

Poly[[tetraquadi- μ_4 -oxalato- μ_2 -oxalato-dineodymium(III)] dihydrate]

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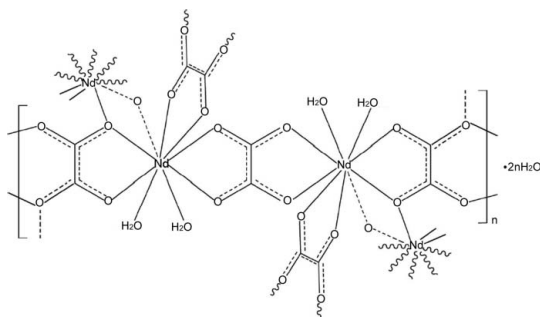
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.019; wR factor = 0.045; data-to-parameter ratio = 12.6.

The title compound, $\{[\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}\}_n$, was synthesized hydrothermally in the presence of bis(carboxyethylgermanium) sesquioxide. It is isostructural with the corresponding Pr compound [Yang *et al.* (2009). *Acta Cryst. E* **65**, m1152–m1153]. The Nd^{3+} cation is nine-coordinated and its coordination polyhedron can be described as a distorted tricapped trigonal prism. Two Nd^{3+} ions are connected by two O atoms from two oxalate ions to give a dinuclear Nd_2 unit. The unit is further linked to four others *via* four oxalate ions yielding a layerparallel to $(0\bar{1}1)$. The linkages between the layers by neighbouring oxalate anions lead to a three-dimensional framework with channels along the c axis. The coordinating and free water molecules are located in the channels and make contact with each other and the host framework by weak $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For the application of lanthanide compounds, see: Kido & Okamoto (2002). For background to lanthanide oxalates, see: Kahwa *et al.* (1984); Trombe & Jaud (2003); Wang *et al.* (2008). For the isostructural Pr compound, see: Yang *et al.* (2009).



Experimental

Crystal data

$[\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$
 $M_r = 660.64$
 Triclinic, $P\bar{1}$
 $a = 6.036$ (3) Å
 $b = 7.603$ (3) Å
 $c = 8.906$ (4) Å
 $\alpha = 98.386$ (6)°
 $\beta = 99.742$ (3)°
 $\gamma = 96.802$ (5)°
 $V = 394.2$ (3) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 6.61$ mm⁻¹
 $T = 293$ K
 $0.05 \times 0.05 \times 0.05$ mm

Data collection

Rigaku SCXmini diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
 $T_{\min} = 0.758$, $T_{\max} = 1.000$
 2997 measured reflections
 1721 independent reflections
 1600 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$
 $wR(F^2) = 0.045$
 $S = 1.04$
 1721 reflections
 137 parameters
 9 restraints
 All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 1.01$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.06$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1W}-\text{H1}\cdots\text{O5}^i$	0.84 (2)	2.00 (3)	2.681 (4)	138 (4)
$\text{O1W}-\text{H1}\cdots\text{O3}^i$	0.84 (2)	2.55 (3)	3.244 (4)	141 (4)
$\text{O1W}-\text{H2}\cdots\text{O3W}$	0.82 (2)	2.01 (2)	2.833 (4)	175 (5)
$\text{O2W}-\text{H3}\cdots\text{O3}^{ii}$	0.83 (2)	2.20 (3)	2.919 (4)	145 (4)
$\text{O2W}-\text{H4}\cdots\text{O3W}^{ii}$	0.83 (2)	2.00 (2)	2.809 (4)	165 (4)
$\text{O3W}-\text{H5}\cdots\text{O4}^{iii}$	0.82 (2)	2.04 (2)	2.827 (4)	159 (5)
$\text{O3W}-\text{H6}\cdots\text{O6}^{iv}$	0.85 (2)	2.10 (4)	2.835 (4)	146 (5)

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

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2122).

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supplementary materials

Acta Cryst. (2012). E68, m289 [doi:10.1107/S1600536812005016]

Poly[[tetraaquad- μ_4 -oxalato- μ_2 -oxalato-dineodymium(III)] dihydrate]**Gao-Juan Cao, Cheng Rong, Qing-lu Li and Wen-Jing Jiang****Comment**

The current interest in designing and making lanthanide compounds has been excited not only by their impressive structural but also by their application in optoelectronic field (Kido & Okamoto, 2002). In our work on the preparation of lanthanide-organogermanate compounds, an unexpected lanthanide oxalate $\{[\text{Nd}(\text{C}_2\text{O}_4)_{1.5}(\text{H}_2\text{O})_2]\text{H}_2\text{O}\}_n$, was obtained. Although the synthesis methods are different, it is isostructural with the corresponding Pr compound (Yang *et al.*, 2009).

Crystal structure determination by X-ray diffraction was performed on a SCXmini-CCD diffractometer equipped with a graphite-monochromatic $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation using an ω scan mode at 273 K. The crystallographic analysis reveals that the asymmetric unit of this compound contains one independent Nd atom, six O atoms, three C atoms and three water molecules. The Nd^{3+} cation is nine-coordinated and is described as distorted tricapped trigonal prism: six O atoms from three $\text{C}_2\text{O}_4^{2-}$ ligands, one O atom from one $\text{C}_2\text{O}_4^{2-}$ and two water molecules. Two Nd^{3+} ions are connected by two O atoms from two oxalates to give a dinuclear Nd_2 unit. The unit is further connected four others *via* four oxalates to form a layer. The linkages between the layers by oxalates lead to a three-dimensional framework with channels along *a* axis, as shown in Fig.2. The coordinated and free water molecules is located in the channels and contact with each other and host framework by $\text{O}—\text{H}\cdots\text{O}$ hydrogen bonds (Fig.3.).

Experimental

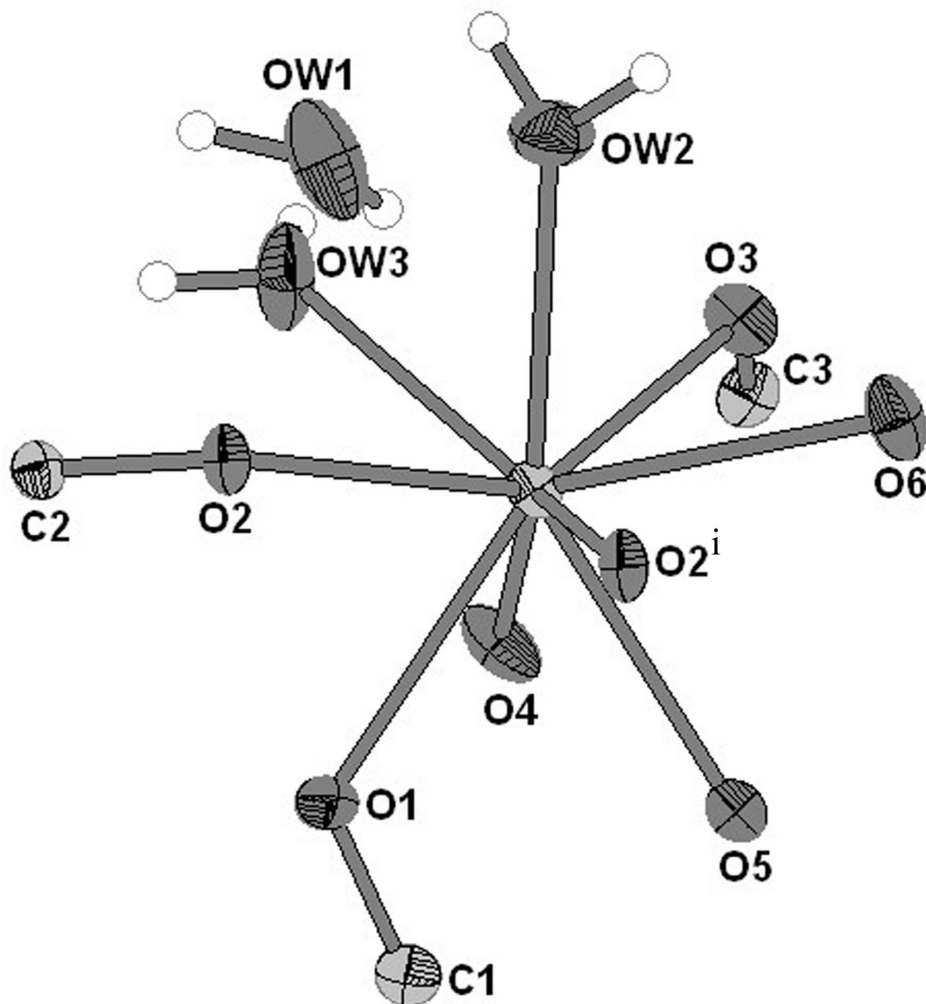
A mixture of $\text{H}_2\text{E}_2\text{Ge}_2\text{O}_3$ (bis(carboxyethylgermanium) sesquioxide) (0.085 g), Nd_2O_3 (0.090 g), $\text{H}_2\text{C}_2\text{O}_4$ (0.090 g) and H_2O (10 ml) was stirred for about 30 min, then sealed in a 25 ml Teflonlined bomb at 170°C for 7 days, cooled to room temperature. Pink prismatic crystals of the title compound were obtained by filtration (yield about 55% based on $\text{H}_2\text{C}_2\text{O}_4$), washed with distilled water, and dried in air. The $\text{H}_2\text{E}_2\text{Ge}_2\text{O}_3$ ligand plays a key role in the formation of the title compound although it is not present in the final product. If $\text{H}_2\text{E}_2\text{Ge}_2\text{O}_3$ ligand was not added, we obtained a different neodymium oxalate reported reviously (Trombe & Jaud, 2003). Elemental analysis calcd (%) for $\text{C}_6\text{H}_{12}\text{Nd}_2\text{O}_{18}$: C, 10.91; H, 1.83; Found: C, 10.87; H, 1.88.

Refinement

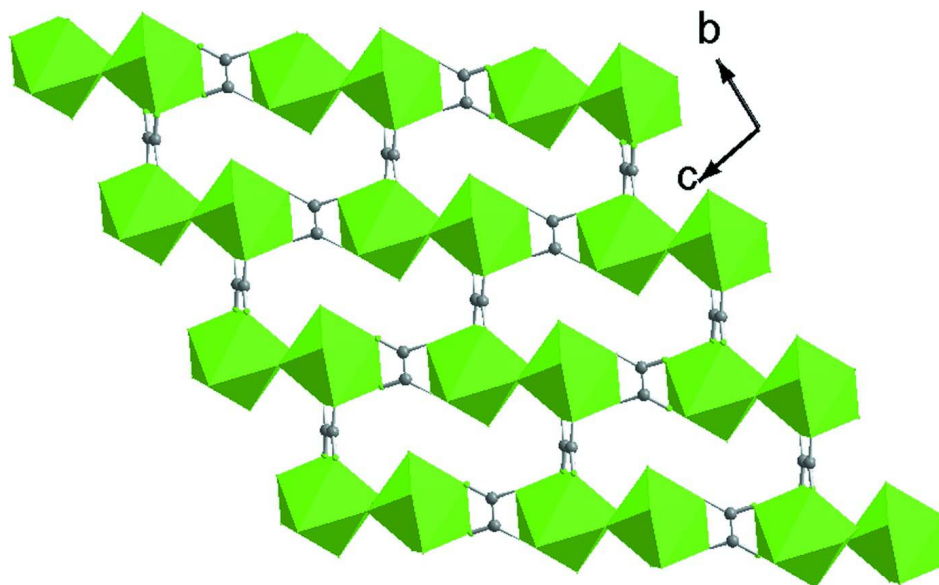
All non-hydrogen atoms were refined anisotropically. The water H atoms were located in a difference Fourier map and refined with a distance restraint of $\text{O}—\text{H} = 0.85 \text{ \AA}$, and $\text{H}—\text{H} = 1.32 \text{ \AA}$ within the water molecules and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Computing details

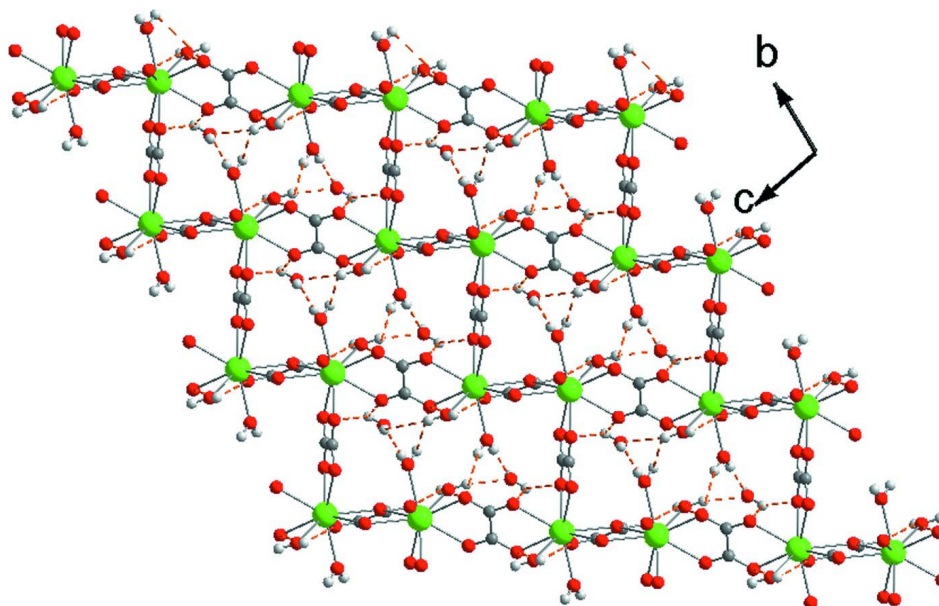
Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear* (Rigaku, 2007); data reduction: *CrystalClear* (Rigaku, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

**Figure 1**

The asymmetric unit of the title complex, together with additional O2 atom to complete the coordination of the Nd³⁺ cation. Symmetry operation (i) $1-x, 2-y, 2-z$. Displacement ellipsoids are plotted at the 50% probability level. H atoms are shown as small circles of arbitrary radii.


Figure 2

The three-dimensional framework of the title complex with channels viewed along the a axis.


Figure 3

Hydrogen bonds with dashed lines in the title compound viewed along the a axis.

Poly[[tetraaquadi- μ_4 -oxalato- μ_2 -oxalato-dineodymium(III)] dihydrate]

Crystal data

$[\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$

$M_r = 660.64$

Triclinic, $P\bar{1}$

Hall symbol: $-\text{P } 1$

$a = 6.036$ (3) Å

$b = 7.603$ (3) Å

$c = 8.906$ (4) Å

$\alpha = 98.386$ (6)°

$\beta = 99.742$ (3)°

$\gamma = 96.802$ (5)°

$V = 394.2$ (3) Å³

$Z = 1$

$F(000) = 312$
 $D_x = 2.783 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 1101 reflections
 $\theta = 2.4\text{--}27.5^\circ$

$\mu = 6.61 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Prism, pink
 $0.05 \times 0.05 \times 0.05 \text{ mm}$

Data collection

Rigaku SCXmini
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2004)
 $T_{\min} = 0.758$, $T_{\max} = 1.000$

2997 measured reflections
 1721 independent reflections
 1600 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.3^\circ$
 $h = -7 \rightarrow 7$
 $k = -9 \rightarrow 9$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.019$
 $wR(F^2) = 0.045$
 $S = 1.04$
 1721 reflections
 137 parameters
 9 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0267P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.01 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.06 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick,
 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0250 (12)

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Nd	0.50918 (3)	0.80732 (2)	0.795455 (19)	0.01243 (9)
O1	0.3007 (4)	0.6414 (3)	0.9553 (3)	0.0197 (5)
O2	0.2687 (4)	1.0032 (3)	0.9482 (3)	0.0159 (5)
O3	0.6296 (4)	0.7244 (3)	0.5432 (3)	0.0194 (5)
O4	0.7188 (4)	0.5888 (3)	0.9155 (3)	0.0218 (5)
O5	0.9212 (4)	0.8988 (3)	0.8085 (3)	0.0210 (5)
O6	0.3574 (5)	0.4917 (3)	0.6531 (3)	0.0227 (5)
C1	0.3797 (6)	0.5159 (4)	1.0114 (4)	0.0160 (7)
C2	0.0540 (5)	0.9720 (4)	0.9295 (4)	0.0138 (6)
C3	0.5789 (6)	0.5661 (4)	0.4686 (4)	0.0163 (7)

O1W	0.1774 (4)	0.8272 (4)	0.5951 (3)	0.0303 (7)
H1	0.052 (5)	0.846 (6)	0.618 (5)	0.045*
H2	0.145 (7)	0.765 (6)	0.509 (3)	0.045*
O2W	0.5617 (5)	1.0983 (4)	0.7077 (3)	0.0283 (6)
H3	0.461 (5)	1.144 (6)	0.658 (5)	0.042*
H4	0.680 (4)	1.171 (5)	0.722 (6)	0.042*
O3W	0.0780 (5)	0.6307 (4)	0.2901 (4)	0.0390 (8)
H5	0.105 (8)	0.550 (6)	0.226 (5)	0.059*
H6	-0.065 (3)	0.620 (7)	0.277 (6)	0.059*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Nd	0.01250 (11)	0.01253 (11)	0.01129 (11)	-0.00015 (6)	0.00267 (6)	-0.00003 (6)
O1	0.0213 (13)	0.0226 (13)	0.0199 (12)	0.0078 (10)	0.0081 (10)	0.0099 (10)
O2	0.0100 (11)	0.0192 (12)	0.0172 (11)	0.0004 (9)	0.0032 (9)	-0.0006 (9)
O3	0.0231 (13)	0.0158 (12)	0.0170 (12)	-0.0022 (10)	0.0058 (10)	-0.0027 (10)
O4	0.0176 (13)	0.0249 (13)	0.0272 (13)	0.0047 (10)	0.0086 (10)	0.0123 (11)
O5	0.0137 (11)	0.0311 (14)	0.0140 (11)	-0.0038 (10)	0.0023 (9)	-0.0034 (10)
O6	0.0303 (14)	0.0191 (12)	0.0172 (12)	-0.0045 (10)	0.0128 (10)	-0.0047 (10)
C1	0.0177 (17)	0.0169 (16)	0.0125 (15)	0.0023 (13)	0.0028 (13)	-0.0001 (13)
C2	0.0131 (15)	0.0123 (14)	0.0153 (16)	0.0008 (12)	0.0025 (12)	0.0014 (13)
C3	0.0155 (16)	0.0179 (17)	0.0135 (15)	0.0021 (13)	0.0000 (12)	0.0000 (13)
O1W	0.0161 (13)	0.0518 (19)	0.0197 (13)	0.0077 (12)	0.0025 (10)	-0.0053 (13)
O2W	0.0261 (15)	0.0227 (14)	0.0342 (16)	-0.0029 (11)	-0.0005 (12)	0.0112 (12)
O3W	0.0284 (16)	0.0440 (18)	0.0356 (17)	-0.0137 (14)	0.0118 (13)	-0.0141 (14)

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

Nd—O1	2.441 (3)	O5—C2 ⁱⁱⁱ	1.241 (4)
Nd—O2W	2.455 (3)	O6—C3 ^{iv}	1.248 (4)
Nd—O4	2.462 (3)	C1—O4 ⁱⁱ	1.258 (5)
Nd—O5	2.480 (3)	C1—C1 ⁱⁱ	1.542 (7)
Nd—O1W	2.481 (3)	C2—O5 ^v	1.241 (4)
Nd—O3	2.494 (3)	C2—C2 ^{vi}	1.539 (6)
Nd—O6	2.530 (3)	C3—O6 ^{iv}	1.248 (4)
Nd—O2 ⁱ	2.576 (2)	C3—C3 ^{iv}	1.532 (7)
Nd—O2	2.601 (2)	O1W—H1	0.839 (19)
O1—C1	1.246 (4)	O1W—H2	0.823 (19)
O2—C2	1.267 (4)	O2W—H3	0.830 (18)
O2—Nd ⁱ	2.576 (2)	O2W—H4	0.827 (19)
O3—C3	1.263 (4)	O3W—H5	0.824 (19)
O4—C1 ⁱⁱ	1.258 (5)	O3W—H6	0.845 (19)
O1—Nd—O2W	142.79 (9)	O4—Nd—O2	120.99 (8)
O1—Nd—O4	66.13 (8)	O5—Nd—O2	122.26 (8)
O2W—Nd—O4	142.62 (9)	O1W—Nd—O2	76.88 (8)
O1—Nd—O5	132.18 (8)	O3—Nd—O2	146.24 (8)
O2W—Nd—O5	71.58 (9)	O6—Nd—O2	122.82 (8)
O4—Nd—O5	71.43 (9)	O2 ⁱ —Nd—O2	65.42 (9)

O1—Nd—O1W	97.08 (10)	C1—O1—Nd	120.1 (2)
O2W—Nd—O1W	70.46 (10)	C2—O2—Nd ⁱ	118.3 (2)
O4—Nd—O1W	142.10 (10)	C2—O2—Nd	123.74 (19)
O5—Nd—O1W	130.44 (10)	Nd ⁱ —O2—Nd	114.58 (8)
O1—Nd—O3	134.13 (8)	C3—O3—Nd	121.0 (2)
O2W—Nd—O3	77.81 (9)	C1 ⁱⁱ —O4—Nd	119.4 (2)
O4—Nd—O3	92.73 (9)	C2 ⁱⁱⁱ —O5—Nd	123.2 (2)
O5—Nd—O3	67.13 (8)	C3 ^{iv} —O6—Nd	120.3 (2)
O1W—Nd—O3	74.66 (9)	O1—C1—O4 ⁱⁱ	126.2 (3)
O1—Nd—O6	70.15 (8)	O1—C1—C1 ⁱⁱ	117.3 (4)
O2W—Nd—O6	132.48 (9)	O4 ⁱⁱ —C1—C1 ⁱⁱ	116.5 (4)
O4—Nd—O6	69.77 (9)	O5 ^v —C2—O2	126.3 (3)
O5—Nd—O6	114.40 (8)	O5 ^v —C2—C2 ^{vi}	116.4 (4)
O1W—Nd—O6	72.59 (10)	O2—C2—C2 ^{vi}	117.2 (3)
O3—Nd—O6	64.28 (8)	O6 ^{iv} —C3—O3	125.9 (3)
O1—Nd—O2 ⁱ	85.95 (9)	O6 ^{iv} —C3—C3 ^{iv}	117.0 (4)
O2W—Nd—O2 ⁱ	81.77 (9)	O3—C3—C3 ^{iv}	117.1 (4)
O4—Nd—O2 ⁱ	77.35 (8)	Nd—O1W—H1	122 (3)
O5—Nd—O2 ⁱ	63.77 (7)	Nd—O1W—H2	124 (3)
O1W—Nd—O2 ⁱ	137.60 (8)	H1—O1W—H2	105 (3)
O3—Nd—O2 ⁱ	130.55 (8)	Nd—O2W—H3	126 (3)
O6—Nd—O2 ⁱ	144.97 (8)	Nd—O2W—H4	128 (3)
O1—Nd—O2	67.11 (8)	H3—O2W—H4	106 (3)
O2W—Nd—O2	75.84 (10)	H5—O3W—H6	105 (3)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1 \cdots O5 ^v	0.84 (2)	2.00 (3)	2.681 (4)	138 (4)
O1W—H1 \cdots O3 ^v	0.84 (2)	2.55 (3)	3.244 (4)	141 (4)
O1W—H2 \cdots O3W	0.82 (2)	2.01 (2)	2.833 (4)	175 (5)
O2W—H3 \cdots O3 ^{vii}	0.83 (2)	2.20 (3)	2.919 (4)	145 (4)
O2W—H4 \cdots O3W ^{vii}	0.83 (2)	2.00 (2)	2.809 (4)	165 (4)
O3W—H5 \cdots O4 ^{iv}	0.82 (2)	2.04 (2)	2.827 (4)	159 (5)
O3W—H6 \cdots O6 ^{viii}	0.85 (2)	2.10 (4)	2.835 (4)	146 (5)

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