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β-Strontium carbodiimide

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(N–C) = 0.005 Å
R factor = 0.017
wR factor = 0.041
Data-to-parameter ratio = 12.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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Colourless single crystals of β-SrNCN were grown from reactive iodide/cyanide/azide fluxes in tantalum containers and structurally characterized by X-ray diffraction. Trigonal β-SrNCN is isotypic with CaNCN and contains alternating layers of strontium cations and linear NCN^{2-} anions oriented perpendicular to the layers. The Sr cations are octahedrally coordinated by carbodiimide N atoms, with Sr—N = 2.623 (2) Å and C═N = 1.232 (5) Å. Sr, C and N atoms have site symmetries of $\bar{3}m$, $\bar{3}m$ and $3m$, respectively.

Comment

At present, two polymorphs of strontium carbodiimide have been reported and they were synthesized using markedly different routes. While single crystals of α-SrNCN were obtained from the reaction of melamine with the metal nitride (Berger & Schnick, 1994), polycrystalline β-SrNCN has been synthesized *via* ammonolysis of $SrCO_3$ at 923 K (Wißmann, 2001). We present here an alternative synthesis of β-SrNCN, resulting in single crystals, and its structure refinement from X-ray diffraction data.

The new route, targeted at the syntheses of various metal cyanamides/carbodiimides, is based on reactive fluxes of the metal halides, sodium cyanide and sodium azide (Liao, Hu *et al.*, 2004; Liao, von Appen & Dronskowski, 2004). Not too surprisingly, both the thermal conditions and nature of the halogen atom play a decisive role for product formation. As a precursor, SrI_2 must be used throughout, but a reaction temperature of 1153 K is needed for synthesizing α-SrNCN, whereas β-SrNCN is obtained at 1073 K. The two polymorphs are then obtained in the form of single crystals.

β-SrNCN crystallizes in the trigonal system and is isostructural with CaNCN (Vannerberg, 1962). Thus, the essential structural feature of β-SrNCN is alternating layers of strontium cations and linear NCN^{2-} anions oriented perpendicular to the metal layers (Fig. 1). All strontium cations are located in layers parallel to the *ab* plane, separated by the NCN^{2-} anions. Similar layer structures are also observed for $Ln_2O_2(NCN)$ (Ln = Ce–Gd; Hashimoto *et al.*, 1996), but the layers in the latter compound are composed of Ln^{3+} cations and oxygen anions, resulting in a layer stoichiometry of $(Ln_2O_2)^{2+}$.

Sr, C and N atoms have site symmetries of $\bar{3}m$, $\bar{3}m$ and $3m$, respectively. The strontium cation is surrounded octahedrally by six NCN^{2-} anions, with an Sr—N distance of 2.623 (2) Å (Table 1). The N—C—N bond lengths and angle [1.232 (5) Å and 180° due to space-group symmetry] are characteristic for a $D_{\infty h}$-shaped NCN^{2-} unit containing two N═C double bonds. These linear anions are oriented parallel to the *c* axis and separate the layers of metal cations. Compared with α-SrNCN,

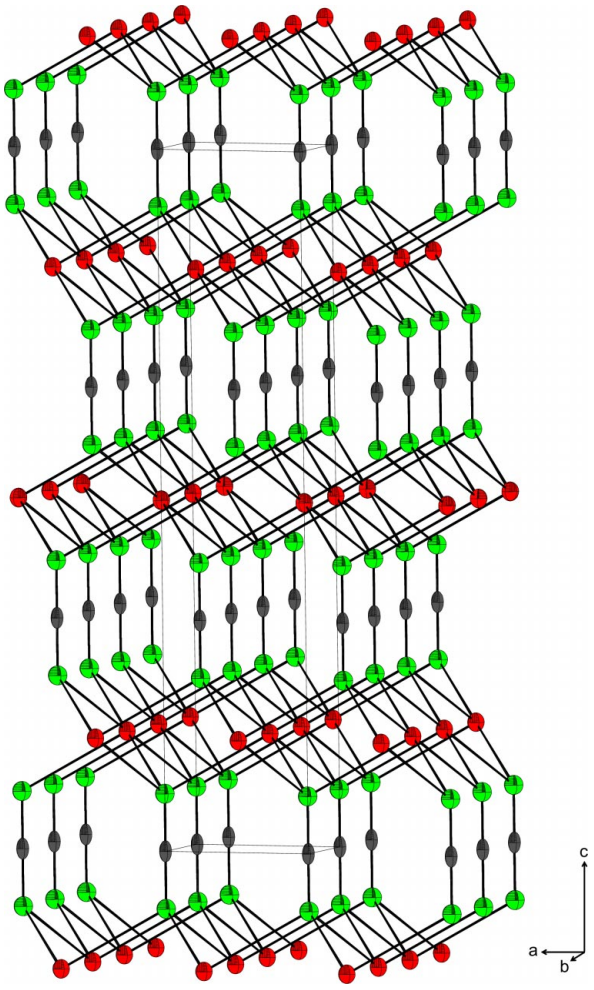

Figure 1
Unit-cell packing in β-SrNCN, with displacement ellipsoids shown at the 50% probability level. Key: Sr atoms red, N atoms green and C atoms grey.

all the averaged interatomic distances are identical within experimental error, but the local symmetry of strontium (approximate octahedral coordination) is slightly lower in the orthorhombic α-phase.

Experimental

Single crystals of β-SrNCN were synthesized following a reported route (Liao, Hu *et al.*, 2004; Liao, von Appen & Dronskowski, 2004). β–SrNCN is obtained upon heating reactive fluxes of SrI_2, NaCN and NaN_3 (2:1:1 ratio) in a tantalum container to 1073 K, followed by slow cooling (6 K min^{-1}) to room temperature. An analogous procedure using the same educts but with a 1:1:1 stoichiometric ratio and a maximum temperature of 1153 K leads to the formation of α–SrNCN.

Crystal data

$SrCN_2$
M_r = 127.65
Trigonal, $R\bar{3}m$
a = 3.9732 (5) Å
c = 15.028 (3) Å
V = 205.45 (5) Å^3
Z = 3
D_x = 3.095 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 893 reflections
θ = 4.1–30.3°
μ = 19.39 mm^{-1}
T = 293 (2) K
Block, colourless
0.08 × 0.06 × 0.06 mm

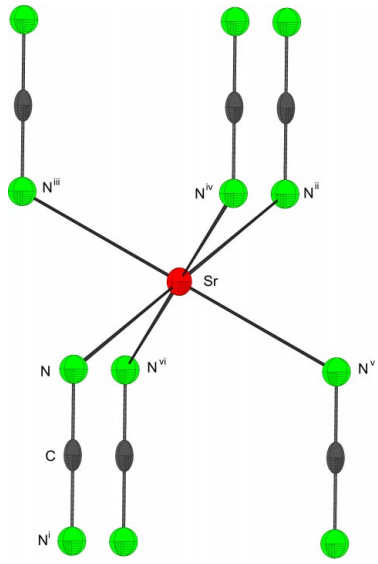

Figure 2
The octahedral Sr atom environment in β-SrNCN. [Symmetry codes: (i) $-x, -y, -z$; (ii) $\frac{2}{3}-x, \frac{4}{3}-y, \frac{1}{3}-z$; (iii) $-\frac{1}{3}-x, \frac{1}{3}-y, \frac{1}{3}-z$; (iv) $\frac{2}{3}-x, \frac{1}{3}-y, \frac{1}{3}-z$; (v) $1+x, 1+y, z$; (vi) $x, 1+y, z$.]

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.246, T_{max} = 0.312
893 measured reflections
97 independent reflections
97 reflections with $I > 2\sigma(I)$
R_{int} = 0.069
θ_{max} = 30.3°
$h = -5 \rightarrow 5$
$k = -5 \rightarrow 5$
$l = -20 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.041
S = 1.07
97 reflections
8 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0153P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sr—N	2.623 (2)	N—C	1.232 (5)
N^{vi}—Sr—N	98.45 (11)	C—N—Sr^{vii}	119.02 (9)
N^{vi}—Sr—N^{iv}	180	Sr^{vii}—N—Sr	98.45 (11)
N—Sr—N^{iv}	81.55 (11)	N^{i}—C—N	180

Symmetry codes: (vi) $x, 1+y, z$; (iv) $\frac{2}{3}-x, \frac{1}{3}-y, \frac{1}{3}-z$; (vii) $x, y-1, z$; (i) $-x, -y, -z$.

The refinement used the atomic coordinates of CaNCN (Vannerberg, 1962) as a starting model, with Sr replacing Ca.

Data collection: *SMART* (Bruker, 1999–2001); cell refinement: *SMART*; data reduction: *SAINT–Plus* (Bruker, 1999–2001); method used to solve structure: atomic coordinates of CaNCN (Vannerberg, 1962) used; program(s) used to refine structure: *SHELXTL* (Sheldrick, 1998); molecular graphics: *ATOMS* (Dowty, 2002); software used to prepare material for publication: *SHELXTL*.

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