

Redetermination of EuScO_3 Volker Kahlenberg,^a Dirk Maier^b and Boža Veličkov^{b*}^aUniversity of Innsbruck, Institute for Mineralogy and Petrography, Innrain 52, 6020 Innsbruck, Austria, and ^bLeibniz-Institute for Crystal Growth, Max-Born-Strasse 2, 12489 Berlin, Germany

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{Sc}-\text{O}) = 0.002$ Å; disorder in main residue; R factor = 0.021; wR factor = 0.051; data-to-parameter ratio = 11.7.

Single crystals of europium(III) scandate(III), with ideal formula EuScO_3 , were grown from the melt using the micro-pulling-down method. The title compound crystallizes in an orthorhombic distorted perovskite-type structure, where Eu occupies the eightfold coordinated A sites (site symmetry m) and Sc resides on the centres of corner-sharing $[\text{ScO}_6]$ octahedra (B sites with site symmetry $\bar{1}$). The structure of EuScO_3 has been reported previously based on powder diffraction data [Liferovich & Mitchell (2004). *J. Solid State Chem.* **177**, 2188–2197]. The results of the current redetermination based on single-crystal diffraction data shows an improvement in the precision of the structural and geometric parameters and reveals a defect-type structure. Site-occupancy refinements indicate an Eu deficiency on the A site coupled with O defects on one of the two O-atom positions. The crystallochemical formula of the investigated sample may thus be written as $A(\square_{0.032}\text{Eu}_{0.968})B\text{ScO}_{2.952}$.

Related literature

Details of the synthesis are described by Maier *et al.* (2007). Rietveld refinements on powders of LnScO_3 with $\text{Ln} = \text{La}^{3+}$ to Ho^{3+} are reported by Liferovich & Mitchell (2004). The crystal structures of the Dy, Gd, Sm and Nd members refined from single-crystal diffraction data have been recently provided by Veličkov *et al.* (2007). The crystal structure of the isotopic TbScO_3 is described by Veličkov *et al.* (2008). Specific geometrical parameters have been calculated by means of the atomic coordinates following the concept of Zhao *et al.* (1993).

Experimental

Crystal data

$\text{Eu}_{0.968}\text{ScO}_{2.952}$	$V = 252.01$ (5) Å ³
$M_r = 239.24$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 5.7554$ (7) Å	$\mu = 26.28$ mm ⁻¹
$b = 7.9487$ (10) Å	$T = 293$ (2) K
$c = 5.5087$ (6) Å	$0.14 \times 0.12 \times 0.02$ mm

Data collection

Stoe IPDS-2 diffractometer	2168 measured reflections
Absorption correction: analytical (Alcock, 1970)	362 independent reflections
$T_{\min} = 0.139$, $T_{\max} = 0.397$	345 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	31 parameters
$wR(F^2) = 0.051$	1 restraint
$S = 1.27$	$\Delta\rho_{\max} = 1.40$ e Å ⁻³
362 reflections	$\Delta\rho_{\min} = -0.84$ e Å ⁻³

Table 1

Selected bond lengths (Å).

Eu1—O1 ⁱ	2.276 (5)	Eu1—O2 ^v	2.845 (3)
Eu1—O2 ⁱⁱ	2.304 (3)	Sc2—O2 ⁱⁱ	2.094 (3)
Eu1—O1 ⁱⁱⁱ	2.375 (5)	Sc2—O2 ^{vi}	2.107 (3)
Eu1—O2 ^{iv}	2.611 (3)	Sc2—O1 ^{vii}	2.1108 (16)

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

Data collection: *X-AREA* (Stoe & Cie, 2006); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS for Windows* (Dowty, 2004); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2214).

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supporting information

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Redetermination of EuScO₃

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S1. Comment

Liferovich & Mitchell (2004) studied the crystal structure of lanthanoid scandates, including EuScO₃, by Rietveld analysis from powder diffraction data. Crystallographic data of DyScO₃, GdScO₃, SmScO₃ and NdScO₃ obtained from single crystals were recently reported by Veličkov *et al.* (2007), and for TbScO₃ by Veličkov *et al.* (2008). Based on these results it was possible to resolve disagreements concerning some structural characteristics and their dependence on the *Ln*-substitution. Whereas Liferovich & Mitchell (2004) observed no obvious continuous evolution, Veličkov *et al.* (2007) were able to show that the geometry and the distortion of the sites are linearly coupled with the size of the lanthanoid in the series from DyScO₃ to NdScO₃. With the structural refinement based on diffraction data collected from single crystalline EuScO₃, the present results provide further data for this series.

The orthorhombic distorted perovskite structure for EuScO₃ (Fig. 1) is confirmed from our refinements. Whereas the lattice parameters for EuScO₃ compare well with the data of Liferovich & Mitchell (2004), the fractional atomic coordinates show deviations of up to 0.006, resulting in slightly different geometrical parameters. The *A*-site is occupied by Eu in an eightfold coordination and has an average bond length of $\langle A-O \rangle = 2.521 \text{ \AA}$ with a polyhedral bond length distortion of ${}^A\Delta_8 = 7.98 \times 10^{-3}$ ($\Delta n = 1/n \sum \{(r_i - r)/r^2\}$). The *B*-site shows bond lengths typical for octahedrally coordinated scandium ($\langle B-O \rangle = 2.104 \text{ \AA}$) and is rather distorted with ${}^B\Delta_6 = 0.015 \times 10^{-3}$ and a bond angle variance of $\delta = 2.61^\circ$. The tilting of the corner sharing octahedra calculated after Zhao *et al.* (1993) are $\theta = 19.70^\circ$ in [110] and $\varnothing = 12.66^\circ$ in [001] directions. From our data we can establish linear trends for the crystallochemical parameters from DyScO₃ to NdScO₃ depending on the *Ln*-substitution.

S2. Experimental

An EuScO₃ fiber was grown using a micro-pulling-down apparatus with induction heating (Maier *et al.*, 2007). The starting material was prepared from 4 N Eu₂O₃ and Sc₂O₃ powders by grinding a total weight of 5 g in a plastic mortar and pressing the mixture into pellets. An 5 ml iridium crucible with 500 mg of the starting material was placed on an iridium after-heater and heated by the inductor coil of a 10 kW rf Generator. The crucible after-heater arrangement was surrounded by a zirconia fiber tube and a high-purity alumina tube for thermal insulation. The experiments were carried out in a vacuum-tight steel chamber. It was evacuated before each experiment to 5×10^{-3} mbar and filled with 5 N argon gas. Subsequently, a constant flow of about 900 ml/min was kept. During growth the height of the molten zone and consequently the diameter of the fiber (~1 mm) was carefully controlled by manually increasing or decreasing the rf-power. Several starting compositions with different Eu to Sc ratios were tested, resulting in the optimal batch with 47.5 mol% Eu₂O₃ and 52.5 mol% Sc₂O₃.

The grown single-crystal was colourless. A part of the single-crystal fiber was crushed and the irregular shaped fragments were screened using a polarizing light microscope to find a sample of good optical quality for the diffraction experiments.

S3. Refinement

Site occupation refinements indicated deviations from full occupancy on the Eu1 (*A*-site) and the O2 sites. For the final refinement cycle a constraint ensuring charge neutrality was included. The crystallochemical formula of the investigated sample can thus be written as $A(\square_{0.032}\text{Eu}_{0.968})^B\text{ScO}_{2.952}$. The highest peak and deepest hole of the difference Fourier map are located 0.84 Å and 1.42 Å away from the Eu1 position. In contrast to the previous Rietveld refinement, where the *Pbnm* setting of space group no. 62 was chosen, the standard setting *Pnma* was used for the present redetermination.

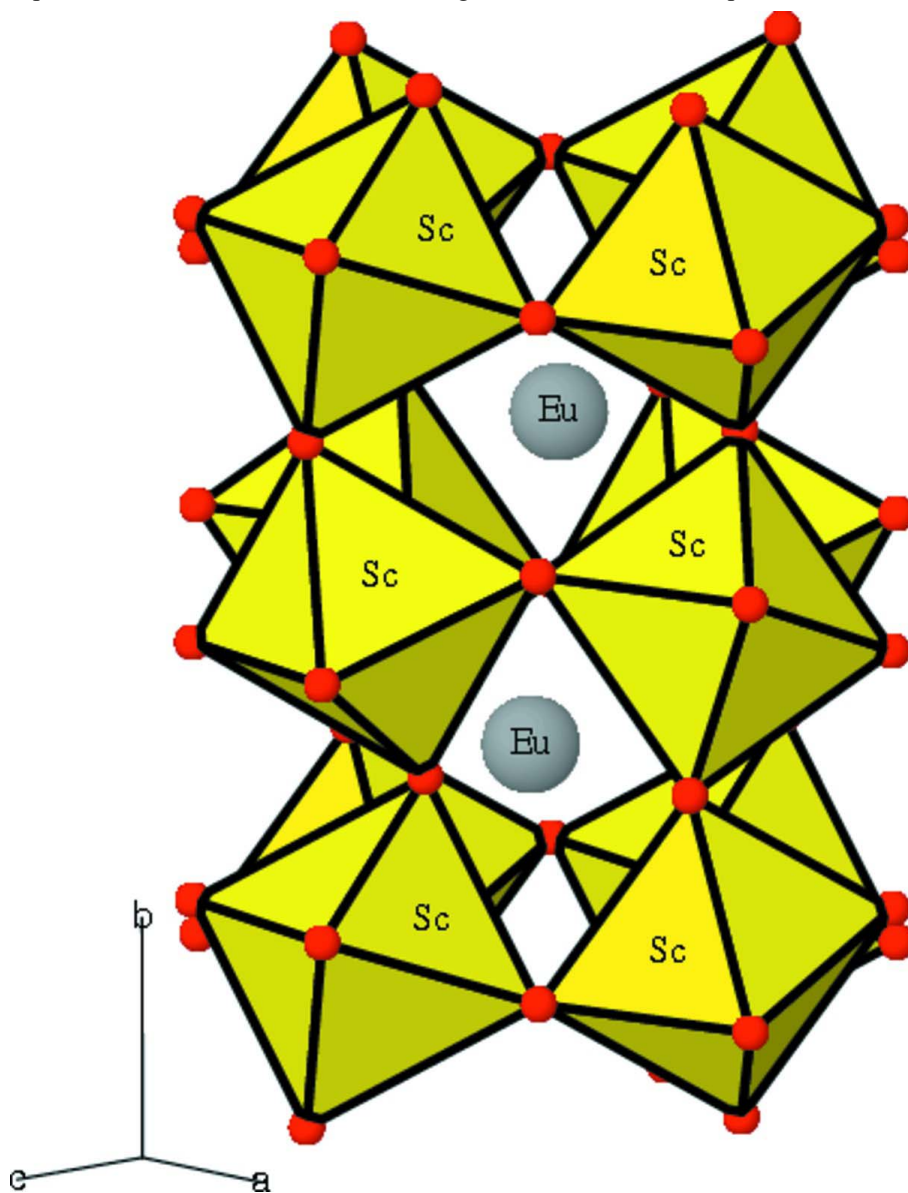


Figure 1

The orthorhombic perovskite structure of EuScO_3 is characterized by a tilted corner sharing ScO_6 framework incorporating the 8-fold coordinated Eu sites. The ScO_6 octahedra are yellow, the Eu atoms are given in grey and the O atoms are presented in red.

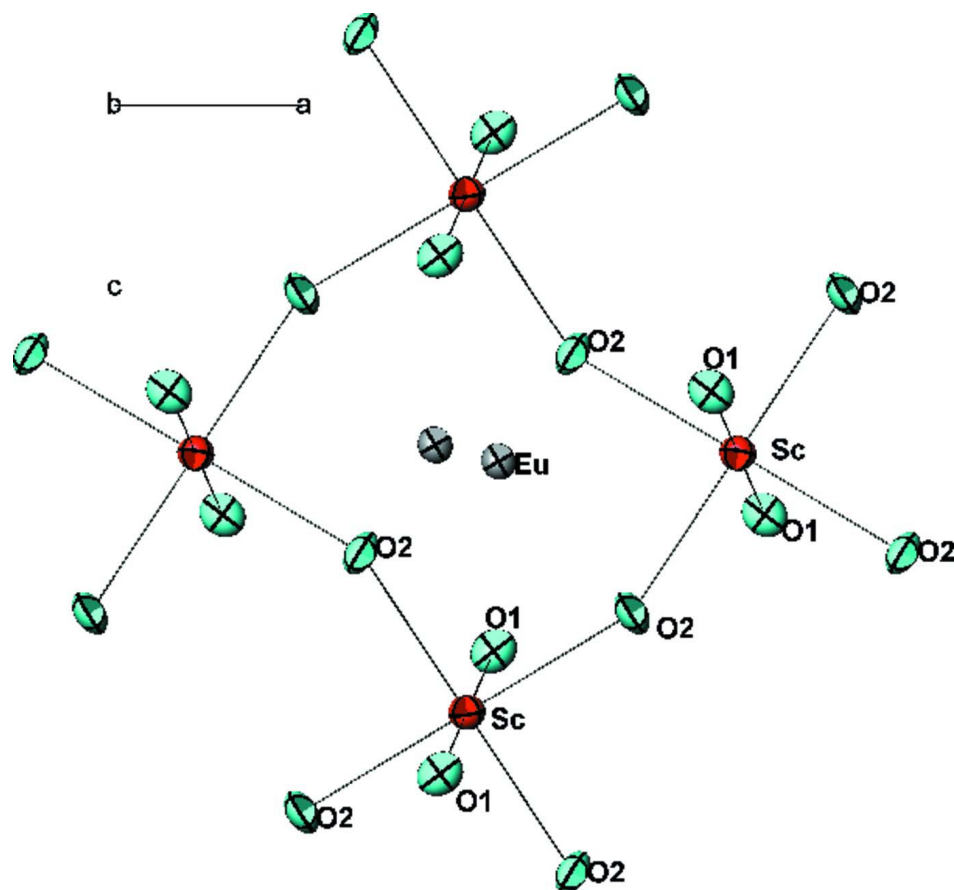


Figure 2

Projection of the EuScO_3 structure along $[010]$, showing the Eu atoms and the Sc coordination with displacement ellipsoids at the 80% probability level.

europium(III) scandate(III)

Crystal data

$\text{Eu}_{0.968}\text{ScO}_{2.952}$

$M_r = 239.24$

Orthorhombic, $Pnma$

Hall symbol: $-P\ 2ac\ 2n$

$a = 5.7554\ (7)\ \text{\AA}$

$b = 7.9487\ (10)\ \text{\AA}$

$c = 5.5087\ (6)\ \text{\AA}$

$V = 252.01\ (5)\ \text{\AA}^3$

$Z = 4$

$F(000) = 422.4$

$D_x = 6.307\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2218 reflections

$\theta = 2.6\text{--}29.2^\circ$

$\mu = 26.28\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Platy fragment, colourless

$0.14 \times 0.12 \times 0.02\ \text{mm}$

Data collection

Stoe IPDS-2
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $6.67\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: analytical
(Alcock, 1970)

$T_{\min} = 0.139$, $T_{\max} = 0.397$

2168 measured reflections

362 independent reflections

345 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$

$\theta_{\max} = 29.1^\circ$, $\theta_{\min} = 4.5^\circ$
 $h = -7 \rightarrow 7$

$k = -10 \rightarrow 9$
 $l = -7 \rightarrow 7$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.051$
 $S = 1.27$
 362 reflections
 31 parameters
 1 restraint
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 $w = 1/[\sigma^2(F_o^2) + (0.0211P)^2 + 0.9412P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.011$
 $\Delta\rho_{\max} = 1.40 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.84 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.113 (5)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Eu1	0.05854 (5)	0.25	0.01589 (6)	0.0090 (2)	0.9677 (13)
Sc2	0	0	0.5	0.0078 (3)	
O1	0.4506 (8)	0.25	0.8815 (9)	0.0111 (9)	
O2	0.1954 (6)	0.9378 (4)	0.8078 (6)	0.0112 (7)	0.9758 (10)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Eu1	0.0070 (3)	0.0102 (3)	0.0098 (3)	0	0.00051 (11)	0
Sc2	0.0064 (6)	0.0079 (6)	0.0090 (6)	0.0006 (6)	0.0000 (3)	0.0000 (3)
O1	0.011 (2)	0.008 (2)	0.014 (2)	0	-0.0025 (17)	0
O2	0.0096 (16)	0.0121 (17)	0.0119 (14)	-0.0019 (12)	-0.0018 (11)	0.0005 (12)

Geometric parameters (\AA , $^\circ$)

Eu1—O1 ⁱ	2.276 (5)	Sc2—O2 ⁱⁱ	2.094 (3)
Eu1—O2 ⁱⁱ	2.304 (3)	Sc2—O2 ^{xii}	2.094 (3)
Eu1—O2 ⁱⁱⁱ	2.304 (3)	Sc2—O2 ^{vi}	2.107 (3)
Eu1—O1 ^{iv}	2.375 (5)	Sc2—O2 ^{xiii}	2.107 (3)
Eu1—O2 ^v	2.611 (3)	Sc2—O1 ^{xiv}	2.1108 (16)
Eu1—O2 ^{vi}	2.611 (3)	Sc2—O1 ^x	2.1108 (16)
Eu1—O2 ^{vii}	2.845 (3)	Sc2—Eu1 ^{xv}	3.2268 (4)
Eu1—O2 ^{viii}	2.845 (3)	Sc2—Eu1 ⁱ	3.2268 (4)

Eu1—Sc2 ^{ix}	3.2268 (4)	Sc2—Eu1 ^{xvi}	3.3428 (4)
Eu1—Sc2 ^x	3.2268 (4)	Sc2—Eu1 ^{xvii}	3.4841 (4)
Eu1—Sc2 ^{xi}	3.3428 (4)	Sc2—Eu1 ^{xviii}	3.4841 (4)
Eu1—Sc2	3.3428 (4)		
O1 ⁱ —Eu1—O2 ⁱⁱ	103.43 (12)	O2 ^{xii} —Sc2—O2 ^{vi}	90.88 (6)
O1 ⁱ —Eu1—O2 ⁱⁱⁱ	103.43 (12)	O2 ⁱⁱ —Sc2—O2 ^{xiii}	90.88 (6)
O2 ⁱⁱ —Eu1—O2 ⁱⁱⁱ	80.77 (17)	O2 ^{xii} —Sc2—O2 ^{xiii}	89.12 (6)
O1 ⁱ —Eu1—O1 ^{iv}	87.69 (11)	O2 ^{vi} —Sc2—O2 ^{xiii}	180
O2 ⁱⁱ —Eu1—O1 ^{iv}	137.24 (9)	O2 ⁱⁱ —Sc2—O1 ^{xiv}	87.46 (16)
O2 ⁱⁱⁱ —Eu1—O1 ^{iv}	137.24 (9)	O2 ^{xii} —Sc2—O1 ^{xiv}	92.54 (16)
O1 ⁱ —Eu1—O2 ^v	137.77 (9)	O2 ^{vi} —Sc2—O1 ^{xiv}	92.67 (15)
O2 ⁱⁱ —Eu1—O2 ^v	117.06 (6)	O2 ^{xiii} —Sc2—O1 ^{xiv}	87.33 (15)
O2 ⁱⁱⁱ —Eu1—O2 ^v	73.38 (8)	O2 ⁱⁱ —Sc2—O1 ^x	92.54 (16)
O1 ^{iv} —Eu1—O2 ^v	71.14 (12)	O2 ^{xii} —Sc2—O1 ^x	87.46 (16)
O1 ⁱ —Eu1—O2 ^{vi}	137.77 (9)	O2 ^{vi} —Sc2—O1 ^x	87.33 (15)
O2 ⁱⁱ —Eu1—O2 ^{vi}	73.38 (8)	O2 ^{xiii} —Sc2—O1 ^x	92.67 (15)
O2 ⁱⁱⁱ —Eu1—O2 ^{vi}	117.06 (6)	O1 ^{xiv} —Sc2—O1 ^x	180
O1 ^{iv} —Eu1—O2 ^{vi}	71.14 (12)	Sc2 ^{xix} —O1—Sc2 ^{xv}	140.6 (2)
O2 ^v —Eu1—O2 ^{vi}	69.74 (15)	Sc2 ^{xix} —O1—Eu1 ^{xx}	105.10 (13)
O1 ⁱ —Eu1—O2 ^{vii}	71.82 (8)	Sc2 ^{xv} —O1—Eu1 ^{xx}	105.10 (13)
O2 ⁱⁱ —Eu1—O2 ^{vii}	77.31 (12)	Sc2 ^{xix} —O1—Eu1 ^{xviii}	91.82 (14)
O2 ⁱⁱⁱ —Eu1—O2 ^{vii}	155.61 (9)	Sc2 ^{xv} —O1—Eu1 ^{xviii}	91.82 (14)
O1 ^{iv} —Eu1—O2 ^{vii}	67.12 (8)	Eu1 ^{xx} —O1—Eu1 ^{xviii}	124.0 (2)
O2 ^v —Eu1—O2 ^{vii}	126.63 (6)	Sc2 ^{xxi} —O2—Sc2 ^{xxii}	143.00 (18)
O2 ^{vi} —Eu1—O2 ^{vii}	66.38 (5)	Sc2 ^{xxi} —O2—Eu1 ⁱⁱ	98.83 (13)
O1 ⁱ —Eu1—O2 ^{viii}	71.82 (8)	Sc2 ^{xxii} —O2—Eu1 ⁱⁱ	117.90 (14)
O2 ⁱⁱ —Eu1—O2 ^{viii}	155.61 (9)	Sc2 ^{xxi} —O2—Eu1 ^{xxii}	85.85 (11)
O2 ⁱⁱⁱ —Eu1—O2 ^{viii}	77.31 (12)	Sc2 ^{xxii} —O2—Eu1 ^{xxii}	89.57 (12)
O1 ^{iv} —Eu1—O2 ^{viii}	67.12 (8)	Eu1 ⁱⁱ —O2—Eu1 ^{xxii}	103.48 (13)
O2 ^v —Eu1—O2 ^{viii}	66.38 (5)	Sc2 ^{xxi} —O2—Eu1 ^{xxiii}	88.37 (12)
O2 ^{vi} —Eu1—O2 ^{viii}	126.63 (6)	Sc2 ^{xxii} —O2—Eu1 ^{xxiii}	79.82 (10)
O2 ^{vii} —Eu1—O2 ^{viii}	121.45 (13)	Eu1 ⁱⁱ —O2—Eu1 ^{xxiii}	102.69 (12)
O2 ⁱⁱ —Sc2—O2 ^{xii}	180	Eu1 ^{xxii} —O2—Eu1 ^{xxiii}	153.77 (14)
O2 ⁱⁱ —Sc2—O2 ^{vi}	89.12 (6)		

Symmetry codes: (i) $x-1/2, y, -z+1/2$; (ii) $-x, -y+1, -z+1$; (iii) $-x, y-1/2, -z+1$; (iv) $x, y, z-1$; (v) $-x+1/2, y-1/2, z-1/2$; (vi) $-x+1/2, -y+1, z-1/2$; (vii) $x, y-1, z-1$; (viii) $x, -y+3/2, z-1$; (ix) $x+1/2, -y+1/2, -z+1/2$; (x) $-x+1/2, -y, z-1/2$; (xi) $-x, y+1/2, -z+1$; (xii) $x, y-1, z$; (xiii) $x-1/2, y-1, -z+3/2$; (xiv) $x-1/2, y, -z+3/2$; (xv) $-x+1/2, -y, z+1/2$; (xvi) $-x, -y, -z+1$; (xvii) $-x, -y, -z$; (xviii) $x, y, z+1$; (xix) $x+1/2, -y+1/2, -z+3/2$; (xx) $x+1/2, y, -z+1/2$; (xxi) $x, y+1, z$; (xxii) $-x+1/2, -y+1, z+1/2$; (xxiii) $x, y+1, z+1$.