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A-type Ce_2NCl_3

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{Ce}-\text{Cl}) = 0.002$ Å; R factor = 0.035; wR factor = 0.061; data-to-parameter ratio = 19.2.

Cerium(III) nitride chloride, Ce_2NCl_3 , contains *trans*-edge connected $[\text{N}\text{Ce}_4]^{9+}$ tetrahedra (222 symmetry) forming chains parallel to the c axis that are separated by Cl^- anions. The Ce^{3+} cations (*..m* symmetry) are each surrounded by two N^{3-} and six Cl^- anions in a bicapped trigonal prismatic coordination geometry (CN = 8).

Related literature

For isotypic A-type $M_2\text{NCl}_3$ structures, see: Schurz & Schleid (2009) for La; Uhrlandt & Meyer (1995) for Pr. For a comparison of A-, B-, and C-type structures, see: Schurz & Schleid (2009); Schurz (2011).

Experimental

Crystal data

Ce_2NCl_3	$V = 575.42$ (7) Å ³
$M_r = 400.60$	$Z = 4$
Orthorhombic, <i>Ibam</i>	Mo $K\alpha$ radiation
$a = 13.6021$ (9) Å	$\mu = 16.86$ mm ⁻¹
$b = 6.8903$ (5) Å	$T = 293$ K
$c = 6.1396$ (4) Å	0.19 × 0.14 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer	4016 measured reflections
Absorption correction: numerical	385 independent reflections
(<i>X-SHAPE</i> ; Stoe & Cie, 1999)	329 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.085$, $T_{\max} = 0.198$	$R_{\text{int}} = 0.082$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	20 parameters
$wR(F^2) = 0.061$	$\Delta\rho_{\max} = 1.06$ e Å ⁻³
$S = 1.12$	$\Delta\rho_{\min} = -1.09$ e Å ⁻³
385 reflections	

Table 1

Selected bond lengths (Å).

Ce—N ⁱ	2.3414 (4)	Ce—Cl ⁱ	2.9876 (5)
Ce—N	2.3414 (4)	Ce—Cl ⁱⁱⁱ	2.9876 (5)
Ce—Cl ⁱⁱ	2.873 (3)	Ce—Cl ^{iv}	3.3896 (11)
Ce—Cl ²	2.969 (3)	Ce—Cl ^v	3.3896 (11)

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); 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: MG2121).

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supporting information

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A-type Ce_2NCl_3

Christian M. Schurz and Thomas Schleid

S1. Comment

Lanthanide nitride chlorides $M_2\text{NCl}_3$ adopt A-, B-, or C-type structures (Schurz & Schleid, 2009; Schurz, 2011). Ce_2NCl_3 belongs to the short series of orthorhombic A-type structures formed for $M = \text{La}–\text{Pr}$ (Uhrlandt & Meyer, 1995; Schurz & Schleid, 2009). The structure features *trans*-edge connected $[\text{N}\text{Ce}_4]^{9+}$ tetrahedra (222 symmetry) forming straight infinite chains running parallel to the c -axis (Fig. 1). These chains are bundled in a hexagonal arrangement and are interconnected by $(\text{Cl1})^-$ anions (222 symmetry) along $[110]$ and $[\bar{1}10]$, and by $(\text{Cl2})^-$ anions ($\dots m$ symmetry) along $[010]$ (Fig. 2). Both types of chloride anions show a fourfold surrounding of cerium cations, while the coordination geometry of the trivalent cerium cations ($\dots m$ symmetry) can be described as bicapped trigonal prismatic (CN = 8) with two Ce–N and six Ce–Cl contacts (Fig. 3).

S2. Experimental

Light yellow, transparent, needle-shaped crystals of Ce_2NCl_3 were obtained as the main product after a mixture of 0.06 g Ce, 0.13 g CeCl_3 , and 0.01 g NaN_3 , along with 0.30 g NaCl added as a flux, was heated at 850 °C for 7 days in a sealed, evacuated fused-silica vessel.

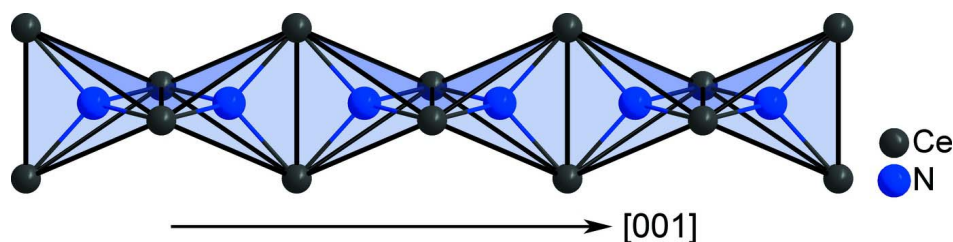


Figure 1

Chains of *trans*-edge connected $[\text{N}\text{Ce}_4]^{9+}$ tetrahedra in A-type Ce_2NCl_3 .

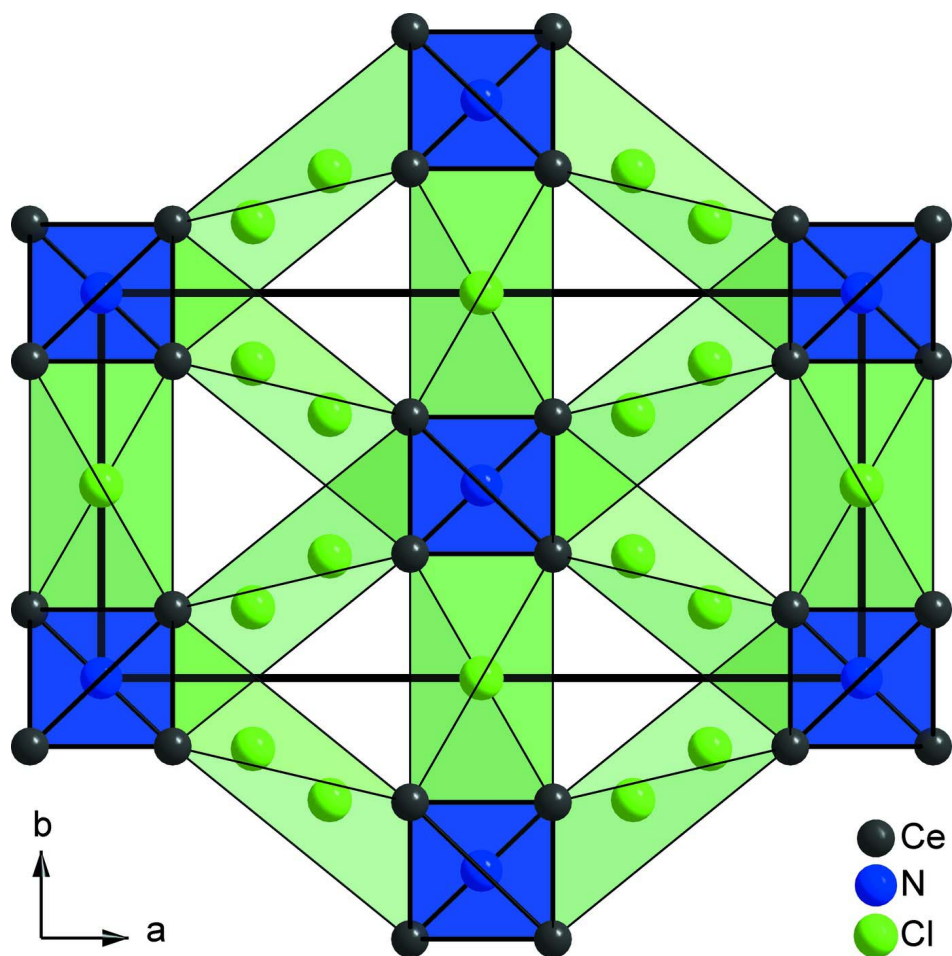


Figure 2
Polyhedral representation of A-type Ce_2NCl_3 .

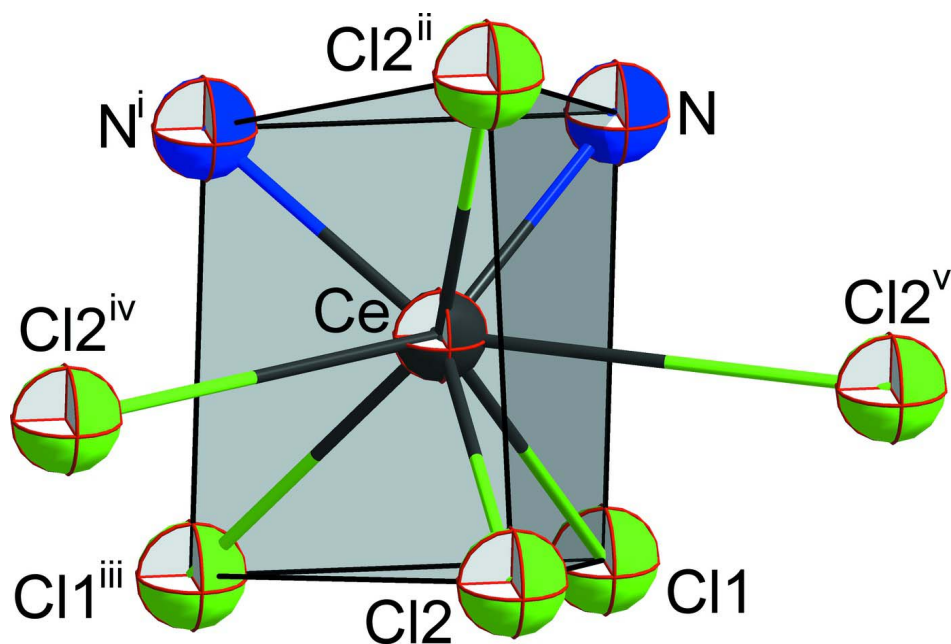


Figure 3

Coordination sphere of Ce atoms in A-type Ce_2NCl_3 . Displacement ellipsoids are drawn at 90% probability level.

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

Cerium(III) nitride trichloride

Crystal data

Ce_2NCl_3

$M_r = 400.60$

Orthorhombic, *Ibam*

Hall symbol: $-1\ 2\ 2c$

$a = 13.6021\ (9)\ \text{\AA}$

$b = 6.8903\ (5)\ \text{\AA}$

$c = 6.1396\ (4)\ \text{\AA}$

$V = 575.42\ (7)\ \text{\AA}^3$

$Z = 4$

$F(000) = 696$

$D_x = 4.624\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71069\ \text{\AA}$

Cell parameters from 19363 reflections

$\theta = 0.4\text{--}28.3^\circ$

$\mu = 16.86\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Needle, light yellow

$0.19 \times 0.14 \times 0.10\ \text{mm}$

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and ϕ scans

Absorption correction: numerical

(*X-SHAPE*; Stoe & Cie, 1999)

$T_{\min} = 0.085, T_{\max} = 0.198$

4016 measured reflections

385 independent reflections

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

$R_{\text{int}} = 0.082$

$\theta_{\max} = 28.1^\circ, \theta_{\min} = 3.0^\circ$

$h = -18 \rightarrow 18$

$k = -9 \rightarrow 9$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.061$
 $S = 1.12$
 385 reflections
 20 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 $w = 1/[\sigma^2(F_o^2) + (0.0169P)^2 + 3.8817P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.06 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.09 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0006 (3)

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	$U_{\text{iso}}^*/U_{\text{eq}}$
Ce	0.09389 (4)	0.17747 (9)	0.0000	0.0243 (3)
N	0.0000	0.0000	0.2500	0.028 (3)
Cl1	0.0000	0.5000	0.2500	0.0330 (8)
Cl2	0.30050 (19)	0.3163 (4)	0.0000	0.0390 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ce	0.0238 (3)	0.0259 (4)	0.0231 (3)	-0.0019 (3)	0.000	0.000
N	0.026 (6)	0.038 (8)	0.022 (6)	0.000	0.000	0.000
Cl1	0.056 (2)	0.0229 (19)	0.0199 (15)	0.000	0.000	0.000
Cl2	0.0319 (14)	0.0361 (15)	0.0489 (15)	-0.0092 (12)	0.000	0.000

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

Ce—N ⁱ	2.3414 (4)	Ce—Ce ^{viii}	3.9934 (7)
Ce—N	2.3414 (4)	Ce—Ce ^{ix}	3.9934 (7)
Ce—Cl2 ⁱⁱ	2.873 (3)	N—Ce ⁱ	2.3414 (4)
Ce—Cl2	2.969 (3)	N—Ce ^{ix}	2.3414 (4)
Ce—Cl1	2.9876 (5)	N—Ce ^{vii}	2.3414 (4)
Ce—Cl1 ⁱⁱⁱ	2.9876 (5)	Cl1—Ce ^x	2.9876 (5)
Ce—Cl2 ^{iv}	3.3896 (11)	Cl1—Ce ^{ix}	2.9876 (5)
Ce—Cl2 ^v	3.3896 (11)	Cl1—Ce ⁱⁱⁱ	2.9876 (5)
Ce—Ce ⁱ	3.5362 (12)	Cl2—Ce ^{xi}	2.873 (3)
Ce—Ce ^{vi}	3.9249 (8)	Cl2—Ce	2.969 (3)

Ce—Ce ^{vii}	3.9249 (8)	Cl2—Ce ^v	3.3896 (11)
N ⁱ —Ce—N	81.923 (19)	Ce ⁱ —Ce—Ce ^{vii}	64.473 (17)
N ⁱ —Ce—Cl2 ⁱⁱ	79.66 (4)	Ce ^{vi} —Ce—Ce ^{vii}	102.91 (3)
N—Ce—Cl2 ⁱⁱ	79.66 (4)	N ⁱ —Ce—Ce ^{viii}	31.484 (13)
N ⁱ —Ce—Cl2	133.21 (3)	N—Ce—Ce ^{viii}	98.92 (2)
N—Ce—Cl2	133.21 (3)	Cl2 ⁱⁱ —Ce—Ce ^{viii}	108.65 (3)
Cl2 ⁱⁱ —Ce—Cl2	78.80 (4)	Cl2—Ce—Ce ^{viii}	127.261 (18)
N ⁱ —Ce—Cl1	119.48 (2)	Cl1—Ce—Ce ^{viii}	96.980 (16)
N—Ce—Cl1	79.545 (12)	Cl1 ⁱⁱⁱ —Ce—Ce ^{viii}	48.061 (9)
Cl2 ⁱⁱ —Ce—Cl1	149.085 (6)	Ce ⁱ —Ce—Ce ^{viii}	62.486 (16)
Cl2—Ce—Cl1	99.49 (5)	Ce ^{vi} —Ce—Ce ^{viii}	53.041 (12)
N ⁱ —Ce—Cl1 ⁱⁱⁱ	79.545 (12)	Ce ^{vii} —Ce—Ce ^{viii}	126.959 (11)
N—Ce—Cl1 ⁱⁱⁱ	119.48 (2)	N ⁱ —Ce—Ce ^{ix}	98.92 (2)
Cl2 ⁱⁱ —Ce—Cl1 ⁱⁱⁱ	149.085 (6)	N—Ce—Ce ^{ix}	31.484 (13)
Cl2—Ce—Cl1 ⁱⁱⁱ	99.49 (5)	Cl2 ⁱⁱ —Ce—Ce ^{ix}	108.65 (3)
Cl1—Ce—Cl1 ⁱⁱⁱ	61.829 (12)	Cl2—Ce—Ce ^{ix}	127.261 (18)
N ⁱ —Ce—Ce ⁱ	40.961 (9)	Cl1—Ce—Ce ^{ix}	48.061 (9)
N—Ce—Ce ⁱ	40.961 (9)	Cl1 ⁱⁱⁱ —Ce—Ce ^{ix}	96.980 (16)
Cl2 ⁱⁱ —Ce—Ce ⁱ	76.24 (6)	Ce ⁱ —Ce—Ce ^{ix}	62.486 (15)
Cl2—Ce—Ce ⁱ	155.05 (6)	Ce ^{vi} —Ce—Ce ^{ix}	126.959 (11)
Cl1—Ce—Ce ⁱ	101.87 (2)	Ce ^{vii} —Ce—Ce ^{ix}	53.041 (11)
Cl1 ⁱⁱⁱ —Ce—Ce ⁱ	101.87 (2)	Ce ^{viii} —Ce—Ce ^{ix}	100.48 (2)
N ⁱ —Ce—Ce ^{vi}	33.054 (12)	Ce ⁱ —N—Ce ^{ix}	113.89 (2)
N—Ce—Ce ^{vi}	100.80 (2)	Ce ⁱ —N—Ce ^{vii}	117.03 (3)
Cl2 ⁱⁱ —Ce—Ce ^{vi}	57.34 (2)	Ce ^{ix} —N—Ce ^{vii}	98.077 (19)
Cl2—Ce—Ce ^{vi}	101.59 (3)	Ce ⁱ —N—Ce	98.077 (19)
Cl1—Ce—Ce ^{vi}	149.920 (11)	Ce ^{ix} —N—Ce	117.03 (3)
Cl1 ⁱⁱⁱ —Ce—Ce ^{vi}	93.536 (8)	Ce ^{vii} —N—Ce	113.89 (2)
Ce ⁱ —Ce—Ce ^{vi}	64.473 (17)	Ce ^x —Cl1—Ce ^{ix}	118.171 (12)
N ⁱ —Ce—Ce ^{vii}	100.80 (2)	Ce ^x —Cl1—Ce ⁱⁱⁱ	83.877 (19)
N—Ce—Ce ^{vii}	33.054 (12)	Ce ^{ix} —Cl1—Ce ⁱⁱⁱ	129.39 (2)
Cl2 ⁱⁱ —Ce—Ce ^{vii}	57.34 (2)	Ce ^x —Cl1—Ce	129.39 (2)
Cl2—Ce—Ce ^{vii}	101.59 (3)	Ce ^{ix} —Cl1—Ce	83.877 (19)
Cl1—Ce—Ce ^{vii}	93.536 (8)	Ce ⁱⁱⁱ —Cl1—Ce	118.171 (13)
Cl1 ⁱⁱⁱ —Ce—Ce ^{vii}	149.920 (11)	Ce ^{xi} —Cl2—Ce	138.81 (11)

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