01	0.024 (4)	0.024 (4)	0.154 (11)	0.012 (4)	-0.017 (3)	0.017 (3)

Geometric parameters (Å, °)

Eu1—O2 <sup>i</sup>	2.425 (4)	S1—K1 <sup>i</sup>	3.6182 (15)
Eu1—O2 <sup>ii</sup>	2.425 (5)	S1—K1 <sup>iv</sup>	3.6579 (19)
Eu1—O4 <sup>iii</sup>	2.428 (5)	K1—O5 <sup>vii</sup>	2.374 (5)
Eu1—O4 <sup>iv</sup>	2.428 (5)	K1—O5 <sup>viii</sup>	2.374 (5)
Eu1—O1	2.449 (10)	K1—O3 <sup>ix</sup>	2.479 (4)
Eu1—O3 <sup>v</sup>	2.514 (4)	K1—O3 <sup>x</sup>	2.479 (4)
Eu1—O3	2.514 (4)	K1—O4 <sup>xi</sup>	2.538 (4)
Eu1—O5	2.518 (4)	K1—O4	2.538 (4)
Eu1—O5 <sup>v</sup>	2.518 (4)	K1—O2	2.830 (4)
Eu1—S1 <sup>v</sup>	3.1210 (11)	K1—O2 <sup>xi</sup>	2.830 (4)
Eu1—S1	3.1210 (11)	K1—S1 <sup>xi</sup>	3.2726 (11)
Eu1—K1 <sup>vi</sup>	4.0356 (12)	K1—S1 <sup>vii</sup>	3.6182 (15)
S1—O4	1.456 (4)	K1—S1 <sup>viii</sup>	3.6182 (15)
S1—O2	1.465 (4)	O4—Eu1 <sup>x</sup>	2.428 (5)

# supporting information

S1—O5	1.470 (5)	O3—K1 <sup>IV</sup>	2.479 (4)
S1—O3	1.484 (4)	$O5-K1^i$	2.374 (5)
S1—K1	3.2726 (11)	O2—Eu1 <sup>vii</sup>	2.425 (4)
$O2^{i}$ —Eu1— $O2^{ii}$	77.6 (2)	K1—S1—K1 <sup>i</sup>	105.93 (4)
$\Omega^{2i}$ Eu1 $\Omega^{4iii}$	73 28 (14)	$04-S1-K1^{iv}$	81.0 (2)
$O2^{ii}$ Fu1 $O4^{iii}$	145 65 (16)	$\Omega^2 = S1 = K1^{iv}$	121.63(18)
$O2^{i}$ Eu1 $O4^{iv}$	145.65(17)	$O_2 S_1 K_1$	121.03(10) 118.38(17)
$O_2 = E_{u1} = O_4$	143.03(17)	$O_2 = S_1 = K_1$	110.30(17)
$O_2^{\text{m}} = E_{\text{u}1} = O_4^{\text{m}}$	/3.28 (14)	03-51-K1	29.00 (17)
04 <sup>m</sup> —Eu1—04 <sup>m</sup>	139.6 (2)		72.58 (2)
O2 <sup>1</sup> —Eu1—O1	141.21 (10)	$K1 - S1 - K1^{W}$	105.03 (4)
O2 <sup>n</sup> —Eu1—O1	141.21 (10)	$K1^{i}$ — $S1$ — $K1^{iv}$	143.32 (5)
O4 <sup>iii</sup> —Eu1—O1	69.82 (12)	$O5^{vii}$ —K1— $O5^{viii}$	128.8 (3)
O4 <sup>iv</sup> —Eu1—O1	69.82 (12)	$O5^{vii}$ —K1— $O3^{ix}$	76.98 (14)
$O2^{i}$ —Eu1— $O3^{v}$	85.25 (14)	O5 <sup>viii</sup> —K1—O3 <sup>ix</sup>	153.95 (18)
$O2^{ii}$ —Eu1—O3 <sup>v</sup>	124.29 (13)	$O5^{vii}$ —K1— $O3^x$	153.95 (18)
$O4^{iii}$ —Eu1— $O3^{v}$	71.15 (14)	$O5^{viii}$ —K1— $O3^{x}$	76.98 (14)
$O4^{iv}$ —Eu1—O3 <sup>v</sup>	96.34 (14)	$O3^{ix}$ —K1—O3 <sup>x</sup>	77.63 (19)
$01$ —Fu1— $03^{v}$	72 05 (9)	$05^{\text{vii}}$ K1-04 <sup>xi</sup>	79 99 (15)
$O^{2i}$ Eul $O^{3}$	124.03(9)	$O5^{\text{viii}}$ K1 $O4^{\text{xi}}$	11370(14)
02 - Eu1 - 03	124.29(13)	$O_{2ix} K_{1} O_{4xi}$	(13.79(14))
02 - Eu1 - 03	05.23(14)	$O_3 = K_1 = O_4$	09.93(14)
$04^{$	90.34 (14)	$03^{$	85.94 (15)
$04^{n}$ —Eu1— $03$	/1.15 (14)	$05^{\text{vii}}$ K1-04	113./9(14)
01—Eu1—O3	72.05 (9)	$O5^{\text{vm}}$ —K1—O4	79.99 (15)
O3 <sup>v</sup> —Eu1—O3	144.10 (18)	$O3^{ix}$ —K1—O4	85.94 (15)
$O2^{i}$ —Eu1—O5	68.88 (14)	O3 <sup>x</sup> —K1—O4	69.93 (14)
O2 <sup>ii</sup> —Eu1—O5	76.38 (15)	O4 <sup>xi</sup> —K1—O4	149.2 (2)
O4 <sup>iii</sup> —Eu1—O5	76.45 (15)	O5 <sup>vii</sup> —K1—O2	64.32 (13)
O4 <sup>iv</sup> —Eu1—O5	119.87 (14)	O5 <sup>viii</sup> —K1—O2	99.13 (14)
O1—Eu1—O5	112.47 (11)	O3 <sup>ix</sup> —K1—O2	88.93 (13)
O3 <sup>v</sup> —Eu1—O5	143.20 (14)	O3 <sup>x</sup> —K1—O2	120.92 (13)
O3—Eu1—O5	55.58 (14)	$O4^{xi}$ K1 $O2$	142.03 (14)
$\Omega^{2i}$ Ful $\Omega^{5v}$	76 38 (15)	04-K1-02	51 72 (13)
$O2^{ii}$ Ful $O5^{v}$	68 88 (14)	$05^{vii}$ K1 $02^{vi}$	99.13 (14)
$O_2 = Eu1 = O_3$	110.87(14)	$O_{5}^{\text{viii}} K_{1} O_{2}^{\text{xi}}$	55.13(14)
$O_4 = Eu1 = O_5^{V}$	76.45.(15)	$O_{2}^{ix} = K_{1} = O_{2}^{xi}$	120.02(13)
$O4^{}Eu1^{}O5^{-}$	70.43(13)	$03^{}$ K1 $02^{}$	120.92(13)
$OI = EuI = OS^{*}$	112.47 (11)	$03^{n}$ K1 $02^{n}$	88.93 (13)
O3 <sup>v</sup> —Eu1—O5 <sup>v</sup>	55.58 (14)	$O4^{xi}$ KI $O2^{xi}$	51.72 (13)
$O3$ —Eu1— $O5^{\circ}$	143.20 (14)	$O4-K1-O2^{x1}$	142.03 (14)
$O5$ —Eu1— $O5^{v}$	135.1 (2)	$O2-K1-O2^{xi}$	142.94 (19)
$O2^{i}$ —Eu1—S1 <sup>v</sup>	80.93 (10)	$O5^{vii}$ —K1—S1	89.74 (9)
$O2^{ii}$ —Eu1—S1 <sup>v</sup>	96.53 (10)	O5 <sup>viii</sup> —K1—S1	89.12 (10)
O4 <sup>iii</sup> —Eu1—S1 <sup>v</sup>	96.44 (10)	O3 <sup>ix</sup> —K1—S1	87.27 (10)
$O4^{iv}$ —Eu1—S1 <sup>v</sup>	84.68 (10)	O3 <sup>x</sup> —K1—S1	94.81 (10)
O1—Eu1—S1 <sup>v</sup>	91.61 (3)	O4 <sup>xi</sup> —K1—S1	156.52 (12)
$O3^{v}$ —Eu1—S1 $^{v}$	27.98 (9)	O4—K1—S1	25.19 (10)
$O3$ —Eu1— $S1^{v}$	154.22 (9)	O2—K1—S1	26.53 (9)
05—Eu1—S1 <sup>v</sup>	149 79 (11)	$02^{xi} - K1 - S1$	151 64 (10)
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$O5^{v}$ —Eu1—S1 $^{v}$	27.67 (11)	O5 <sup>vii</sup> —K1—S1 <sup>xi</sup>	89.12 (10)
O2 <sup>i</sup> —Eu1—S1	96.53 (10)	O5 <sup>viii</sup> —K1—S1 <sup>xi</sup>	89.74 (9)
O2 <sup>ii</sup> —Eu1—S1	80.93 (10)	$O3^{ix}$ —K1—S1 <sup>xi</sup>	94.81 (10)
O4 <sup>iii</sup> —Eu1—S1	84.68 (10)	$O3^{x}$ —K1—S1 <sup>xi</sup>	87.27 (10)
O4 <sup>iv</sup> —Eu1—S1	96.44 (10)	$O4^{xi}$ — $K1$ — $S1^{xi}$	25.19 (10)
O1—Eu1—S1	91.61 (3)	O4—K1—S1 <sup>xi</sup>	156.52 (12)
O3 <sup>v</sup> —Eu1—S1	154.22 (9)	O2—K1—S1 <sup>xi</sup>	151.64 (10)
O3—Eu1—S1	27.98 (9)	$O2^{xi}$ —K1—S1 <sup>xi</sup>	26.53 (9)
O5—Eu1—S1	27.67 (11)	S1—K1—S1 <sup>xi</sup>	177.34 (9)
O5 <sup>v</sup> —Eu1—S1	149.79 (11)	O5 <sup>vii</sup> —K1—S1 <sup>vii</sup>	15.34 (9)
S1 <sup>v</sup> —Eu1—S1	176.78 (5)	O5 <sup>viii</sup> —K1—S1 <sup>vii</sup>	132.36 (15)
$O2^{i}$ —Eu1—K1 <sup>vi</sup>	69.92 (10)	O3 <sup>ix</sup> —K1—S1 <sup>vii</sup>	73.36 (10)
$O2^{ii}$ —Eu1—K1 <sup>vi</sup>	141.97 (10)	O3 <sup>x</sup> —K1—S1 <sup>vii</sup>	144.15 (11)
O4 <sup>iii</sup> —Eu1—K1 <sup>vi</sup>	36.57 (10)	O4 <sup>xi</sup> —K1—S1 <sup>vii</sup>	64.67 (11)
$O4^{iv}$ —Eu1—K1 <sup>vi</sup>	127.33 (11)	O4—K1—S1 <sup>vii</sup>	127.34 (11)
O1—Eu1—K1 <sup>vi</sup>	73.44 (2)	O2—K1—S1 <sup>vii</sup>	79.43 (9)
$O3^{v}$ —Eu1—K1 <sup>vi</sup>	35.80 (9)	$O2^{xi}$ —K1—S1 <sup>vii</sup>	88.26 (10)
O3—Eu1—K1 <sup>vi</sup>	129.45 (10)	S1—K1—S1 <sup>vii</sup>	104.28 (3)
O5—Eu1—K1 <sup>vi</sup>	108.36 (11)	S1 <sup>xi</sup> —K1—S1 <sup>vii</sup>	74.79 (3)
$O5^{v}$ —Eu1—K1 <sup>vi</sup>	84.42 (10)	$O5^{vii}$ —K1—S1 <sup>viii</sup>	132.36 (15)
S1 <sup>v</sup> —Eu1—K1 <sup>vi</sup>	59.86 (3)	O5 <sup>viii</sup> —K1—S1 <sup>viii</sup>	15.34 (9)
S1—Eu1—K1 <sup>vi</sup>	121.20 (3)	O3 <sup>ix</sup> —K1—S1 <sup>viii</sup>	144.15 (11)
O4—S1—O2	107.5 (2)	O3x—K1—S1 <sup>viii</sup>	73.36 (10)
O4—S1—O5	112.4 (3)	O4 <sup>xi</sup> —K1—S1 <sup>viii</sup>	127.34 (11)
O2—S1—O5	111.0 (3)	O4—K1—S1 <sup>viii</sup>	64.67 (11)
O4—S1—O3	110.6 (3)	O2—K1—S1 <sup>viii</sup>	88.26 (10)
O2—S1—O3	110.1 (3)	O2 <sup>xi</sup> —K1—S1 <sup>viii</sup>	79.43 (9)
O5—S1—O3	105.2 (2)	S1—K1—S1 <sup>viii</sup>	74.79 (3)
O4—S1—Eu1	130.45 (19)	$S1^{xi}$ — $K1$ — $S1^{viii}$	104.28 (3)
O2—S1—Eu1	121.99 (18)	S1 <sup>vii</sup> —K1—S1 <sup>viii</sup>	140.69 (8)
O5—S1—Eu1	52.70 (17)	S1—O4—Eu1 <sup>x</sup>	144.3 (3)
O3—S1—Eu1	52.64 (16)	S1—O4—K1	106.9 (2)
O4—S1—K1	47.92 (18)	Eu1 <sup>x</sup> —O4—K1	108.69 (16)
O2—S1—K1	59.63 (17)	S1—O3—K1 <sup>iv</sup>	133.1 (2)
O5—S1—K1	129.05 (18)	S1—O3—Eu1	99.4 (2)
O3—S1—K1	125.43 (18)	K1 <sup>iv</sup> —O3—Eu1	107.82 (15)
Eu1—S1—K1	177.55 (5)	S1—O5—K1 <sup>i</sup>	139.4 (2)
O4—S1—K1 <sup>i</sup>	106.2 (2)	S1—O5—Eu1	99.6 (2)
$O2-S1-K1^{i}$	91.13 (18)	K1 <sup>i</sup> —O5—Eu1	117.07 (16)
O5—S1—K1 <sup>i</sup>	25.29 (17)	S1—O2—Eu1 <sup>vii</sup>	140.9 (3)
O3—S1—K1 <sup>i</sup>	128.50 (17)	S1—O2—K1	93.8 (2)
Eu1—S1—K1 <sup>i</sup>	76.13 (3)	Eu1 <sup>vii</sup> —O2—K1	104.89 (15)

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