Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

A-type Ce_2NCl_3

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Received 24 May 2011; accepted 14 June 2011

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(Ce–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 $[NCe_4]^{9+}$ 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_2NCl_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, *Ibam*	Mo $K\alpha$ radiation
a = 13.6021 (9) Å	μ = 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 (*X-SHAPE*; Stoe & Cie, 1999)	385 independent reflections
T_{min} = 0.085, T_{max} = 0.198	329 reflections with $I > 2\sigma(I)$
	R_{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—Cl1	2.9876 (5)
Ce—N	2.3414 (4)	Ce—Cl1^{iii}	2.9876 (5)
Ce—Cl2^{ii}	2.873 (3)	Ce—Cl2^{iv}	3.3896 (11)
Ce—Cl2	2.969 (3)	Ce—Cl2^{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*.

This work was supported by the State of Baden-Württemberg (Stuttgart) and the Deutsche Forschungsgemeinschaft (DFG; Frankfurt/Main). We thank Dr Falk Lissner for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: MG2121).

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supplementary materials

Acta Cryst. (2011). E**67**, i42 [**doi:10.1107/S1600536811023105**]

A-type Ce_2NCl_3

C. M. Schurz and **T. Schleid**

Comment

Lanthanide nitride chlorides M_2NCl_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 = La–Pr (Uhrlandt & Meyer, 1995; Schurz & Schleid, 2009). The structure features *trans*-edge connected $[NCe_4]^{9+}$ 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 $(Cl1)^-$ anions (222 symmetry) along [110] and [$\bar{1}$10], and by $(Cl2)^-$ anions (..*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 (..*m* symmetry) can be described as bicapped trigonal prismatic (CN = 8) with two Ce–N and six Ce–Cl contacts (Fig. 3).

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.

Figures

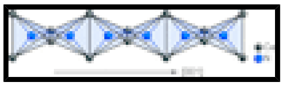

Fig. 1. Chains of *trans*-edge connected $[NCe_4]^{9+}$ tetrahedra in A-type Ce_2NCl_3.

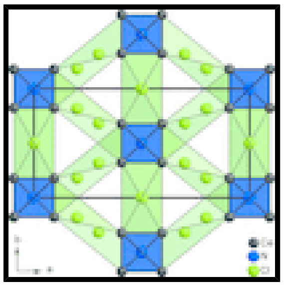

Fig. 2. Polyhedral representation of A-type Ce_2NCl_3.

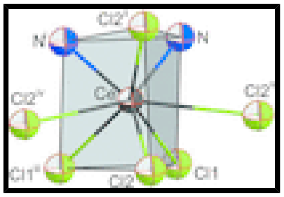

Fig. 3. Coordination sphere of Ce atoms in A-type Ce_2NCl_3. Displacement ellipsoids are drawn at 90% probability level. Symmetry codes: (i) -*x*, -*y*, -*z*; (ii) -*x* + 1/2, *y* - 1/2, *z*; (iii) -*x*, -*y* + 1, -*z*; (iv) -*x* + 1/2, -*y* + 1/2, -*z* + 1/2; (v) -*x* + 1/2, -*y* + 1/2, *z* + 1/2.

Cerium(III) nitride trichloride

Crystal data

Ce_2NCl_3

$M_r = 400.60$

Orthorhombic, *Ibam*

Hall symbol: -I 2 2c

$a = 13.6021\ (9)$ Å

$b = 6.8903\ (5)$ Å

$c = 6.1396\ (4)$ Å

$V = 575.42\ (7)$ Å^3

$Z = 4$

$F(000) = 696$

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

Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å

Cell parameters from 19363 reflections

$\theta = 0.4$–$28.3°$

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

$T = 293$ K

Needle, light yellow

0.19 × 0.14 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer

Radiation source: fine-focus sealed tube

graphite

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 $I > 2\sigma(I)$

$R_{int} = 0.082$

$\theta_{max} = 28.1°$, $\theta_{min} = 3.0°$

$h = -18 \rightarrow 18$

$k = -9 \rightarrow 9$

$l = -8 \rightarrow 8$

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 $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 1.06$ e Å^{-3}

$\Delta\rho_{min} = -1.09$ e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

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 (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
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 (Å^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 (Å, °)

Ce—N$^{\rm i}$	2.3414 (4)	Ce—Ce$^{\rm viii}$	3.9934 (7)
Ce—N	2.3414 (4)	Ce—Ce$^{\rm ix}$	3.9934 (7)
Ce—Cl2$^{\rm ii}$	2.873 (3)	N—Ce$^{\rm i}$	2.3414 (4)
Ce—Cl2	2.969 (3)	N—Ce$^{\rm ix}$	2.3414 (4)
Ce—Cl1	2.9876 (5)	N—Ce$^{\rm vii}$	2.3414 (4)
Ce—Cl1$^{\rm iii}$	2.9876 (5)	Cl1—Ce$^{\rm x}$	2.9876 (5)
Ce—Cl2$^{\rm iv}$	3.3896 (11)	Cl1—Ce$^{\rm ix}$	2.9876 (5)
Ce—Cl2$^{\rm v}$	3.3896 (11)	Cl1—Ce$^{\rm iii}$	2.9876 (5)
Ce—Ce$^{\rm i}$	3.5362 (12)	Cl2—Ce$^{\rm xi}$	2.873 (3)
Ce—Ce$^{\rm vi}$	3.9249 (8)	Cl2—Ce	2.969 (3)
Ce—Ce$^{\rm vii}$	3.9249 (8)	Cl2—Ce$^{\rm v}$	3.3896 (11)
N$^{\rm i}$—Ce—N	81.923 (19)	Ce$^{\rm i}$—Ce—Ce$^{\rm vii}$	64.473 (17)
N$^{\rm i}$—Ce—Cl2$^{\rm ii}$	79.66 (4)	Ce$^{\rm vi}$—Ce—Ce$^{\rm vii}$	102.91 (3)
N—Ce—Cl2$^{\rm ii}$	79.66 (4)	N$^{\rm i}$—Ce—Ce$^{\rm viii}$	31.484 (13)
N$^{\rm i}$—Ce—Cl2	133.21 (3)	N—Ce—Ce$^{\rm viii}$	98.92 (2)
N—Ce—Cl2	133.21 (3)	Cl2$^{\rm ii}$—Ce—Ce$^{\rm viii}$	108.65 (3)
Cl2$^{\rm ii}$—Ce—Cl2	78.80 (4)	Cl2—Ce—Ce$^{\rm viii}$	127.261 (18)
N$^{\rm i}$—Ce—Cl1	119.48 (2)	Cl1—Ce—Ce$^{\rm viii}$	96.980 (16)
N—Ce—Cl1	79.545 (12)	Cl1$^{\rm iii}$—Ce—Ce$^{\rm viii}$	48.061 (9)
Cl2$^{\rm ii}$—Ce—Cl1	149.085 (6)	Ce$^{\rm i}$—Ce—Ce$^{\rm viii}$	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) $-x+1/2, y+1/2, z$.

Fig. 1

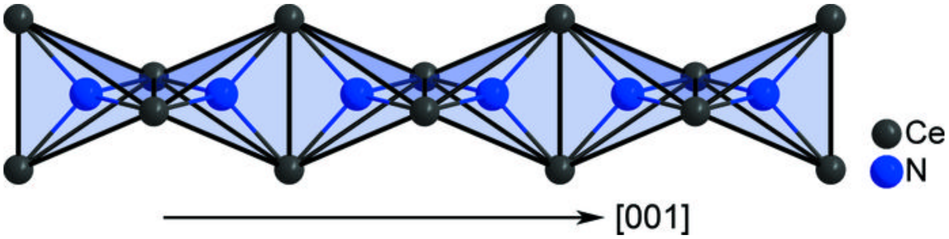

Fig. 2

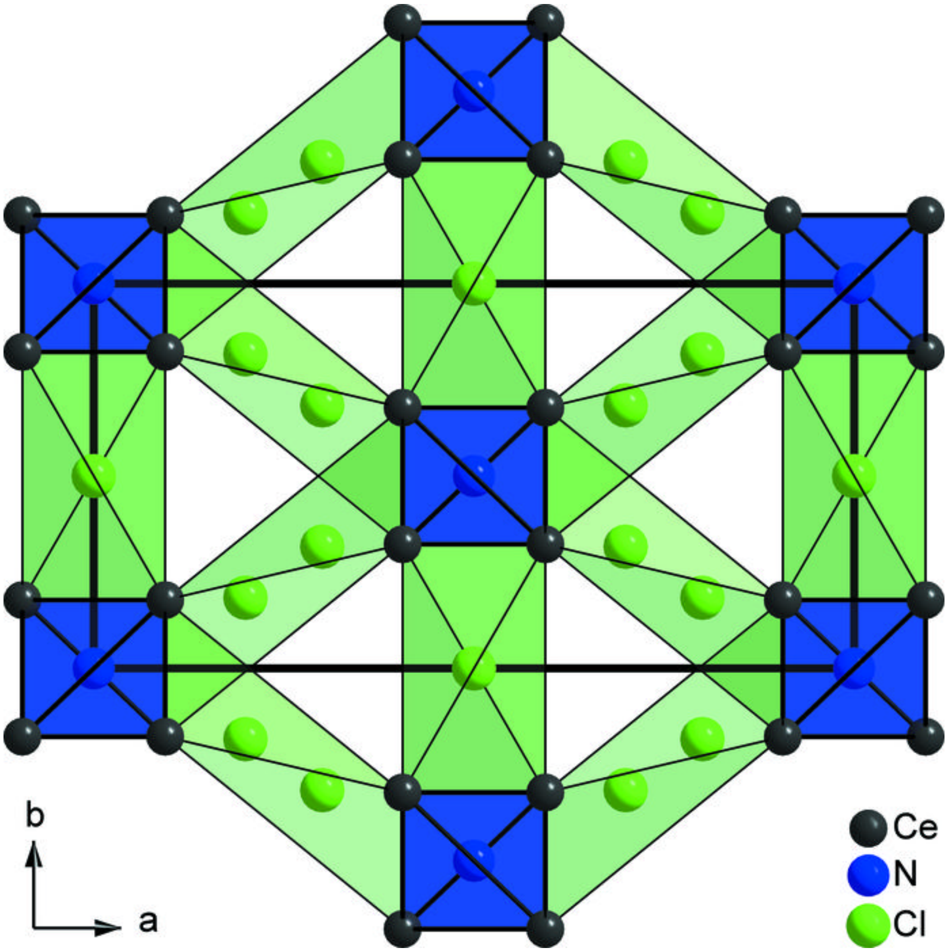

Fig. 3