

## C-type Nd<sub>2</sub>Se<sub>3</sub>

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 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{Nd}-\text{Se}) = 0.0005$  Å;  $R$  factor = 0.026;  $wR$  factor = 0.060; data-to-parameter ratio = 31.4.

The title compound, neodymium sesquiselenide, is isotopic with the other known rare-earth metal(III) selenides  $M_2\text{Se}_3$  ( $M = \text{La}-\text{Pr}$  and  $\text{Sm}-\text{Lu}$ ) with the cubic C-type structure. It adopts a cation-defective  $\text{Th}_3\text{P}_4$ -type arrangement with close to 8/9 of the unique neodymium-cation site occupied, leading to the composition  $\text{Nd}_{2.667}\text{Se}_4$  ( $Z = 4$ ) or  $\text{Nd}_2\text{Se}_3$  ( $Z = 5.333$ ), respectively. The  $\text{Nd}^{3+}$  cations are thus surrounded by eight selenide anions, forming trigonal  $[\text{NdSe}_8]^{13-}$  dodecahedra, whereas the  $\text{Se}^{2-}$  anions exhibit a sixfold coordination, but due to the under-occupation of neodymium, each one is statistically surrounded by only 5.333 cations. The crystal studied was a merohedral twin with a 0.31 (6):0.69 (6) domain ratio.

### Related literature

For the structural family with the cation-defective  $\text{Th}_3\text{P}_4$ -type arrangement, see: Pardo *et al.* (1963); Flahaut *et al.* (1965); Lashkarev & Paderno (1965). For the rare-earth sesquiselenides  $M_2\text{Se}_3$  with  $M = \text{La}-\text{Pr}$  and  $\text{Sm}-\text{Lu}$ , see: Grundmeier & Urland (1995); Folchnandt (1997); Folchnandt & Schleid (2001); Folchnandt *et al.* (2004).

### Experimental

#### Crystal data

$\text{Nd}_{2.667}\text{Se}_4$	$Z = 4$
$M_r = 700.48$	Mo $K\alpha$ radiation
Cubic, $I\bar{4}3d$	$\mu = 40.39$ mm <sup>-1</sup>
$a = 8.8632$ (6) Å	$T = 293$ K
$V = 696.26$ (8) Å <sup>3</sup>	$0.03 \times 0.03 \times 0.02$ mm

#### Data collection

Stoe IPDS-I diffractometer	8964 measured reflections
Absorption correction: numerical ( <i>X-SHAPE</i> ; Stoe & Cie, 1999)	220 independent reflections
$T_{\min} = 0.305$ , $T_{\max} = 0.401$	214 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.065$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	$\Delta\rho_{\text{max}} = 1.01$ e Å <sup>-3</sup>
$wR(F^2) = 0.060$	$\Delta\rho_{\text{min}} = -2.11$ e Å <sup>-3</sup>
$S = 1.22$	Absolute structure: Flack (1983), 92 Friedel pairs
220 reflections	Flack parameter: 0.31 (6)
7 parameters	

**Table 1**

Selected bond lengths (Å).

Nd–Se <sup>i</sup> (4×)	2.9675 (5)	Nd–Se (4×)	3.1732 (6)
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 Symmetry codes: (i)  $-x + \frac{1}{2}, -y, z + \frac{1}{2}$ .

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: MG2064).

### References

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**supplementary materials**

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## C-type Nd<sub>2</sub>Se<sub>3</sub>

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### Comment

C-type Nd<sub>2</sub>Se<sub>3</sub> (Fig. 1) belongs to a structural family with the cation-defect Th<sub>3</sub>P<sub>4</sub>-type arrangement (Pardo *et al.*, 1963; Flahaut *et al.*, 1965; Lashkarev & Paderno, 1965) adopted by rare-earth sesquiselenides M<sub>2</sub>Se<sub>3</sub> with M = La – Pr and Sm – Lu (Grundmeier & Urland, 1995; Folchnandt, 1997; Folchnandt & Schleid, 2001; Folchnandt *et al.*, 2004) following the general formula M<sub>2.667</sub>□<sub>0.333</sub>Se<sub>4</sub>. The Nd<sup>3+</sup> cations occupy the 12a position, whereas selenium resides at the 16c position. Despite the fact that out of the 12 possible cationic sites (per 16 Se<sup>2-</sup> and unit cell), only 10.667 are allowed to be occupied to realise the composition Nd<sub>2</sub>Se<sub>3</sub> (with Z = 5.333, *i.e.* M<sub>2.667</sub>□<sub>0.333</sub>Se<sub>4</sub> with Z = 4); these exhibit the coordination number 8 with respect to the selenide anions. The [NdSe<sub>8</sub>]<sup>13-</sup> coordination polyhedra can be described as trigonal dodecahedra with  $\bar{4}$ -symmetry (Fig. 2). On average, the Se<sup>2-</sup> anions are surrounded by 5.333 Nd<sup>3+</sup> cations in a trigonal hemiprism of symmetry  $\bar{3}$ . with faces rotated 38.2° with respect to each other (Fig. 3).

### Experimental

Ruby-red, multifaceted, transparent crystals of Nd<sub>2</sub>Se<sub>3</sub> were obtained from stoichiometric reaction of the elements in the presence of CsCl as a flux, placed within a torch-sealed evacuated fused-silica vessel. The mixture was heated at 1123 K for seven days, followed by cooling to ambient temperature with 10 K/h.

### Figures

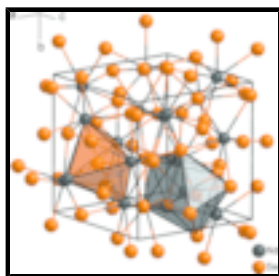


Fig. 1. Crystal structure of C-Type Nd<sub>2</sub>Se<sub>3</sub>.

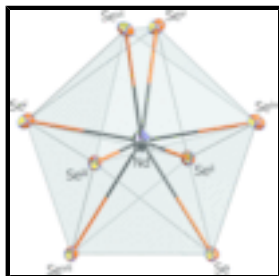


Fig. 2. Coordination sphere of the Nd<sup>3+</sup> cation in the shape of a trigonal dodecahedron. Displacement ellipsoids are drawn at 95% probability level. [Symmetry codes: (i)  $-x + 1/2, -y, z + 1/2$ ; (ii)  $y + 1/4, x + 1/4, z + 1/4$ ; (iii)  $y + 1/4, -x - 1/4, -z + 1/4$ ; (iv)  $-x + 1/2, y, -z$ ; (v)  $-y + 3/4, -x + 1/4, z + 1/4$ ; (vi)  $-y + 3/4, x - 1/4, -z + 1/4$ ; (vii)  $x, -y, -z + 1/2$ .]

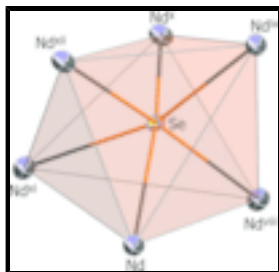


Fig. 3. Coordination sphere of the  $\text{Se}^{2-}$  anion. Due to the under-occupation of the neodymium site, each selenium is surrounded by 5.333  $\text{Nd}^{3+}$  cations. Displacement ellipsoids are drawn at 95% probability level. [Symmetry codes: (viii)  $y, -z, -x + 1/2$ ; (ix)  $-x + 1/2, -y, z - 1/2$ ; (x)  $-y - 1/4, x - 1/4, -z + 1/4$ ; (xi)  $y, z, x$ ; (xii)  $y + 1/4, -x + 3/4, -z + 1/4$ .]

## dineodymium(III) triselenide

### Crystal data

$\text{Nd}_{2.667}\text{Se}_4$

$M_r = 700.48$

Cubic,  $I\bar{4}3d$

Hall symbol: I -4bd 2c 3

$a = 8.8632(6) \text{ \AA}$

$b = 8.8632(6) \text{ \AA}$

$c = 8.8632(6) \text{ \AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 90^\circ$

$V = 696.26(8) \text{ \AA}^3$

$Z = 4$

$F_{000} = 1184$

$D_x = 6.682 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 5000 reflections

$\theta = 1.0\text{--}32.7^\circ$

$\mu = 40.39 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Block, red

$0.03 \times 0.03 \times 0.03 \text{ mm}$

### Data collection

Stoe IPDS-I  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293 \text{ K}$

imaging plate detector system scans

Absorption correction: numerical  
(X-SHAPE; Stoe & Cie, 1999)

$T_{\min} = 0.305, T_{\max} = 0.401$

8964 measured reflections

220 independent reflections

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

$R_{\text{int}} = 0.065$

$\theta_{\max} = 32.7^\circ$

$\theta_{\min} = 5.6^\circ$

$h = -13 \rightarrow 13$

$k = -13 \rightarrow 13$

$l = -13 \rightarrow 13$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.060$

$$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.007$$

$$\Delta\rho_{\max} = 1.01 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\min} = -2.11 \text{ e \AA}^{-3}$$

$S = 1.22$

220 reflections

7 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Extinction correction: SHELXL97 (Sheldrick, 2008),

$F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0086 (7)

Absolute structure: Flack (1983), 92 Friedel pairs

Flack parameter: 0.31 (6)

### 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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Nd	0.3750	0.0000	0.2500	0.0053 (2)	0.89
Se	0.07261 (5)	0.07261 (5)	0.07261 (5)	0.0028 (3)	

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Nd	0.0066 (3)	0.0046 (3)	0.0046 (3)	0.000	0.000	0.000
Se	0.0028 (3)	0.0028 (3)	0.0028 (3)	0.00063 (16)	0.00063 (16)	0.00063 (16)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Nd—Se <sup>i</sup>	2.9675 (5)	Nd—Se	3.1732 (6)
Nd—Se <sup>ii</sup>	2.9675 (5)	Se—Nd <sup>viii</sup>	2.9675 (5)
Nd—Se <sup>iii</sup>	2.9675 (5)	Se—Nd <sup>ix</sup>	2.9675 (5)
Nd—Se <sup>iv</sup>	2.9675 (5)	Se—Nd <sup>x</sup>	2.9675 (5)
Nd—Se <sup>v</sup>	3.1732 (6)	Se—Nd <sup>xi</sup>	3.1732 (6)
Nd—Se <sup>vi</sup>	3.1732 (6)	Se—Nd <sup>xii</sup>	3.1732 (6)
Nd—Se <sup>vii</sup>	3.1732 (6)		
Se <sup>i</sup> —Nd—Se <sup>ii</sup>	91.403 (3)	Se <sup>ii</sup> —Nd—Se	77.283 (2)
Se <sup>i</sup> —Nd—Se <sup>iii</sup>	91.403 (3)	Se <sup>iii</sup> —Nd—Se	87.467 (16)
Se <sup>ii</sup> —Nd—Se <sup>iii</sup>	162.00 (2)	Se <sup>iv</sup> —Nd—Se	67.092 (10)
Se <sup>i</sup> —Nd—Se <sup>iv</sup>	162.00 (2)	Se <sup>v</sup> —Nd—Se	135.510 (1)
Se <sup>ii</sup> —Nd—Se <sup>iv</sup>	91.403 (3)	Se <sup>vi</sup> —Nd—Se	135.510 (1)

## supplementary materials

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Se <sup>iii</sup> —Nd—Se <sup>iv</sup>	91.403 (3)	Se <sup>vii</sup> —Nd—Se	64.738 (1)
Se <sup>i</sup> —Nd—Se <sup>v</sup>	77.284 (2)	Nd <sup>viii</sup> —Se—Nd <sup>ix</sup>	88.609 (17)
Se <sup>ii</sup> —Nd—Se <sup>v</sup>	67.092 (10)	Nd <sup>viii</sup> —Se—Nd <sup>x</sup>	88.609 (17)
Se <sup>iii</sup> —Nd—Se <sup>v</sup>	130.811 (11)	Nd <sup>ix</sup> —Se—Nd <sup>x</sup>	88.609 (17)
Se <sup>iv</sup> —Nd—Se <sup>v</sup>	87.468 (16)	Nd <sup>viii</sup> —Se—Nd <sup>xi</sup>	107.535 (2)
Se <sup>i</sup> —Nd—Se <sup>vi</sup>	87.468 (16)	Nd <sup>ix</sup> —Se—Nd <sup>xi</sup>	162.372 (6)
Se <sup>ii</sup> —Nd—Se <sup>vi</sup>	130.811 (11)	Nd <sup>x</sup> —Se—Nd <sup>xi</sup>	84.849 (2)
Se <sup>iii</sup> —Nd—Se <sup>vi</sup>	67.092 (10)	Nd <sup>viii</sup> —Se—Nd <sup>xii</sup>	162.372 (6)
Se <sup>iv</sup> —Nd—Se <sup>vi</sup>	77.283 (2)	Nd <sup>ix</sup> —Se—Nd <sup>xii</sup>	84.849 (2)
Se <sup>v</sup> —Nd—Se <sup>vi</sup>	64.739 (1)	Nd <sup>x</sup> —Se—Nd <sup>xii</sup>	107.534 (2)
Se <sup>i</sup> —Nd—Se <sup>vii</sup>	67.092 (10)	Nd <sup>xi</sup> —Se—Nd <sup>xii</sup>	81.565 (16)
Se <sup>ii</sup> —Nd—Se <sup>vii</sup>	87.468 (16)	Nd <sup>viii</sup> —Se—Nd	84.849 (2)
Se <sup>iii</sup> —Nd—Se <sup>vii</sup>	77.283 (2)	Nd <sup>ix</sup> —Se—Nd	107.535 (2)
Se <sup>iv</sup> —Nd—Se <sup>vii</sup>	130.810 (11)	Nd <sup>x</sup> —Se—Nd	162.372 (6)
Se <sup>v</sup> —Nd—Se <sup>vii</sup>	135.510 (1)	Nd <sup>xi</sup> —Se—Nd	81.565 (16)
Se <sup>vi</sup> —Nd—Se <sup>vii</sup>	135.510 (1)	Nd <sup>xii</sup> —Se—Nd	81.565 (16)
Se <sup>i</sup> —Nd—Se	130.811 (11)		

Symmetry codes: (i)  $-x+1/2, -y, z+1/2$ ; (ii)  $y+1/4, x+1/4, z+1/4$ ; (iii)  $y+1/4, -x-1/4, -z+1/4$ ; (iv)  $-x+1/2, y, -z$ ; (v)  $-y+3/4, -x+1/4, z+1/4$ ; (vi)  $-y+3/4, x-1/4, -z+1/4$ ; (vii)  $x, -y, -z+1/2$ ; (viii)  $y, -z, -x+1/2$ ; (ix)  $-x+1/2, -y, z-1/2$ ; (x)  $-y-1/4, x-1/4, -z+1/4$ ; (xi)  $y, z, x$ ; (xii)  $y+1/4, -x+3/4, -z+1/4$ .

Fig. 1

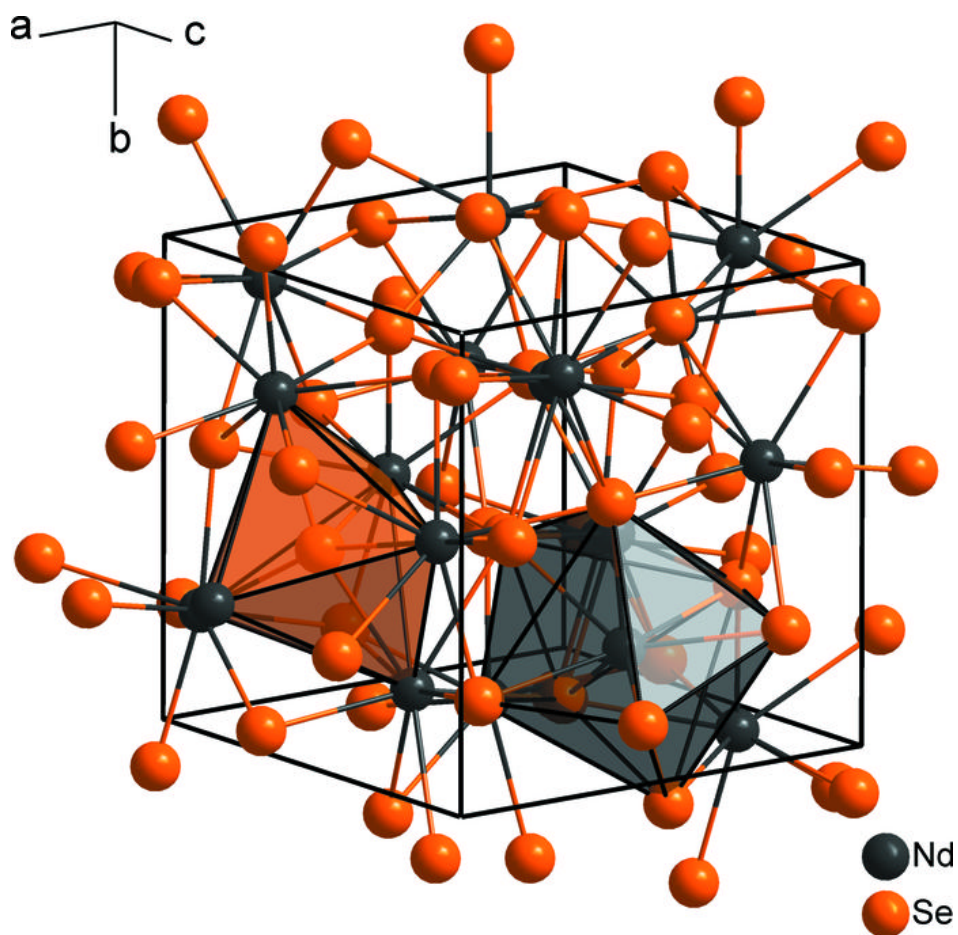


Fig. 2

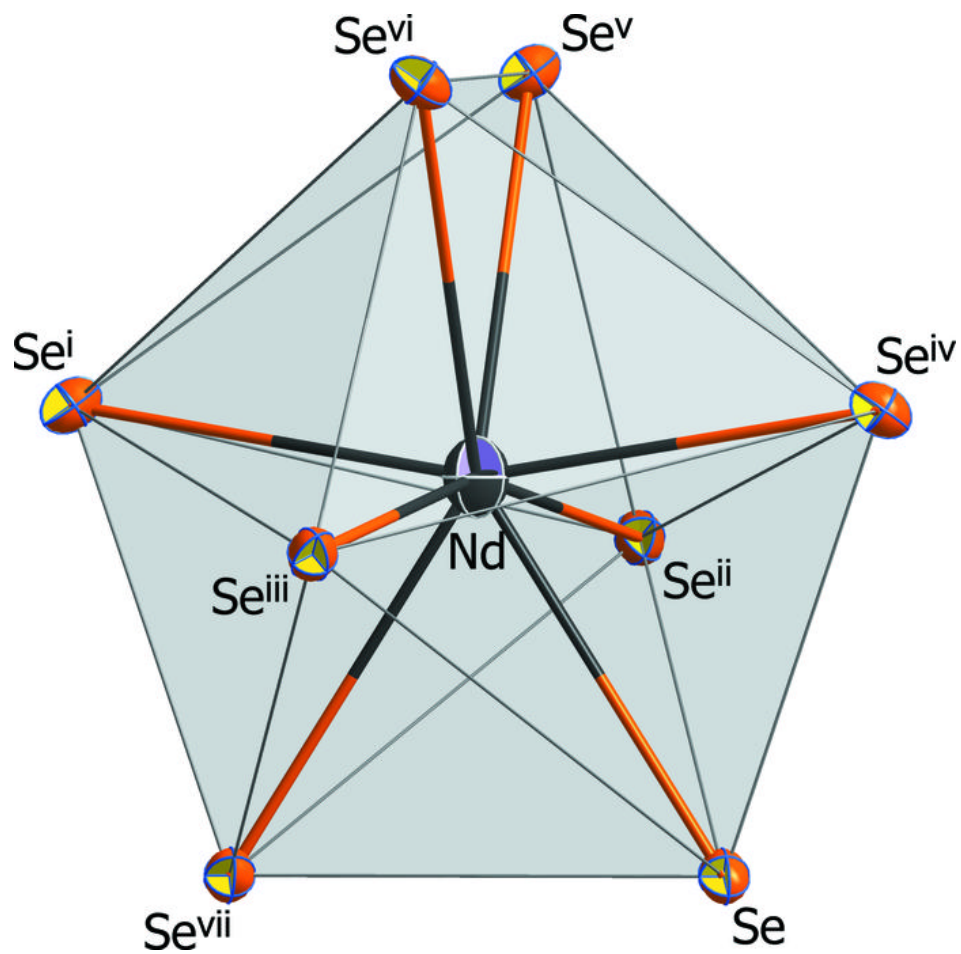




Fig. 3

