

C-type Nd₂Se₃

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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 Th_3P_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 Nd_2Se_3 ($Z = 5.333$), respectively. The Nd^{3+} cations are thus surrounded by eight selenide anions, forming trigonal $[\text{NdSe}_8]^{13-}$ dodecahedra, whereas the 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 Th_3P_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, $I\bar{4}3d$	$\mu = 40.39 \text{ mm}^{-1}$
$a = 8.8632$ (6) Å	$T = 293$ K
$V = 696.26$ (8) Å ³	$0.03 \times 0.03 \times 0.02$ mm

Data collection

Stoe IPDS-I diffractometer
Absorption correction: numerical
(*X-SHAPE*; Stoe & Cie, 1999)
 $T_{\text{min}} = 0.305$, $T_{\text{max}} = 0.401$

8964 measured reflections
220 independent reflections
214 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.065$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.060$
 $S = 1.22$
220 reflections
7 parameters

$\Delta\rho_{\text{max}} = 1.01 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -2.11 \text{ e \AA}^{-3}$
Absolute structure: Flack (1983), 92
Friedel pairs
Flack parameter: 0.31 (6)

Table 1

Selected bond lengths (Å).

Nd–Se ⁱ (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).

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supporting information

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S1. Comment

C-type Nd₂Se₃ (Fig. 1) belongs to a structural family with the cation-defect Th₃P₄-type arrangement (Pardo *et al.*, 1963; Flahaut *et al.*, 1965; Lashkarev & Paderno, 1965) adopted by rare-earth sesquiselenides M₂Se₃ with M = La – Pr and Sm – Lu (Grundmeier & Urland, 1995; Folchnandt, 1997; Folchnandt & Schleid, 2001; Folchnandt *et al.*, 2004) following the general formula M_{2.667}□_{0.333}Se₄. The Nd³⁺ 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 Se²⁻ and unit cell), only 10.667 are allowed to be occupied to realise the composition Nd₂Se₃ (with Z = 5.333, *i.e.* M_{2.667}□_{0.333}Se₄ with Z = 4); these exhibit the coordination number 8 with respect to the selenide anions. The [NdSe₈]¹³⁻ coordination polyhedra can be described as trigonal dodecahedra with $\bar{4}$ -symmetry (Fig. 2). On average, the Se²⁻ anions are surrounded by 5.333 Nd³⁺ cations in a trigonal hemiprism of symmetry .3. with faces rotated 38.2° with respect to each other (Fig. 3).

S2. Experimental

Ruby-red, multifaceted, transparent crystals of Nd₂Se₃ 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.

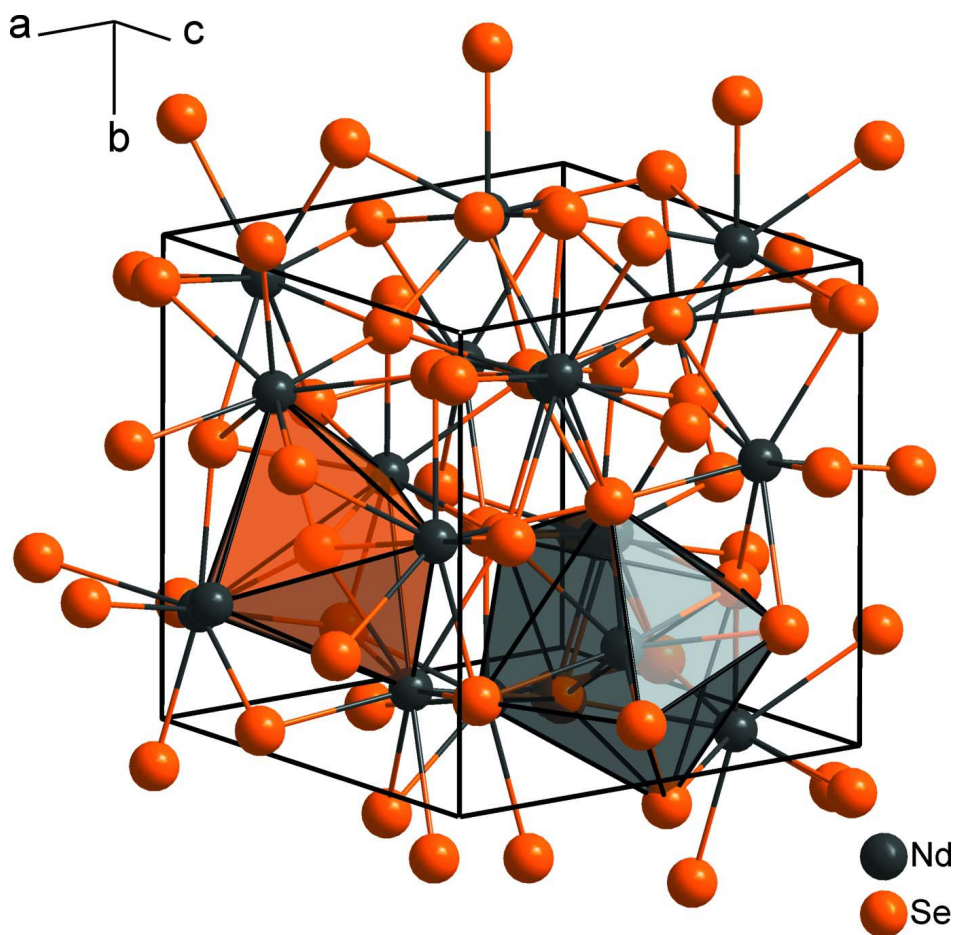


Figure 1
Crystal structure of C-Type Nd_2Se_3 .

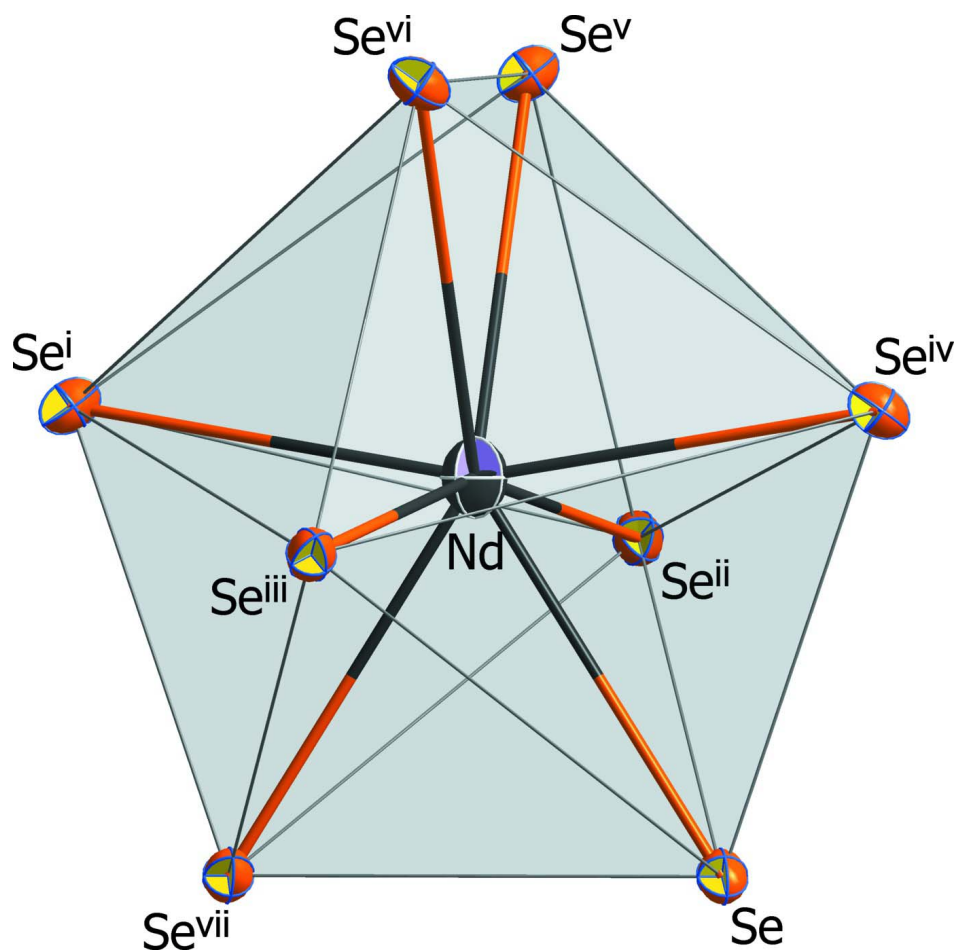


Figure 2

Coordination sphere of the Nd³⁺ 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) $x, -y, -z + 1/2$.]

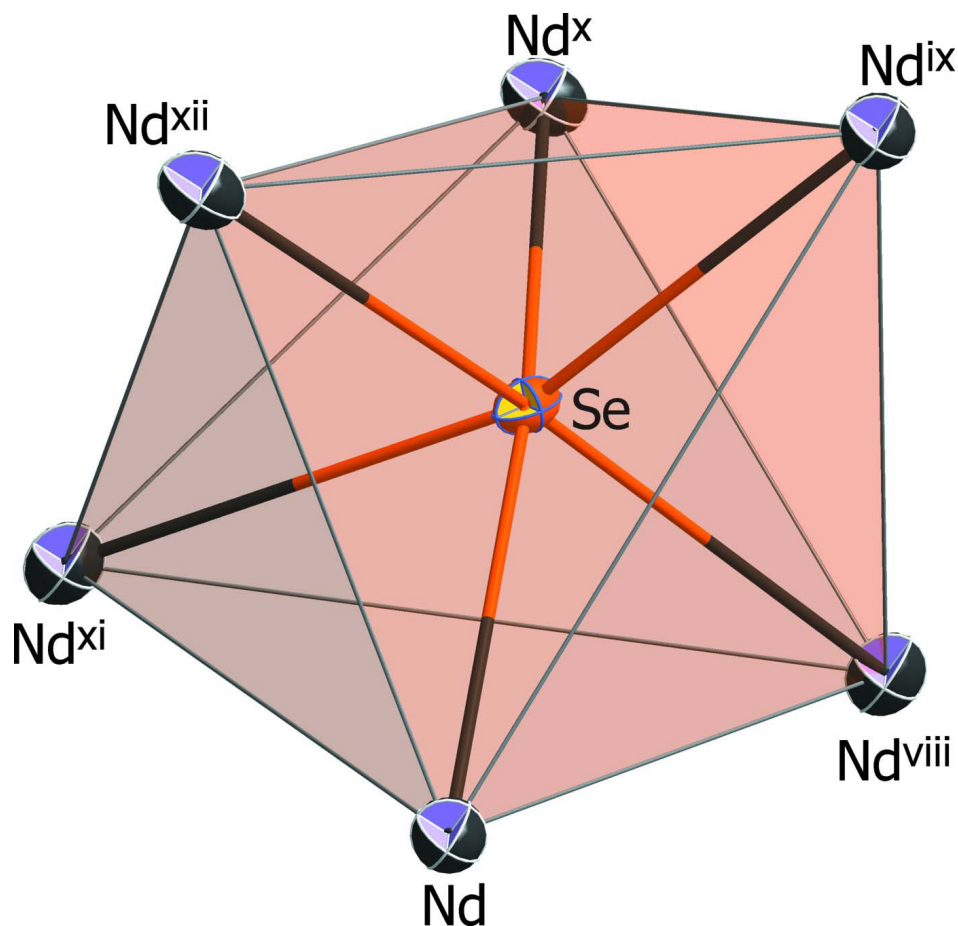


Figure 3

Coordination sphere of the Se^{2-} anion. Due to the under-occupation of the neodymium site, each selenium is surrounded by 5.333 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, $\bar{I}43d$

Hall symbol: I -4bd 2c 3

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

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

$Z = 4$

$F(000) = 1184$

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

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

Graphite monochromator

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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.065$
 $\theta_{\text{max}} = 32.7^\circ$, $\theta_{\text{min}} = 5.6^\circ$

$h = -13 \rightarrow 13$
 $k = -13 \rightarrow 13$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.060$
 $S = 1.22$
 220 reflections
 7 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.007$
 $\Delta\rho_{\text{max}} = 1.01 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -2.11 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0086 (7)
 Absolute structure: Flack (1983), 92 Friedel
 pairs
 Absolute structure 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 (Å^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	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 (Å^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 (Å , $^\circ$)

Nd—Se ⁱ	2.9675 (5)	Nd—Se	3.1732 (6)
Nd—Se ⁱⁱ	2.9675 (5)	Se—Nd ^{viii}	2.9675 (5)
Nd—Se ⁱⁱⁱ	2.9675 (5)	Se—Nd ^{ix}	2.9675 (5)
Nd—Se ^{iv}	2.9675 (5)	Se—Nd ^x	2.9675 (5)
Nd—Se ^v	3.1732 (6)	Se—Nd ^{xi}	3.1732 (6)
Nd—Se ^{vi}	3.1732 (6)	Se—Nd ^{xii}	3.1732 (6)
Nd—Se ^{vii}	3.1732 (6)		
Se ⁱ —Nd—Se ⁱⁱ	91.403 (3)	Se ⁱⁱ —Nd—Se	77.283 (2)

Se ⁱ —Nd—Se ⁱⁱⁱ	91.403 (3)	Se ⁱⁱⁱ —Nd—Se	87.467 (16)
Se ⁱⁱ —Nd—Se ⁱⁱⁱ	162.00 (2)	Se ^{iv} —Nd—Se	67.092 (10)
Se ⁱ —Nd—Se ^{iv}	162.00 (2)	Se ^v —Nd—Se	135.510 (1)
Se ⁱⁱ —Nd—Se ^{iv}	91.403 (3)	Se ^{vi} —Nd—Se	135.510 (1)
Se ⁱⁱⁱ —Nd—Se ^{iv}	91.403 (3)	Se ^{vii} —Nd—Se	64.738 (1)
Se ⁱ —Nd—Se ^v	77.284 (2)	Nd ^{viii} —Se—Nd ^{ix}	88.609 (17)
Se ⁱⁱ —Nd—Se ^v	67.092 (10)	Nd ^{viii} —Se—Nd ^x	88.609 (17)
Se ⁱⁱⁱ —Nd—Se ^v	130.811 (11)	Nd ^{ix} —Se—Nd ^x	88.609 (17)
Se ^{iv} —Nd—Se ^v	87.468 (16)	Nd ^{viii} —Se—Nd ^{xi}	107.535 (2)
Se ⁱ —Nd—Se ^{vi}	87.468 (16)	Nd ^{ix} —Se—Nd ^{xi}	162.372 (6)
Se ⁱⁱ —Nd—Se ^{vi}	130.811 (11)	Nd ^x —Se—Nd ^{xi}	84.849 (2)
Se ⁱⁱⁱ —Nd—Se ^{vi}	67.092 (10)	Nd ^{viii} —Se—Nd ^{xii}	162.372 (6)
Se ^{iv} —Nd—Se ^{vi}	77.283 (2)	Nd ^{ix} —Se—Nd ^{xii}	84.849 (2)
Se ^v —Nd—Se ^{vi}	64.739 (1)	Nd ^x —Se—Nd ^{xii}	107.534 (2)
Se ⁱ —Nd—Se ^{vii}	67.092 (10)	Nd ^{xi} —Se—Nd ^{xii}	81.565 (16)
Se ⁱⁱ —Nd—Se ^{vii}	87.468 (16)	Nd ^{viii} —Se—Nd	84.849 (2)
Se ⁱⁱⁱ —Nd—Se ^{vii}	77.283 (2)	Nd ^{ix} —Se—Nd	107.535 (2)
Se ^{iv} —Nd—Se ^{vii}	130.810 (11)	Nd ^x —Se—Nd	162.372 (6)
Se ^v —Nd—Se ^{vii}	135.510 (1)	Nd ^{xi} —Se—Nd	81.565 (16)
Se ^{vi} —Nd—Se ^{vii}	135.510 (1)	Nd ^{xii} —Se—Nd	81.565 (16)
Se ⁱ —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) $y+1/4, -x+3/4, -z+1/4$.