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# Synthesis and crystal structure of a new polymorph of potassium europium(III) bis(sulfate) monohydrate, $\mathrm{KEu}\left(\mathrm{SO}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}$ 

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The mixed-metal sulfate, $\mathrm{KEu}\left(\mathrm{SO}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}$, has been obtained as a new polymorph using hydrothermal conditions. The crystal structure is isotypic with $\mathrm{NaCe}\left(\mathrm{SO}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}$ and shows a three-dimensional connectivity of the tetrahedral sulfate units with $\mathrm{Eu}^{\mathrm{III}}$ and $\mathrm{K}^{\mathrm{I}}$ ions. Tricapped trigonal-prismatic $\mathrm{EuO}_{9}$ units and square-antiprismatic $\mathrm{KO}_{8}$ units link the $\mathrm{SO}_{4}$ tetrahedra, building the threedimensional 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 $P 2_{1} / c$ 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 (Ramya 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 $\mathrm{Eu}^{\text {III }}$ ions and the $\mathrm{SO}_{4}{ }^{2-}$ units. Green, yellow and red spheres represent $\mathrm{Eu}, \mathrm{S}$ 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 $\mathrm{KEu}\left(\mathrm{SO}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}$ that is isotypic with trigonal $\mathrm{NaCe}\left(\mathrm{SO}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}$ (Blackburn \& Gerkin, 1995).


Figure 2
Three-dimensional framework observed by connectivity between the $K^{1}$ ions and the $\mathrm{SO}_{4}{ }^{2-}$ units. Cyan, yellow and red spheres represent $\mathrm{K}, \mathrm{S}$ and O sites, respectively.


Figure 3
Overall three-dimensional connectivity between the $\mathrm{Eu}^{\text {III }}$ ions, the $\mathrm{K}^{\mathrm{I}}$ ions and the $\mathrm{SO}_{4}{ }^{2-}$ units. Green, cyan, yellow and red spheres represent $\mathrm{Eu}, \mathrm{K}, \mathrm{S}$ and O sites, respectively

## 2. Structural commentary

The asymmetric unit of trigonal $\mathrm{KEu}\left(\mathrm{SO}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}$ 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 $\mathrm{Eu}^{\text {III }}$ 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 $\mathrm{Eu}-\mathrm{O}$ bond lengths range from 2.425 (4) to 2.518 (4) $\AA$ with an average of $2.469 \AA$. The resulting three-dimensional $\mathrm{Eu} / \mathrm{SO}_{4}$ framework is displayed in Fig. 1. The $K^{1}$ ion is eightcoordinated by six sulfate units, again two chelating and four in a monodentate way, leading to a square-antiprismatic $\mathrm{KO}_{8}$ coordination polyhedron with $\mathrm{K}-\mathrm{O}$ distances ranging from 2.374 (5) to 2.830 (4) $\AA$ and an average of $2.556 \AA$. 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) $\AA$ and $\mathrm{O}-$ S-O angles of $105.2(2)-112.4$ (3) ${ }^{\circ}$. 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 $\mathrm{NaCe}\left(\mathrm{SO}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}$ (Blackburn \& Gerkin, 1995). It should be noted that the reported structure of $\mathrm{NaEu}\left(\mathrm{SO}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}(\mathrm{Wu} \& \mathrm{Liu}$, 2006) shows the same space-group type, very similar lattice parameters, and unexpectedly also very similar $\mathrm{Na}-\mathrm{O}$ distances in comparison with the $\mathrm{K}-\mathrm{O}$ distances of the title compound. The previously reported $\mathrm{KEu}\left(\mathrm{SO}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}$ polymorph crystallizes in space group $P 2_{1} / c$ (Kazmierczak \& Höppe, 2010) and in comparison shows a similar connectivity and respective coordination polyhedra.


Figure 4
Three-dimensional node connectivity of the title compound. Green, cyan and yellow spheres represent the Eu and K sites and the $\mathrm{SO}_{4}$ 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 $\mathrm{EuO}_{9}, \mathrm{KO}_{8}$ and $\mathrm{SO}_{4}$ 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 $3^{12} .4^{14} \cdot 5^{12} \cdot 6^{7}$. 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. $\mathrm{Eu}\left(\mathrm{COOCH}_{3}\right)_{3} \cdot x \mathrm{H}_{2} \mathrm{O}$ ( $0.329 \mathrm{~g}, 1 \mathrm{mmol}$ ) was dissolved in 10 ml water. Then $\mathrm{K}_{2} \mathrm{SO}_{4}$ ( $0.348 \mathrm{~g}, 2 \mathrm{mmol}$ ) was added to the solution, which was stirred for 30 mins. Finally, piperazine $(0.043 \mathrm{~g}, 0.5 \mathrm{mmol})$ 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
$M_{\text {r }}$
Crystal system, space group
Temperature (K)
$a, c(\AA)$
$V\left(\AA^{3}\right)$
Z
Radiation type
$\mu\left(\mathrm{mm}^{-1}\right)$
Crystal size (mm)
Data collection
Diffractometer
Absorption correction
$T_{\text {min }}, T_{\text {max }}$
No. of measured, independent and observed $[I>2 \sigma(I)$ ] reflections
$R_{\text {int }}$
$(\sin \theta / \lambda)_{\text {max }}\left(\AA^{-1}\right)$
Refinement
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right], w R\left(F^{2}\right), S$
No. of reflections
No. of parameters
$\Delta \rho_{\text {max }}, \Delta \rho_{\text {min }}\left(\mathrm{e} \AA^{-3}\right)$
Absolute structure
Absolute structure parameter

## $\mathrm{KEu}\left(\mathrm{SO}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}$

399.18

Trigonal, $P 3_{1} 21$
293
6.9065 (2), 12.7802 (5)
527.94 (3)

3
Mo $K \alpha$
10.12
$0.14 \times 0.12 \times 0.08$

Bruker SMART CCD area detector
Multi-scan (SADABS; Sheldrick, 1996)
0.332, 0.498

3856, 848, 823
0.032
0.674
$0.024,0.058,1.07$
848
56
1.16, - 0.86

Flack (1983)
-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

# Synthesis and crystal structure of a new polymorph of potassium europium(III) bis(sulfate) monohydrate, $\mathrm{KEu}\left(\mathrm{SO}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}$ 

## 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

$\mathrm{KEu}\left(\mathrm{SO}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}$
$M_{r}=399.18$
Trigonal, $P 3_{1} 21$
Hall symbol: P 31 2"
$a=6.9065$ (2) $\AA$
$c=12.7802(5) \AA$
$V=527.94(3) \AA^{3}$
$Z=3$
$F(000)=558$

## 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)
$T_{\text {min }}=0.332, T_{\text {max }}=0.498$

## Refinement

Refinement on $F^{2}$
Least-squares matrix: full
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.024$
$w R\left(F^{2}\right)=0.058$
$S=1.07$
848 reflections
56 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
$D_{\mathrm{x}}=3.767 \mathrm{Mg} \mathrm{m}^{-3}$
Mo $K \alpha$ radiation, $\lambda=0.71073 \AA$
Cell parameters from 848 reflections
$\theta=3.4-28.6^{\circ}$
$\mu=10.12 \mathrm{~mm}^{-1}$
$T=293 \mathrm{~K}$
Block like, light yellow
$0.14 \times 0.12 \times 0.08 \mathrm{~mm}$

3856 measured reflections
848 independent reflections
823 reflections with $I>2 \sigma(I)$
$R_{\text {int }}=0.032$
$\theta_{\text {max }}=28.6^{\circ}, \theta_{\text {min }}=3.4^{\circ}$
$h=-9 \rightarrow 9$
$k=-8 \rightarrow 9$
$l=-16 \rightarrow 17$

Secondary atom site location: difference Fourier map
H -atom parameters not defined
$w=1 /\left[\sigma^{2}\left(F_{\mathrm{o}}^{2}\right)+(0.026 P)^{2}+3.0791 P\right]$
where $P=\left(F_{\mathrm{o}}{ }^{2}+2 F_{\mathrm{c}}{ }^{2}\right) / 3$
$(\Delta / \sigma)_{\max }<0.001$
$\Delta \rho_{\text {max }}=1.16$ e $\AA^{-3}$
$\Delta \rho_{\text {min }}=-0.86$ e $\AA^{-3}$
Absolute structure: Flack (1983)
Absolute structure parameter: -0.02 (3)

## 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 $\mathrm{F}^{2}$ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on $\mathrm{F}^{2}$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $\mathrm{F}^{2}$. The threshold expression of $\mathrm{F}^{2}>2 \sigma\left(\mathrm{~F}^{2}\right)$ is used only for calculating R-factors (gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $\mathrm{F}^{2}$ 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 ( $\AA^{2}$ )

|  | $x$ | $y$ | $z$ | $U_{\mathrm{iso}} * / U_{\mathrm{eq}}$ |
| :--- | :--- | :--- | :--- | :--- |
| Eu1 | $0.56354(7)$ | $0.56354(7)$ | 0.5000 | $0.00972(12)$ |
| S1 | $0.5565(2)$ | $0.5452(2)$ | $0.25595(8)$ | $0.0068(2)$ |
| 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 | $0.4906(8)$ | $0.3578(8)$ | $0.3288(3)$ | $0.0155(10)$ |
| O1 | $0.9181(15)$ | $0.9181(15)$ | 0.5000 | $0.068(4)$ |
| O2 | $0.7533(7)$ | $0.5868(7)$ | $0.1949(3)$ | $0.0165(10)^{*}$ |

Atomic displacement parameters $\left(\AA^{2}\right)$

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 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 | $0.013(2)$ | $0.025(3)$ | $0.0128(18)$ | $0.012(2)$ | $-0.0075(17)$ | $-0.0030(18)$ |
| O3 | $0.020(2)$ | $0.010(2)$ | $0.0136(18)$ | $0.008(2)$ | $-0.0018(16)$ | $-0.0061(15)$ |
| O5 | $0.022(3)$ | $0.016(2)$ | $0.014(2)$ | $0.013(2)$ | $0.0000(17)$ | $0.0023(16)$ |
| O1 | $0.024(4)$ | $0.024(4)$ | $0.154(11)$ | $0.012(4)$ | $-0.017(3)$ | $0.017(3)$ |

## Geometric parameters ( $\left({ }^{\circ},{ }^{\circ}\right)$

| Eu1-O2 ${ }^{\text {i }}$ | 2.425 (4) | $\mathrm{S} 1-\mathrm{K} 1^{\mathrm{i}}$ | 3.6182 (15) |
| :---: | :---: | :---: | :---: |
| Eu1-O2ii | 2.425 (5) | S1-K1 ${ }^{\text {iv }}$ | 3.6579 (19) |
| Eu1-O4 $4^{\text {iii }}$ | 2.428 (5) | $\mathrm{K} 1-\mathrm{O} 5^{\text {vii }}$ | 2.374 (5) |
| Eu1-O4 $4^{\text {iv }}$ | 2.428 (5) | $\mathrm{K} 1-\mathrm{O} 5^{\text {viii }}$ | 2.374 (5) |
| Eu1-O1 | 2.449 (10) | $\mathrm{K} 1-\mathrm{O} 3{ }^{\text {ix }}$ | 2.479 (4) |
| Eu1-O3v | 2.514 (4) | $\mathrm{K} 1-\mathrm{O} 3^{\text {x }}$ | 2.479 (4) |
| Eu1-O3 | 2.514 (4) | $\mathrm{K} 1-\mathrm{O} 4^{\text {xi }}$ | 2.538 (4) |
| Eu1-O5 | 2.518 (4) | $\mathrm{K} 1-\mathrm{O} 4$ | 2.538 (4) |
| Eu1-O5v | 2.518 (4) | $\mathrm{K} 1-\mathrm{O} 2$ | 2.830 (4) |
| Eu1-S1v | 3.1210 (11) | $\mathrm{K} 1-\mathrm{O} 2{ }^{\text {xi }}$ | 2.830 (4) |
| Eu1-S1 | 3.1210 (11) | $\mathrm{K} 1-\mathrm{S} 1^{\text {xi }}$ | 3.2726 (11) |
| Eu1-K1 ${ }^{\text {vi }}$ | 4.0356 (12) | $\mathrm{K} 1-\mathrm{S} 1^{\text {vii }}$ | 3.6182 (15) |
| S1-O4 | 1.456 (4) | $\mathrm{K} 1-\mathrm{S} 1^{\text {viii }}$ | 3.6182 (15) |
| S1-O2 | 1.465 (4) | O4-Eu1 ${ }^{\text {x }}$ | 2.428 (5) |


| S1-O5 | 1.470 (5) |
| :---: | :---: |
| S1-O3 | 1.484 (4) |
| S1-K1 | 3.2726 (11) |
| $\mathrm{O} 2{ }^{\text {i }}$ - $\mathrm{Eu} 1-\mathrm{O} 2^{\text {ii }}$ | 77.6 (2) |
| $\mathrm{O} 2^{\text {i }}$-Eu1-O4 ${ }^{\text {iii }}$ | 73.28 (14) |
| $\mathrm{O} 2^{\text {ii- }}$ Eu1-O4 $4^{\text {iii }}$ | 145.65 (16) |
| $\mathrm{O} 2{ }^{\text {i }}$ - $\mathrm{Eu} 1-\mathrm{O} 4^{\text {iv }}$ | 145.65 (17) |
| $\mathrm{O} 2{ }^{\text {ii }}-\mathrm{Eu} 1-\mathrm{O} 4{ }^{\text {iv }}$ | 73.28 (14) |
| O4iii-Eu1-O4 $4^{\text {iv }}$ | 139.6 (2) |
| $\mathrm{O} 2 \mathrm{i}-\mathrm{Eu} 1-\mathrm{O} 1$ | 141.21 (10) |
| $\mathrm{O} 2 \mathrm{ii}-\mathrm{Eu} 1-\mathrm{O} 1$ | 141.21 (10) |
| O4iii-Eu1-O1 | 69.82 (12) |
| $\mathrm{O} 4{ }^{\text {iv }}-\mathrm{Eu} 1-\mathrm{O} 1$ | 69.82 (12) |
| $\mathrm{O} 2{ }^{\text {i}}-\mathrm{Eu} 1-\mathrm{O}^{\text {v }}$ | 85.25 (14) |
| $\mathrm{O} 2^{\text {ii }}$-Eu1-O3 ${ }^{\text {v }}$ | 124.29 (13) |
| $\mathrm{O} 4{ }^{\text {iii }}$ - $\mathrm{Eu} 1-\mathrm{O}^{\text {v }}$ | 71.15 (14) |
| $\mathrm{O} 4^{\text {iv }}-\mathrm{Eu} 1-\mathrm{O}^{\text {v }}$ | 96.34 (14) |
| $\mathrm{O} 1-\mathrm{Eu} 1-\mathrm{O}^{\text {v }}$ | 72.05 (9) |
| O2 ${ }^{\text {i }}$ - Eu1-O3 | 124.29 (13) |
| $\mathrm{O} 2 \mathrm{ii}-\mathrm{Eu} 1-\mathrm{O} 3$ | 85.25 (14) |
| O4iii-Eu1-O3 | 96.34 (14) |
| O4 ${ }^{\text {iv }}$-Eu1-O3 | 71.15 (14) |
| O1-Eu1-O3 | 72.05 (9) |
| O3v-Eu1-O3 | 144.10 (18) |
| O2i-ELu1-O5 | 68.88 (14) |
| $\mathrm{O} 2 \mathrm{ii}-\mathrm{Eu} 1-\mathrm{O} 5$ | 76.38 (15) |
| O4iii-Eu1-O5 | 76.45 (15) |
| O4 $4^{\text {iv }}$-Eu1-O5 | 119.87 (14) |
| O1-Eu1-O5 | 112.47 (11) |
| $\mathrm{O} 3{ }^{\text {v}}-\mathrm{Eu} 1-\mathrm{O} 5$ | 143.20 (14) |
| O3-Eu1-O5 | 55.58 (14) |
| $\mathrm{O} 2{ }^{\mathrm{i}}-\mathrm{Eu} 1-\mathrm{O} 5^{\text {v}}$ | 76.38 (15) |
| $\mathrm{O} 2{ }^{\text {ii }}-\mathrm{Eu} 1-\mathrm{O}^{\text {v }}$ | 68.88 (14) |
| O4 ${ }^{\text {iii }}$-Eu1-O5 ${ }^{\text {v }}$ | 119.87 (14) |
| O4 ${ }^{\text {iv }}$ - Eu1-O5 ${ }^{\text {v }}$ | 76.45 (15) |
| O1-Eu1-O5 ${ }^{\text {v }}$ | 112.47 (11) |
| O3 ${ }^{\text {v }}$ - $\mathrm{Eu} 1-\mathrm{O} 5^{\text {v }}$ | 55.58 (14) |
| O3-Eu1-O5 ${ }^{\text {v }}$ | 143.20 (14) |
| O5-Eu1-O5 ${ }^{\text {v }}$ | 135.1 (2) |
| $\mathrm{O} 2 \mathrm{i}-\mathrm{Eu} 1-\mathrm{S} 1^{\text {v }}$ | 80.93 (10) |
| $\mathrm{O} 2{ }^{\text {ii }}-\mathrm{Eu} 1-\mathrm{S} 1^{v}$ | 96.53 (10) |
| $\mathrm{O} 4{ }^{\text {iii }}$ - $\mathrm{Eu} 1-\mathrm{S} 1^{\mathrm{v}}$ | 96.44 (10) |
| $\mathrm{O} 4^{\text {iv }}-\mathrm{Eu} 1-\mathrm{S} 1^{\text {v }}$ | 84.68 (10) |
| O1-Eu1-S1 ${ }^{\text {v }}$ | 91.61 (3) |
| O3 ${ }^{\text {- }}$ - $\mathrm{Eu} 1-\mathrm{S1}{ }^{\text {v }}$ | 27.98 (9) |
| O3-Eu1-S1 ${ }^{\text {v }}$ | 154.22 (9) |
| O5-Eu1-S1 ${ }^{\text {v }}$ | 149.79 (11) |


| $\mathrm{O} 3-\mathrm{K} 1^{\mathrm{iv}}$ | $2.479(4)$ |
| :--- | :--- |
| $\mathrm{O} 5-\mathrm{K} 1^{\mathrm{i}}$ | $2.374(5)$ |
| $\mathrm{O} 2-\mathrm{Eu} 1^{\text {vii }}$ | $2.425(4)$ |

105.93 (4)
81.0 (2)
121.63 (18)
118.38 (17)
29.66 (17)
72.58 (2)
105.03 (4)
143.32 (5)
128.8 (3)
76.98 (14)
153.95 (18)
153.95 (18)
76.98 (14)
77.63 (19)
79.99 (15)
113.79 (14)
69.93 (14)
85.94 (15)
113.79 (14)
79.99 (15)
85.94 (15)
69.93 (14)
149.2 (2)
64.32 (13)
99.13 (14)
88.93 (13)
120.92 (13)
142.03 (14)
51.72 (13)
99.13 (14)
64.32 (13)
120.92 (13)
88.93 (13)
51.72 (13)
142.03 (14)
142.94 (19)
89.74 (9)
89.12 (10)
87.27 (10)
94.81 (10)
156.52 (12)
25.19 (10)
26.53 (9)
151.64 (10)

| O5 ${ }^{\text {v }}$-Eu1-S1 ${ }^{\text {v }}$ | 27.67 (11) |
| :---: | :---: |
| O2i-Eu1-S1 | 96.53 (10) |
| O2ii-Eu1-S1 | 80.93 (10) |
| O4iii-EEu1-S1 | 84.68 (10) |
| O4 ${ }^{\text {iv }}$-Eu1-S1 | 96.44 (10) |
| O1-Eu1-S1 | 91.61 (3) |
| $\mathrm{O} 3{ }^{v}-\mathrm{Eu} 1-\mathrm{S} 1$ | 154.22 (9) |
| O3-Eu1-S1 | 27.98 (9) |
| O5-Eu1-S1 | 27.67 (11) |
| O5 ${ }^{\text {- }} \mathrm{Eu} 1-\mathrm{S} 1$ | 149.79 (11) |
| S12-Eu1-S1 | 176.78 (5) |
| O2i-Eu1-K1 ${ }^{\text {vi }}$ | 69.92 (10) |
| $\mathrm{O} 2 \mathrm{ii}-\mathrm{Eu} 1-\mathrm{K} 1^{\text {vi }}$ | 141.97 (10) |
| O4iii-Eu1-K1 ${ }^{\text {vi }}$ | 36.57 (10) |
| O4v ${ }^{\text {iv }} \mathrm{Eu} 1-\mathrm{K} 1^{\text {vi }}$ | 127.33 (11) |
| O1-Eu1-K1 ${ }^{\text {vi }}$ | 73.44 (2) |
| O3v-Eu1-K1 ${ }^{\text {vi }}$ | 35.80 (9) |
| O3-Eu1-K1 ${ }^{\text {vi }}$ | 129.45 (10) |
| O5-Eu1-K1 ${ }^{\text {vi }}$ | 108.36 (11) |
| O5v-Eu1-K1 ${ }^{\text {vi }}$ | 84.42 (10) |
| S1 ${ }^{\text {v }}$-Eu1-K1 $1^{\text {vi }}$ | 59.86 (3) |
| S1-Eu1-K1 ${ }^{\text {vi }}$ | 121.20 (3) |
| $\mathrm{O} 4-\mathrm{S} 1-\mathrm{O} 2$ | 107.5 (2) |
| $\mathrm{O} 4-\mathrm{S} 1-\mathrm{O} 5$ | 112.4 (3) |
| $\mathrm{O} 2-\mathrm{S} 1-\mathrm{O} 5$ | 111.0 (3) |
| $\mathrm{O} 4-\mathrm{S} 1-\mathrm{O} 3$ | 110.6 (3) |
| $\mathrm{O} 2-\mathrm{S} 1-\mathrm{O} 3$ | 110.1 (3) |
| O5-S1-O3 | 105.2 (2) |
| O4-S1-Eu1 | 130.45 (19) |
| O2-S1-Eu1 | 121.99 (18) |
| O5-S1-Eu1 | 52.70 (17) |
| O3-S1-Eu1 | 52.64 (16) |
| O4-S1-K1 | 47.92 (18) |
| O2-S1-K1 | 59.63 (17) |
| O5-S1-K1 | 129.05 (18) |
| O3-S1-K1 | 125.43 (18) |
| Eu1-S1-K1 | 177.55 (5) |
| O4-S1-K1 ${ }^{\text {i }}$ | 106.2 (2) |
| $\mathrm{O} 2-\mathrm{S} 1-\mathrm{K} 1^{\text {i }}$ | 91.13 (18) |
| O5-S1-K1 ${ }^{\text {i }}$ | 25.29 (17) |
| O3-S1-K1 ${ }^{\text {i }}$ | 128.50 (17) |
| Eu1-S1-K1 ${ }^{\text {i }}$ | 76.13 (3) |


| O5 ${ }^{\text {vii }} \mathrm{K} 1-\mathrm{S} 1^{\text {xi }}$ | 89.12 (10) |
| :---: | :---: |
| O5 ${ }^{\text {viii }}$-K1-S1 ${ }^{\text {xi }}$ | 89.74 (9) |
| $\mathrm{O} 3{ }^{\mathrm{ix}}-\mathrm{K} 1-\mathrm{S} 1^{\text {xi }}$ | 94.81 (10) |
| O3 ${ }^{\text {x }}$-K1-S1 ${ }^{\text {xi }}$ | 87.27 (10) |
| O4 ${ }^{\text {xi }}-\mathrm{K} 1-\mathrm{S} 1^{\text {xi }}$ | 25.19 (10) |
| $\mathrm{O} 4-\mathrm{K} 1-\mathrm{S} 1^{\text {xi }}$ | 156.52 (12) |
| $\mathrm{O} 2-\mathrm{K} 1-\mathrm{S} 1^{\text {xi }}$ | 151.64 (10) |
| $\mathrm{O} 2{ }^{\text {xi }}-\mathrm{K} 1-\mathrm{S} 1^{\text {xi }}$ | 26.53 (9) |
| $\mathrm{S} 1-\mathrm{K} 1-\mathrm{S} 1^{\text {xi }}$ | 177.34 (9) |
| O5 ${ }^{\text {vii }}$-K1—S1 ${ }^{\text {vii }}$ | 15.34 (9) |
| O5viii-K1-S1 ${ }^{\text {vii }}$ | 132.36 (15) |
| O3 ${ }^{\text {ix }}$ - $\mathrm{K} 1-\mathrm{S} 1^{\text {vii }}$ | 73.36 (10) |
| O3 ${ }^{\text {x }}-\mathrm{K} 1-\mathrm{S} 1^{\text {vii }}$ | 144.15 (11) |
| $\mathrm{O} 4{ }^{\text {xi}}-\mathrm{K} 1-\mathrm{S} 1^{\text {vii }}$ | 64.67 (11) |
| O4-K1-S1 ${ }^{\text {vii }}$ | 127.34 (11) |
| O2-K1-S1 ${ }^{\text {vii }}$ | 79.43 (9) |
| $\mathrm{O} 2{ }^{\text {xi }}$ - $\mathrm{K} 1-\mathrm{S} 1^{\text {vii }}$ | 88.26 (10) |
| S1-K1-S1 ${ }^{\text {vii }}$ | 104.28 (3) |
| S1 ${ }^{\text {xi }}-\mathrm{K} 1-\mathrm{S} 1^{\text {vii }}$ | 74.79 (3) |
| O5vii-K1-S1 ${ }^{\text {viii }}$ | 132.36 (15) |
| O5 ${ }^{\text {viii }} \mathrm{K} 1-\mathrm{S} 1^{\text {viii }}$ | 15.34 (9) |
| O3 ${ }^{\text {ix }}-\mathrm{K} 1-\mathrm{S} 1^{\text {viii }}$ | 144.15 (11) |
| O3 ${ }^{\text {x }}$-K1-S1 ${ }^{\text {viii }}$ | 73.36 (10) |
| O4 ${ }^{\text {xi }}$-K1-S1 ${ }^{\text {viii }}$ | 127.34 (11) |
| O4-K1-S1 ${ }^{\text {viii }}$ | 64.67 (11) |
| $\mathrm{O} 2-\mathrm{K} 1-\mathrm{S} 1^{\text {viii }}$ | 88.26 (10) |
| $\mathrm{O} 2^{\text {xi}}-\mathrm{K} 1-\mathrm{S} 1^{\text {viii }}$ | 79.43 (9) |
| S1-K1-S1 ${ }^{\text {viii }}$ | 74.79 (3) |
| S1 ${ }^{\text {xi }}-\mathrm{K} 1-\mathrm{S} 1^{\text {viii }}$ | 104.28 (3) |
| S1 ${ }^{\text {vii }}$-K1-S1 ${ }^{\text {viii }}$ | 140.69 (8) |
| S1-O4-Eu1 ${ }^{\text {x }}$ | 144.3 (3) |
| S1-O4-K1 | 106.9 (2) |
| Eu1 ${ }^{\text {- }}$ O4-K1 | 108.69 (16) |
| S1-O3-K1 ${ }^{\text {iv }}$ | 133.1 (2) |
| S1-O3-Eu1 | 99.4 (2) |
| $\mathrm{K} 1{ }^{\text {iv}}-\mathrm{O} 3-\mathrm{Eu} 1$ | 107.82 (15) |
| S1-O5-K1 ${ }^{\text {i }}$ | 139.4 (2) |
| S1-O5-Eu1 | 99.6 (2) |
| K1-O5-Eu1 | 117.07 (16) |
| S1-O2-Eu1 ${ }^{\text {vii }}$ | 140.9 (3) |
| S1-O2-K1 | 93.8 (2) |
| Eu1 ${ }^{\text {vii }}$-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) $-x+1,-x+y,-z+1 / 3$; (x) $-x+y,-x+1, z-1 / 3$; (xi) $y, x,-z$.

