

Caesium neodymium sulfate, $\text{CsNd}(\text{SO}_4)_2$

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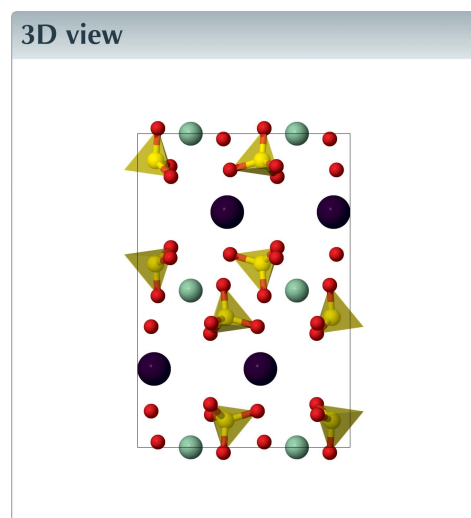
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The crystal structure of caesium neodymium(III) sulfate, $\text{CsNd}(\text{SO}_4)_2$, was determined from intensity data collected on a Rigaku tabletop XtaLAB mini II diffractometer at the International Union of Crystallography Congress 2017, in Hyderabad, India. $\text{CsNd}(\text{SO}_4)_2$ is the fourth crystal structure to be reported in the $\text{CsPr}(\text{SO}_4)_2$ family: the Cs and Nd atoms have site symmetries of 2.. and ..2, respectively. In the extended structure, NdO_8 square antiprisms and SO_4 tetrahedra are connected into layers, which propagate in the (101) plane and CsO_{14} polyhedra connect the layers into a three-dimensional network.



Structure description

Double salts of the form $M^+ \text{REE}^{3+}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ (where M^+ is an alkali metal cation, usually Rb^+ or Cs^+) were first reported by Bukovec and coworkers in a series of articles in the 1970s (*e.g.* Bukovec & Golič, 1975; Bukovec *et al.*, 1977, 1978). It was not possible to determine the crystal structures for all of these compounds (*e.g.* Bukovec *et al.*, 1980). Double salts have often been studied for the properties that result from two different cations in combination (*e.g.* Meyn *et al.*, 1993). $\text{CsNd}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ was studied for its dehydration kinetics, resulting in the decomposition products of $\text{CsNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and then $\text{CsNd}(\text{SO}_4)_2$; however, no crystal structure has been reported for the latter two compounds (Bukovec *et al.*, 1980). $\text{CsNd}(\text{SO}_4)_2$ is isostructural with three other compounds with reported crystal structures, namely $\text{CsPr}(\text{SO}_4)_2$ (Bukovec *et al.*, 1978), $\text{RbDy}(\text{SO}_4)_2$ (Sarukhanyan *et al.*, 1984) and a bismuth-chromate analogue, $\text{RbBi}(\text{CrO}_4)_2$ (Riou *et al.*, 1984).

The crystal structure of $\text{CsNd}(\text{SO}_4)_2$ is an infinite, three dimensional framework. The structure may be considered as a layered structure, incorporating layers of edge- and corner-linked SO_4 and NdO_8 polyhedra in the *ac* plane, with fourteen-coordinate Cs^+ cations bridging the layers with seven Cs—O bonds to each layer (Table 1; Figs. 1 and 2).

Table 1
Selected bond lengths (Å).

Cs1—O3	3.161 (8)	Nd1—O2 ⁱⁱ	2.464 (8)
Cs1—O2 ⁱ	3.223 (9)	Nd1—O3	2.522 (8)
Cs1—O3 ⁱⁱⁱ	3.254 (8)	Nd1—O4 ⁱⁱⁱ	2.566 (9)
Cs1—O4 ⁱⁱⁱ	3.305 (8)	S1—O3	1.472 (8)
Cs1—O1 ⁱ	3.316 (8)	S1—O1	1.480 (8)
Cs1—O2 ^{iv}	3.444 (9)	S1—O4	1.487 (9)
Cs1—O1	3.570 (9)	S1—O2	1.491 (7)
Nd1—O1 ^v	2.456 (8)		

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, y, -z + 1$; (iii) $-x + \frac{3}{2}, -y + 1, z$; (iv) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (v) $x, y, z + 1$.

Isostructural networks have been reported (three with crystal structures) as discussed above.

The bond-valence sums for all cationic elements are slightly low, especially the metallic elements Cs and Nd. Bond-valence sums for Cs (0.851 to 0.892) and Nd (2.749 to 2.756) especially are poor, whether using the values of Brown & Altermatt (1985) or the revised values of Gagné & Hawthorne (2015). It would be of interest to study the bond-valence behaviour of each element in more detail, in a fashion similar to the studies on Pb (Krivovichev & Brown, 2001), Tl (Locock & Burns, 2004) and Te (Mills & Christy, 2013), among others. Specific studies on Cs and Nd should generate bond-valence sums closer to the expected values of 1 and 3 valence units.

Synthesis and crystallization

CsNd(SO₄)₂ was synthesized from a complex mixture of several inorganic compounds dissolved in diluted sulfuric acid (Sigma Aldrich, initial purity 99.999%, pH = -1 after dilution), including caesium nitrate (Sigma Aldrich, 99%) and neodymium(III) oxide (Sigma Aldrich, 99.9%). Initial hydrothermal synthesis at 200°C did not yield any crystals. Subsequently, the vessel was left at room temperature over a period of months. During this time, pale-purple plate-like

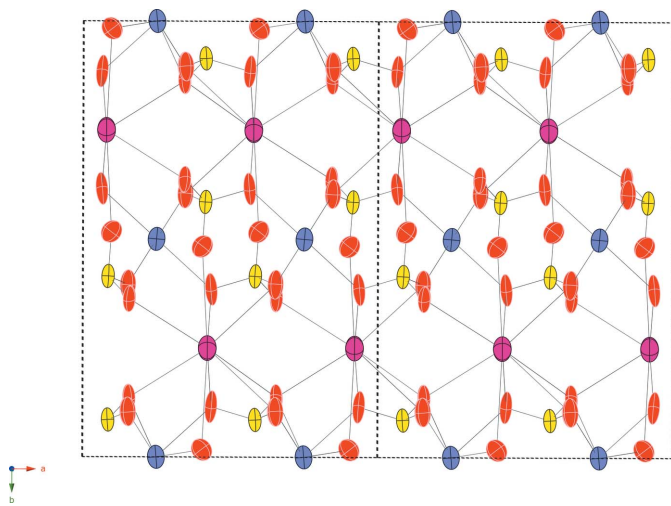


Figure 1
Displacement ellipsoid (90% probability level) representation of two unit cells of CsNd(SO₄)₂: O atoms are red, S atoms yellow, Cs magenta and Nd pale-lavender.

crystals were observed growing on the bottom of the Teflon vessel. Single crystal X-ray diffraction showed these to be crystals of the title compound.

Refinement

Considering the relatively simple nature of the crystal structure of CsNd(SO₄)₂, the structure determination was complicated due to complex twinning observed in some crystals. This twinning was observed on crystals run on the micro-focus MX1 and MX2 macromolecular beamlines of the Australian Synchrotron. The extraneous diffraction spots led to the pseudo-hexagonal unit cell $a = 10.902$ (2), $b = 13.934$ (3), $c = 10.957$ (2) Å, $\alpha = \beta = 90^\circ$, $\gamma = 119.73$ (3) and $V = 1445.4$ (5) Å³. This cell was shown to be a transposition of the *Pnma* cell due to twinning of CsNd(SO₄)₂ crystals by using the *JANA2006* crystallographic program (Petříček *et al.*, 2014). Firstly, the program searched for higher symmetry supercells, which may induce reticular twinning, but no such cells were found. An averaging procedure was then performed, which takes into account twinning by sygonic and also metric merohedry. This procedure showed that R_{int} values were significantly lower for the orthorhombic *mmm* Laue symmetry group (0.07) rather than any hexagonal Laue group (0.4). Finally, the space-group test, which took twinning matrices into account, showed that the space group *Pnna* had the best figure of merit, consistent with the space group determined from a non-twinned crystal fragment (see below). Using *JANA2006*, the crystal was found to be comprised of three twin components. A CIF of the structure model refined from the twinned crystal using synchrotron diffraction data on the MX1 beamline (Cowieson *et al.*, 2015) may be found in the supporting information. The first component was found to have a twin volume fraction of 0.271 (3) and matrix of $[1\ 0\ 0 / 0\ 1\ 0 / 0\ 0\ 1]$, the second

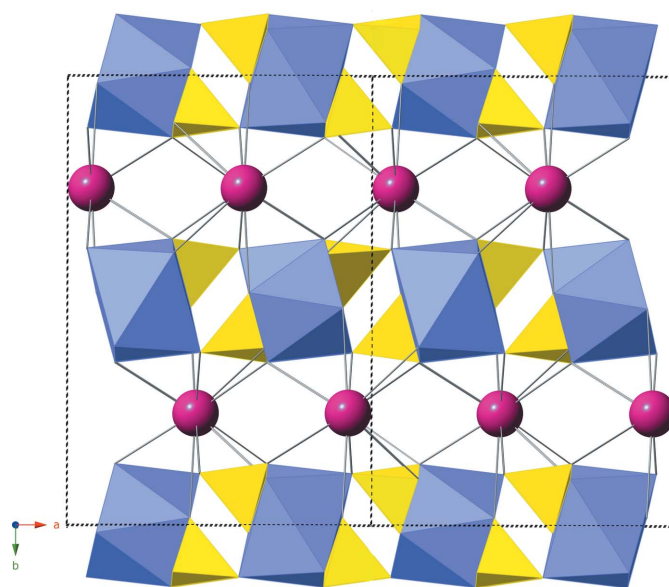


Figure 2
Polyhedral representation of CsNd(SO₄)₂. Sulfate tetrahedra are yellow, NdO₈ polyhedra are pale-lavender and Cs⁺ cations in magenta. Outlines of the unit cell are shown as dotted black lines.

Table 2

Bond-valence sums (in valence units) for atoms in CsNd(SO₄)₂.

	Cs1	Nd1	S1	Σ
O1	0.084 (×2↓), 0.045 (×2↓)	0.386 (×2↓)	1.471	1.986
O2	0.105 (×2↓), 0.061 (×2↓)	0.378 (×2↓)	1.431	1.975
O3	0.122 (×2↓), 0.097 (×2↓)	0.323 (×2↓)	1.501	2.043
O4	0.086 (×2↓)	0.287 (×2↓)	1.445	1.818
Σ	0.851	2.749	5.848	

0.00048 (10) and $[\frac{1}{2} 0 \frac{1}{2} / 0 1 0 / -\frac{3}{2} 0 \frac{1}{2}]$ and the third 0.729 (3) and $[-\frac{1}{2} 0 \frac{1}{2} / 0 1 0 / -\frac{3}{2} 0 -\frac{1}{2}]$. Practically, the second twin component has a negligible effect on the twinning, and the crystal is best considered to be a two-component twin with the two components in a 27:73 ratio.

Whilst it was possible to solve the structure after the treatment of twinning, the final values of R_1 and wR_2 at convergence were higher than those obtained from a non-twinning fragment. The crystal structure reported here was solved on a Rigaku XtaLAB mini II diffractometer at the International Union of Crystallography Congress 2017, Hyderabad, India, using a single, non-twinning crystal fragment. This crystal was obtained by crushing a large, highly twinned, pale-purple crystalline mass in oil, and mounting a smaller, single fragment (dimensions 0.024 × 0.024 × 0.053 μm) that floated away after crushing.

Structure solution was carried out by direct methods using *SHELXT* (Sheldrick, 2015a) and structure refinement by full-matrix least-squares was implemented by *SHELXL* (Sheldrick, 2015b) in the OLEX2 environment (Dolomanov *et al.*, 2009). Full collection and refinement details are shown in Table 2. The residual Fourier peaks are relatively large (3.61 e Å⁻³ maximum, -3.20 e Å⁻³ minimum), but not unreasonably so for small inorganic crystals with heavy scattering elements. A bond-valence summary is shown in Table 2, using the parameters of Gagné & Hawthorne (2015) for S—O, Cs—O and Nd—O bonds.

Full crystal data, data collection and structure refinement details are summarized in Table 3.

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Table 3

Experimental details.

Crystal data	CsNd(SO ₄) ₂
Chemical formula	469.27
M_r	Orthorhombic, <i>Pnna</i>
Crystal system, space group	293
Temperature (K)	9.574 (2), 14.115 (3), 5.4666 (11)
a, b, c (Å)	738.7 (3)
V (Å ³)	4
Z	Mo $K\alpha$
Radiation type	12.46
μ (mm ⁻¹)	0.05 × 0.02 × 0.02
Crystal size (mm)	
Data collection	Rigaku XtaLAB Mini II
Diffractometer	Gaussian (<i>ABSPACK</i> in <i>CrysAlis PRO</i> ; Rigaku OD, 2017)
Absorption correction	0.554, 0.759
T_{\min}, T_{\max}	3915, 1092, 771
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	0.102
R_{int}	0.712
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.064, 0.170, 1.04
No. of reflections	1092
No. of parameters	56
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	3.61, -3.20

Computer programs: *CrysAlis PRO* (Rigaku OD, 2017), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2016/6* (Sheldrick, 2015b), *CrystalMaker* (Palmer, 2009) and *publCIF* (Westrip, 2010).

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full crystallographic data

IUCrData (2018). 3, x180169 [https://doi.org/10.1107/S2414314618001694]

Caesium neodymium sulfate, CsNd(SO₄)₂

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caesium neodymium(III) sulfate

Crystal data

CsNd(SO ₄) ₂	$D_x = 4.219 \text{ Mg m}^{-3}$
$M_r = 469.27$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Orthorhombic, <i>Pnna</i>	Cell parameters from 968 reflections
$a = 9.574 (2) \text{ \AA}$	$\theta = 2.9\text{--}29.9^\circ$
$b = 14.115 (3) \text{ \AA}$	$\mu = 12.46 \text{ mm}^{-1}$
$c = 5.4666 (11) \text{ \AA}$	$T = 293 \text{ K}$
$V = 738.7 (3) \text{ \AA}^3$	Fragment, pale purple
$Z = 4$	$0.05 \times 0.02 \times 0.02 \text{ mm}$
$F(000) = 844$	

Data collection

Rigaku XtaLAB Mini II diffractometer	3915 measured reflections
Radiation source: fine-focus sealed X-ray tube	1092 independent reflections
CCD plate scans	771 reflections with $I > 2\sigma(I)$
Absorption correction: gaussian	$R_{\text{int}} = 0.102$
(<i>ABSPACK</i> in Crys Alis PRO; Rigaku OD, 2017)	$\theta_{\text{max}} = 30.4^\circ$, $\theta_{\text{min}} = 2.9^\circ$
$T_{\text{min}} = 0.554$, $T_{\text{max}} = 0.759$	$h = -13 \rightarrow 13$
	$k = -20 \rightarrow 18$
	$l = -5 \rightarrow 7$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0907P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.170$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 3.61 \text{ e \AA}^{-3}$
1092 reflections	$\Delta\rho_{\text{min}} = -3.20 \text{ e \AA}^{-3}$
56 parameters	
0 restraints	

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cs1	0.92197 (10)	0.750000	0.250000	0.0213 (3)

Nd1	0.750000	0.500000	0.68152 (16)	0.0165 (3)
S1	0.5851 (3)	0.58533 (19)	0.2371 (6)	0.0149 (6)
O1	0.6532 (9)	0.6041 (6)	-0.0010 (13)	0.0190 (17)
O2	0.4359 (7)	0.6153 (7)	0.2254 (16)	0.0226 (19)
O3	0.6571 (8)	0.6370 (5)	0.4342 (14)	0.0169 (17)
O4	0.5960 (9)	0.4831 (6)	0.2998 (16)	0.0201 (19)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs1	0.0134 (5)	0.0257 (5)	0.0248 (6)	0.000	0.000	0.0007 (5)
Nd1	0.0119 (4)	0.0224 (5)	0.0152 (5)	-0.0009 (4)	0.000	0.000
S1	0.0066 (11)	0.0228 (14)	0.0153 (14)	-0.0009 (9)	0.0005 (11)	0.0001 (12)
O1	0.010 (4)	0.035 (4)	0.012 (4)	0.000 (4)	0.002 (3)	-0.002 (4)
O2	0.006 (3)	0.043 (5)	0.018 (5)	0.003 (4)	0.001 (3)	0.005 (4)
O3	0.007 (4)	0.028 (4)	0.015 (4)	-0.003 (3)	-0.002 (3)	-0.006 (3)
O4	0.018 (4)	0.020 (4)	0.022 (5)	-0.003 (3)	0.004 (4)	0.003 (3)

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

Cs1—O3	3.161 (8)	Cs1—O1 ⁱ	3.570 (9)
Cs1—O3 ⁱ	3.161 (8)	Nd1—O1 ^{viii}	2.456 (8)
Cs1—O2 ⁱⁱ	3.223 (9)	Nd1—O1 ^{ix}	2.456 (8)
Cs1—O2 ⁱⁱⁱ	3.223 (9)	Nd1—O2 ^{iv}	2.464 (8)
Cs1—O3 ^{iv}	3.254 (8)	Nd1—O2 ^x	2.464 (8)
Cs1—O3 ^v	3.254 (8)	Nd1—O3	2.522 (8)
Cs1—O4 ^{vi}	3.305 (8)	Nd1—O3 ^{vi}	2.522 (8)
Cs1—O4 ^{vii}	3.305 (8)	Nd1—O4 ^{vi}	2.566 (9)
Cs1—O1 ⁱⁱ	3.316 (8)	Nd1—O4	2.566 (9)
Cs1—O1 ⁱⁱⁱ	3.316 (8)	S1—O3	1.472 (8)
Cs1—O2 ^v	3.444 (9)	S1—O1	1.480 (8)
Cs1—O2 ^{iv}	3.444 (9)	S1—O4	1.487 (9)
Cs1—O1	3.570 (9)	S1—O2	1.491 (7)
O3—Cs1—O3 ⁱ	73.3 (3)	O3—S1—O1	110.4 (5)
O3—Cs1—O2 ⁱⁱ	94.3 (2)	O3—S1—O4	106.2 (5)
O3 ⁱ —Cs1—O2 ⁱⁱ	89.56 (19)	O1—S1—O4	110.2 (5)
O3—Cs1—O2 ⁱⁱⁱ	89.56 (19)	O3—S1—O2	109.8 (5)
O3 ⁱ —Cs1—O2 ⁱⁱⁱ	94.3 (2)	O1—S1—O2	109.5 (5)
O2 ⁱⁱ —Cs1—O2 ⁱⁱⁱ	175.3 (3)	O4—S1—O2	110.6 (5)
O3—Cs1—O3 ^{iv}	97.97 (16)	O3—S1—Nd1	52.3 (3)
O3 ⁱ —Cs1—O3 ^{iv}	166.2 (3)	O1—S1—Nd1	121.9 (3)
O2 ⁱⁱ —Cs1—O3 ^{iv}	80.4 (2)	O4—S1—Nd1	54.1 (4)
O2 ⁱⁱⁱ —Cs1—O3 ^{iv}	96.3 (2)	O2—S1—Nd1	128.6 (4)
O3—Cs1—O3 ^v	166.2 (3)	O3—S1—Nd1 ^x	120.9 (3)
O3 ⁱ —Cs1—O3 ^v	97.97 (16)	O1—S1—Nd1 ^x	125.8 (4)
O2 ⁱⁱ —Cs1—O3 ^v	96.3 (2)	O4—S1—Nd1 ^x	72.4 (4)
O2 ⁱⁱⁱ —Cs1—O3 ^v	80.4 (2)	O2—S1—Nd1 ^x	38.3 (4)

O3 ^{iv} —Cs1—O3 ^v	92.5 (3)	Nd1—S1—Nd1 ^x	103.51 (8)
O3—Cs1—O4 ^{vi}	55.2 (2)	O3—S1—Nd1 ^{xi}	125.0 (3)
O3 ⁱ —Cs1—O4 ^{vi}	119.1 (2)	O1—S1—Nd1 ^{xi}	29.7 (3)
O2 ⁱⁱ —Cs1—O4 ^{vi}	121.5 (2)	O4—S1—Nd1 ^{xi}	80.8 (4)
O2 ⁱⁱⁱ —Cs1—O4 ^{vi}	58.8 (2)	O2—S1—Nd1 ^{xi}	118.4 (4)
O3 ^{iv} —Cs1—O4 ^{vi}	60.3 (2)	Nd1—S1—Nd1 ^{xi}	107.56 (7)
O3 ^v —Cs1—O4 ^{vi}	124.6 (2)	Nd1 ^x —S1—Nd1 ^{xi}	113.33 (8)
O3—Cs1—O4 ^{vii}	119.1 (2)	O3—S1—Cs1 ^{xii}	113.3 (3)
O3 ⁱ —Cs1—O4 ^{vii}	55.2 (2)	O1—S1—Cs1 ^{xii}	57.6 (3)
O2 ⁱⁱ —Cs1—O4 ^{vii}	58.8 (2)	O4—S1—Cs1 ^{xii}	140.4 (4)
O2 ⁱⁱⁱ —Cs1—O4 ^{vii}	121.5 (2)	O2—S1—Cs1 ^{xii}	54.0 (4)
O3 ^{iv} —Cs1—O4 ^{vii}	124.6 (2)	Nd1—S1—Cs1 ^{xii}	165.42 (9)
O3 ^v —Cs1—O4 ^{vii}	60.3 (2)	Nd1 ^x —S1—Cs1 ^{xii}	85.59 (6)
O4 ^{vi} —Cs1—O4 ^{vii}	174.0 (3)	Nd1 ^{xi} —S1—Cs1 ^{xii}	78.39 (6)
O3—Cs1—O1 ⁱⁱ	135.92 (19)	O3—S1—Cs1 ^{xiii}	51.4 (3)
O3 ⁱ —Cs1—O1 ⁱⁱ	110.7 (2)	O1—S1—Cs1 ^{xiii}	133.7 (4)
O2 ⁱⁱ —Cs1—O1 ⁱⁱ	43.53 (19)	O4—S1—Cs1 ^{xiii}	115.7 (4)
O2 ⁱⁱⁱ —Cs1—O1 ⁱⁱ	132.05 (19)	O2—S1—Cs1 ^{xiii}	59.1 (4)
O3 ^{iv} —Cs1—O1 ⁱⁱ	68.0 (2)	Nd1—S1—Cs1 ^{xiii}	82.85 (7)
O3 ^v —Cs1—O1 ⁱⁱ	56.75 (19)	Nd1 ^x —S1—Cs1 ^{xiii}	75.37 (6)
O4 ^{vi} —Cs1—O1 ⁱⁱ	128.2 (2)	Nd1 ^{xi} —S1—Cs1 ^{xiii}	163.41 (8)
O4 ^{vii} —Cs1—O1 ⁱⁱ	56.7 (2)	Cs1 ^{xiii} —S1—Cs1 ^{xiii}	88.59 (6)
O3—Cs1—O1 ⁱⁱⁱ	110.7 (2)	O3—S1—Cs1	47.0 (3)
O3 ⁱ —Cs1—O1 ⁱⁱⁱ	135.92 (19)	O1—S1—Cs1	63.5 (3)
O2 ⁱⁱ —Cs1—O1 ⁱⁱⁱ	132.05 (19)	O4—S1—Cs1	120.4 (4)
O2 ⁱⁱⁱ —Cs1—O1 ⁱⁱⁱ	43.53 (19)	O2—S1—Cs1	127.8 (4)
O3 ^{iv} —Cs1—O1 ⁱⁱⁱ	56.75 (19)	Nd1—S1—Cs1	78.61 (6)
O3 ^v —Cs1—O1 ⁱⁱⁱ	68.0 (2)	Nd1 ^x —S1—Cs1	162.66 (9)
O4 ^{vi} —Cs1—O1 ⁱⁱⁱ	56.7 (2)	Nd1 ^{xi} —S1—Cs1	81.72 (6)
O4 ^{vii} —Cs1—O1 ⁱⁱⁱ	128.2 (2)	Cs1 ^{xiii} —S1—Cs1	89.34 (6)
O1 ⁱⁱ —Cs1—O1 ⁱⁱⁱ	96.2 (3)	Cs1 ^{xiii} —S1—Cs1	87.95 (6)
O3—Cs1—O2 ^v	125.10 (19)	O3—S1—Cs1 ^{vi}	119.4 (3)
O3 ⁱ —Cs1—O2 ^v	59.14 (19)	O1—S1—Cs1 ^{vi}	101.5 (3)
O2 ⁱⁱ —Cs1—O2 ^v	110.1 (3)	O4—S1—Cs1 ^{vi}	13.4 (4)
O2 ⁱⁱⁱ —Cs1—O2 ^v	69.7 (3)	O2—S1—Cs1 ^{vi}	105.7 (4)
O3 ^{iv} —Cs1—O2 ^v	133.29 (18)	Nd1—S1—Cs1 ^{vi}	67.16 (5)
O3 ^v —Cs1—O2 ^v	42.33 (18)	Nd1 ^x —S1—Cs1 ^{vi}	68.67 (5)
O4 ^{vi} —Cs1—O2 ^v	128.3 (2)	Nd1 ^{xi} —S1—Cs1 ^{vi}	71.75 (5)
O4 ^{vii} —Cs1—O2 ^v	52.0 (2)	Cs1 ^{xiii} —S1—Cs1 ^{vi}	127.29 (7)
O1 ⁱⁱ —Cs1—O2 ^v	88.46 (19)	Cs1 ^{xiii} —S1—Cs1 ^{vi}	124.77 (7)
O1 ⁱⁱⁱ —Cs1—O2 ^v	88.6 (2)	Cs1—S1—Cs1 ^{vi}	126.57 (6)
O3—Cs1—O2 ^{iv}	59.14 (19)	S1—O1—Nd1 ^{xi}	132.9 (5)
O3 ⁱ —Cs1—O2 ^{iv}	125.10 (19)	S1—O1—Cs1 ^{xii}	100.3 (4)
O2 ⁱⁱ —Cs1—O2 ^{iv}	69.7 (3)	Nd1 ^{xi} —O1—Cs1 ^{xii}	109.5 (2)
O2 ⁱⁱⁱ —Cs1—O2 ^{iv}	110.1 (3)	S1—O1—Cs1	94.8 (4)
O3 ^{iv} —Cs1—O2 ^{iv}	42.33 (18)	Nd1 ^{xi} —O1—Cs1	110.2 (3)
O3 ^v —Cs1—O2 ^{iv}	133.29 (18)	Cs1 ^{xiii} —O1—Cs1	106.3 (2)
O4 ^{vi} —Cs1—O2 ^{iv}	52.0 (2)	S1—O1—Nd1	40.3 (3)

O4 ^{vii} —Cs1—O2 ^{iv}	128.3 (2)	Nd1 ^{xi} —O1—Nd1	110.0 (3)
O1 ⁱⁱ —Cs1—O2 ^{iv}	88.6 (2)	Cs1 ^{xii} —O1—Nd1	138.1 (2)
O1 ⁱⁱⁱ —Cs1—O2 ^{iv}	88.46 (19)	Cs1—O1—Nd1	72.26 (14)
O2 ^v —Cs1—O2 ^{iv}	175.6 (2)	S1—O1—Cs1 ^{xiii}	34.2 (3)
O3—Cs1—O1	41.67 (18)	Nd1 ^{xi} —O1—Cs1 ^{xiii}	167.1 (3)
O3 ⁱ —Cs1—O1	65.81 (19)	Cs1 ^{xii} —O1—Cs1 ^{xiii}	77.87 (15)
O2 ⁱⁱ —Cs1—O1	132.85 (18)	Cs1—O1—Cs1 ^{xiii}	76.74 (13)
O2 ⁱⁱⁱ —Cs1—O1	51.65 (18)	Nd1—O1—Cs1 ^{xiii}	60.79 (9)
O3 ^{iv} —Cs1—O1	114.82 (19)	S1—O2—Nd1 ^x	119.7 (5)
O3 ^v —Cs1—O1	125.26 (19)	S1—O2—Cs1 ^{xii}	104.0 (4)
O4 ^{vi} —Cs1—O1	54.6 (2)	Nd1 ^x —O2—Cs1 ^{xii}	121.7 (3)
O4 ^{vii} —Cs1—O1	120.3 (2)	S1—O2—Cs1 ^{xiii}	99.1 (4)
O1 ⁱⁱ —Cs1—O1	175.8 (2)	Nd1 ^x —O2—Cs1 ^{xiii}	99.5 (3)
O1 ⁱⁱⁱ —Cs1—O1	88.02 (17)	Cs1 ^{xii} —O2—Cs1 ^{xiii}	110.1 (3)
O2 ^v —Cs1—O1	91.51 (19)	S1—O2—Cs1	38.7 (3)
O2 ^{iv} —Cs1—O1	91.69 (18)	Nd1 ^x —O2—Cs1	155.8 (3)
O3—Cs1—O1 ⁱ	65.81 (19)	Cs1 ^{xii} —O2—Cs1	80.60 (16)
O3 ⁱ —Cs1—O1 ⁱ	41.67 (18)	Cs1 ^{xiii} —O2—Cs1	78.74 (15)
O2 ⁱⁱ —Cs1—O1 ⁱ	51.65 (18)	S1—O3—Nd1	100.2 (4)
O2 ⁱⁱⁱ —Cs1—O1 ⁱ	132.85 (18)	S1—O3—Cs1	113.1 (4)
O3 ^{iv} —Cs1—O1 ⁱ	125.26 (19)	Nd1—O3—Cs1	105.9 (3)
O3 ^v —Cs1—O1 ⁱ	114.82 (19)	S1—O3—Cs1 ^{xiii}	107.9 (4)
O4 ^{vi} —Cs1—O1 ⁱ	120.3 (2)	Nd1—O3—Cs1 ^{xiii}	109.6 (3)
O4 ^{vii} —Cs1—O1 ⁱ	54.6 (2)	Cs1—O3—Cs1 ^{xiii}	118.5 (2)
O1 ⁱⁱ —Cs1—O1 ⁱ	88.02 (17)	S1—O3—Cs1 ^{xii}	49.8 (3)
O1 ⁱⁱⁱ —Cs1—O1 ⁱ	175.8 (2)	Nd1—O3—Cs1 ^{xii}	149.9 (3)
O2 ^v —Cs1—O1 ⁱ	91.69 (18)	Cs1—O3—Cs1 ^{xii}	87.65 (17)
O2 ^{iv} —Cs1—O1 ⁱ	91.51 (19)	Cs1 ^{xiii} —O3—Cs1 ^{xii}	85.63 (17)
O1—Cs1—O1 ⁱ	87.8 (3)	S1—O4—Nd1	97.9 (4)
O1 ^{viii} —Nd1—O1 ^{ix}	90.1 (4)	S1—O4—Cs1 ^{vi}	160.6 (5)
O1 ^{viii} —Nd1—O2 ^{iv}	74.4 (3)	Nd1—O4—Cs1 ^{vi}	100.9 (3)
O1 ^{ix} —Nd1—O2 ^{iv}	88.7 (3)	S1—O4—Nd1 ^x	82.4 (4)
O1 ^{viii} —Nd1—O2 ^x	88.7 (3)	Nd1—O4—Nd1 ^x	122.8 (3)
O1 ^{ix} —Nd1—O2 ^x	74.4 (3)	Cs1 ^{vi} —O4—Nd1 ^x	91.3 (2)
O2 ^{iv} —Nd1—O2 ^x	156.2 (4)	S1—O4—Nd1 ^{xi}	75.8 (3)
O1 ^{viii} —Nd1—O3	77.7 (2)	Nd1—O4—Nd1 ^{xi}	120.6 (3)
O1 ^{ix} —Nd1—O3	166.2 (3)	Cs1 ^{vi} —O4—Nd1 ^{xi}	90.6 (2)
O2 ^{iv} —Nd1—O3	81.9 (3)	Nd1 ^x —O4—Nd1 ^{xi}	114.9 (2)
O2 ^x —Nd1—O3	111.2 (3)	S1—O4—Cs1 ^{xiii}	48.1 (3)
O1 ^{viii} —Nd1—O3 ^{vi}	166.2 (3)	Nd1—O4—Cs1 ^{xiii}	73.10 (19)
O1 ^{ix} —Nd1—O3 ^{vi}	77.7 (2)	Cs1 ^{vi} —O4—Cs1 ^{xiii}	143.7 (2)
O2 ^{iv} —Nd1—O3 ^{vi}	111.2 (3)	Nd1 ^x —O4—Cs1 ^{xiii}	65.27 (14)
O2 ^x —Nd1—O3 ^{vi}	81.9 (3)	Nd1 ^{xi} —O4—Cs1 ^{xiii}	123.8 (2)
O3—Nd1—O3 ^{vi}	115.2 (3)	S1—O4—Cs1	44.4 (3)
O1 ^{viii} —Nd1—O4 ^{vi}	137.4 (3)	Nd1—O4—Cs1	66.90 (18)
O1 ^{ix} —Nd1—O4 ^{vi}	114.4 (3)	Cs1 ^{vi} —O4—Cs1	142.6 (2)
O2 ^{iv} —Nd1—O4 ^{vi}	72.0 (3)	Nd1 ^x —O4—Cs1	125.5 (2)
O2 ^x —Nd1—O4 ^{vi}	130.1 (3)	Nd1 ^{xi} —O4—Cs1	69.23 (13)

O3—Nd1—O4 ^{vi}	72.3 (3)	Cs1 ^{xiii} —O4—Cs1	69.26 (11)
O3 ^{vi} —Nd1—O4 ^{vi}	55.4 (3)	S1—O4—Cs1 ^{xii}	28.9 (3)
O1 ^{viii} —Nd1—O4	114.4 (3)	Nd1—O4—Cs1 ^{xii}	126.7 (3)
O1 ^{ix} —Nd1—O4	137.4 (3)	Cs1 ^{vi} —O4—Cs1 ^{xii}	132.0 (2)
O2 ^{iv} —Nd1—O4	130.1 (3)	Nd1 ^x —O4—Cs1 ^{xii}	68.85 (14)
O2 ^x —Nd1—O4	72.0 (3)	Nd1 ^{xi} —O4—Cs1 ^{xii}	62.84 (12)
O3—Nd1—O4	55.4 (3)	Cs1 ^{xiii} —O4—Cs1 ^{xii}	66.96 (11)
O3 ^{vi} —Nd1—O4	72.3 (3)	Cs1—O4—Cs1 ^{xii}	66.87 (10)
O4 ^{vi} —Nd1—O4	71.2 (4)		

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