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Calcium nitride (Ca_2N), a redetermination

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(Ca–N) = 0.0003 Å
R factor = 0.017
wR factor = 0.038
Data-to-parameter ratio = 14.9

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

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Ca_2N adopts the anti-$CdCl_2$ structure in which two sheets of calcium ions enclose a sheet of N^{3-} ions, with each calcium bonded to three N^{3-} at 2.4500 (3) Å and each nitrogen octahedrally coordinated by six calciums. Within one calcium sheet, each metal has three others at 3.2944 (8) Å and a further six at 3.6271 (3) Å. The distance between two calcium layers with no intervening nitrogen layer is 4.3221 (6) Å, and this intervening region contains no observable electron density. Neutron and X-ray powder diffraction studies have shown that the c-axis dimension changes with the synthetic method employed. In the single-crystal, c is significantly lower, reflecting the higher temperature employed in its formation.

Comment

There is considerable interest in the A_2N nitrides of the Group 2 elements due to their unusual formal oxidation state and electrical properties. A previous crystal structure determination (Keve & Skapski, 1968) showed the major features of the Ca_2N structure but could not be completed as the crystals were lost. We have repeated the determination on high quality crystals obtained from an unusual preparative route. Single crystals of Ca_2N were prepared by firstly reacting calcium metal dissolved in an excess of liquid sodium with a positive pressure of nitrogen gas at 723 K for 3 d. The excess sodium was removed by vacuum distillation at 973 K and 10^{-5} Torr leaving a polycrystalline product. The product was then heated at 1393 K for 5 d in a stainless steel crucible lined with cobalt foil and welded shut in an argon atmosphere. Single crystals of the air-sensitive Ca_2N were removed from the crucible in a high-integrity, nitrogen-filled glove-box (O_2 content < 2 p.p.m., H_2O content < 5 p.p.m.) and placed in RS3000 perfluoropolyether for mounting on the diffractometer.

Ca_2N has the anti-$CdCl_2$ structure in which two sheets of calcium ions enclose a sheet of N^{3-} ions and each calcium is bonded to three N^{3-} ions at 2.4500 (3) Å. Each nitrogen is octahedrally coordinated by calciums. Within the layer each calcium has three calcium ions at 3.2944 (8) Å and a further six at 3.6271 (3) Å. The distance between two calcium layer with no intervening nitrogen layers is 4.3221 (6) Å, and this intervening region contains no observable electron density. Neutron and X-ray powder diffraction studies (Gregory *et al.*, 2000) have shown that the c-axis dimension changes according to the synthetic method used: the c dimension of the single-crystal was significantly lower than those of the powders, reflecting the higher temperature employed in the formation of the single crystals.

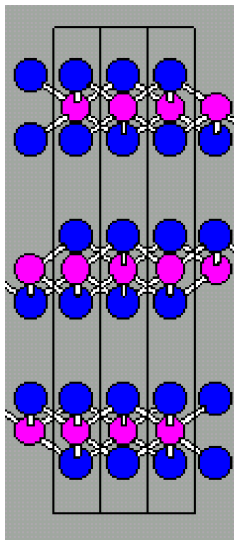

Figure 1
A view of the crystal structure of Ca_2N showing the layer lattice (Ca blue spheres; N pink spheres). The figure was produced using *ATOMS* (Dowty, 1998).

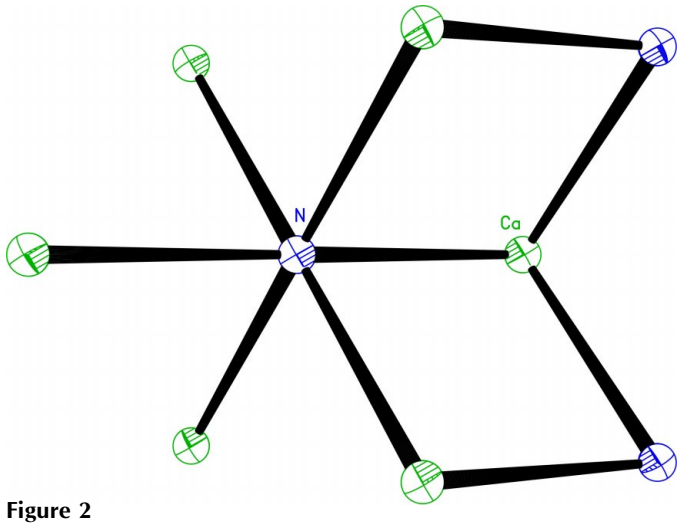

Figure 2
A view showing the atom labelling and the immediate coordination around Ca and N. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Synthetic details are given in the *Comment* section.

Crystal data

Ca_2N
M_r = 94.17
Trigonal, $R\bar{3}m$
a = 3.6271 (3) Å
c = 18.972 (2) Å
V = 216.15 (3) Å^3
Z = 3
D_x = 2.170 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 49 reflections
θ = 12.5–16.5°
μ = 3.61 mm^{-1}
T = 298 (2) K
Sphenoid, dark red
0.24 × 0.16 × 0.16 mm

Data collection

Stoe Stadi-4 four-circle diffractometer
ω/θ scans
Absorption correction: ψ scan (*X-RED*; Stoe & Cie, 1997)
T_{min} = 0.574, T_{max} = 0.652
864 measured reflections
104 independent reflections
99 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 29.9°
$h = -5 \rightarrow 5$
$k = -5 \rightarrow 5$
$l = -25 \rightarrow 25$
3 standard reflections
frequency: 60 min
random variation ±1.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.038
S = 1.28
104 reflections
7 parameters
$w = 1/[\sigma^2(F_o^2) + 0.28P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.063 (8)

Table 1
Selected geometric parameters (Å).

Ca—N	2.4500 (3)	Ca—Ca^{ii}	3.6271 (3)
Ca—Ca^{i}	3.2944 (8)	Ca—Ca^{iii}	4.3221 (6)

Symmetry codes: (i) $\frac{7}{3} - x, \frac{8}{3} - y, \frac{2}{3} - z$; (ii) $x, y - 1, z$; (iii) $\frac{5}{3} - x, \frac{4}{3} - y, \frac{1}{3} - z$.

There were no unusual aspects to the structure analysis.

Data collection: *STADI*4 (Stoe & Cie, 1997); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1997); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2000).

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