inorganic compounds

Ba$_{14}$Cu$_2$In$_4$N$_7$, a new subnitride with isolated nitridocuprate groups and indium clusters

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Single crystals of Ba$_{14}$Cu$_2$In$_4$N$_7$, tetradecabarium dicopper tetraindium heptanitride, were synthesized by slow cooling from 1023 K at 7 MPa of N$_2$ using an Na flux. The compound crystallizes in the monoclinic space group $P2/m$ with $Z = 2$, and contains ^{0}[CuN$_2$] nitridocuprate units and distorted ^{0}[In$_4$] clusters. One Ba atom, not connected to any N atoms, is surrounded by 12 other Ba atoms in a barium cuboctahedron. The structural formula is expressed as (Ba)Ba$_{27}$N$_6$[CuN$_2$]$_4$-[In$_4$]$_2$.

Comment

Some ternary compounds containing nitride polyanions and Zintl anions, such as Ca$_4$In$_2$N and Sr$_4$In$_2$N (Cordier & Rönninger, 1987), Ba$_3$Ge$_2$N$_2$ (Yamane & DiSalvo, 1996), and Sr$_6$Ga$_5$N and Ga$_6$Ga$_5$N (Cordier *et al.*, 1995), have been reported. Recently, we prepared single crystals of a new quaternary compound, Ba$_8$Cu$_3$In$_4$N$_5$, by the Na flux method from a starting melt with a Ba:Cu:In:Na molar ratio of 2:1:1:6 (Yamane *et al.*, 2002). The crystal structure analysis revealed the presence of nitridocuprates of one-dimensional chains, $^1_\infty$[CuN$_{2/2}$], isolated units, ^{0}[CuN$_2$], and one-dimensional indium clusters, $^1_\infty$[In$_2$In$_{4/2}$]. The new title compound, Ba$_{14}$Cu$_2$In$_4$N$_7$, was prepared from a Ba-rich melt (Ba:Cu:In:Na = 6:1:1:6).
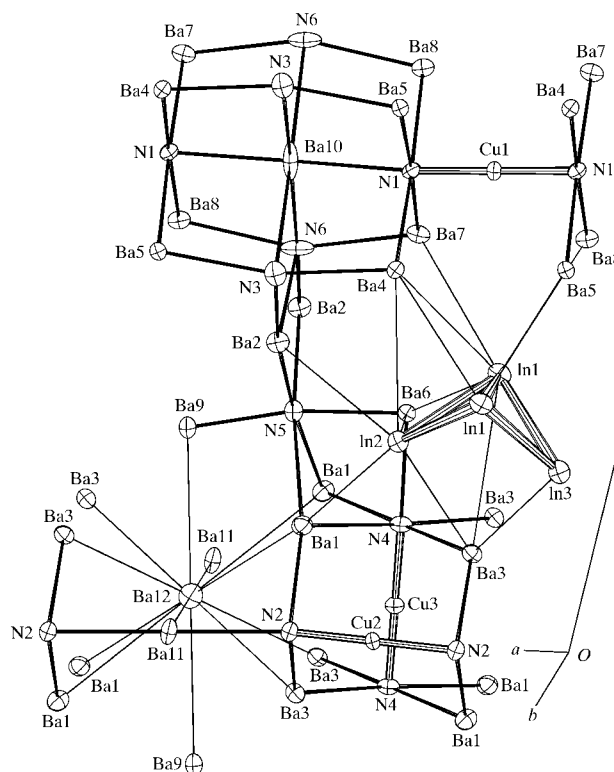
The crystal structure of Ba$_{14}$Cu$_2$In$_4$N$_7$ is shown in Fig. 1. The Ba atoms, except that at the Ba12 site, coordinate with N atoms. Atom Ba9 connects to one N atom (N5), with Ba9—N5 = 2.466 (11) Å, which is the shortest Ba—N distance in Ba$_{14}$Cu$_2$In$_4$N$_7$. A similar short Ba—N interatomic distance was reported for the Ba atom bonded to one N atom in the subnitrides Na$_8$Ba$_{14}$CaN$_6$ [2.463 (3) Å; Vajenine *et al.*, 1999] and Na$_7$Ba$_{14}$CaN$_6$ [2.43 (3) Å; Vajenine & Simon, 2001].

Atoms Ba3, Ba6 and Ba11 are each coordinated to two N atoms. The Ba6—N4 and Ba6—N5 bond lengths are 2.582 (12) and 2.586 (11) Å, respectively, while the Ba3—N and Ba11—N bond lengths are in the range 2.701 (8)–2.787 (8) Å. Atoms Ba1, Ba2, Ba4, Ba5, Ba7 and Ba8 are coordinated to three N atoms, with Ba—N distances in the range 2.662 (9)–2.993 (10) Å. Atom Ba10 is surrounded by six N atoms, with Ba—N distances in the range 2.775 (7)–3.074 (11) Å.

Atom Ba12 is situated in a metal polyhedron (cuboctahedron) of 12 Ba atoms. The interatomic distances between Ba12 and the other Ba atoms are in the range 3.7654 (8)–4.0045 (8) Å, and these are shorter than the Ba—Ba distance in barium metal (Hirst *et al.*, 1956) and close to the Ba—Ba distances observed in BaCuN [$\geq$ 3.747 (2) Å] and Ba$_{16}$[(CuN)$_8$][Cu$_2$N$_3$][Cu$_3$N$_4$] [$\geq$ 3.694 (3) Å] (Niewa & DiSalvo, 1998).

The Cu atoms are linearly coordinated to two N atoms. The N1—Cu1—N1 unit is directed along the *a* axis, while the N2—Cu2—N2 and N4—Cu3—N4 units align alternately along the *b* axis in the directions of the *a* and *c* axes, respectively. The Cu—N distances are in the range 1.890 (7)–1.906 (10) Å. These values are consistent with the Cu—N distance of the N—Cu—N units in Sr$_6$[Cu$_2$N$_3$][CuN$_2$] [1.86 (2) Å; DiSalvo *et al.*, 1997] and Ba$_8$Cu$_3$In$_4$N$_5$ [1.880 (7) Å; Yamane *et al.*, 2002].

Atoms N1, N2 and N4 are coordinated to five Ba atoms and one Cu atom, in Ba$_5$Cu octahedra. Atoms N3, N5 and N6 atoms are coordinated to six Ba atoms, in Ba$_6$ octahedra.

Figure 1
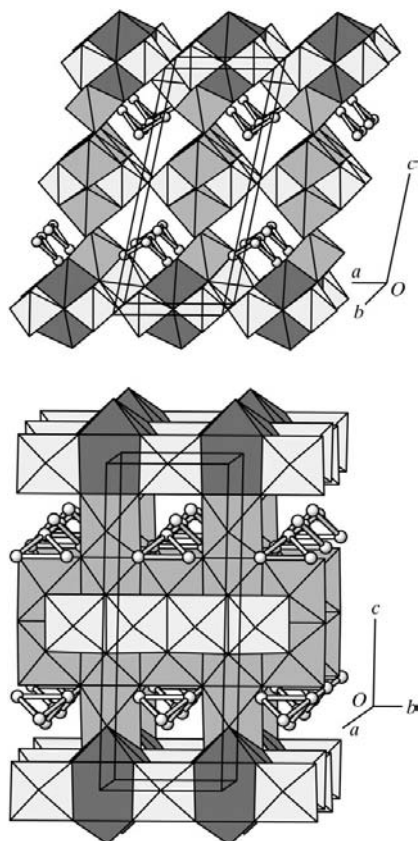The arrangement of atomic positions in the structure of Ba$_{14}$Cu$_2$In$_4$N$_7$, illustrated with 50% probability displacement ellipsoids.

Figure 2
The structure of $Ba_{14}Cu_2In_4N_7$ with N-centred Ba octahedra shown as mid-grey, N-centred Ba and Cu octahedra shown as light grey, Ba12 atom-centred Ba polyhedra shown as dark grey, and In atoms shown as grey circles with bonds.

Fig. 2 illustrates the crystal structure of $Ba_{14}Cu_2In_4N_7$ with the N-centred metal octahedra and Ba12-centred Ba octadecahedra. These polyhedra share apices, edges and planes, and form cages in which distorted tetrahedral In_4 clusters are contained.

The In_4 cluster consists of two In1 atoms and atoms In2 and In3. The In2—In3 distance of 3.7310 (17) Å is longer than the other In—In distances in the cluster [2.9548 (14)– 3.3009 (16) Å], and larger than the distances observed in Zintl compounds of Na_2In [3.068 (1)–3.152 (1) Å; Sevov & Corbett, 1993], NaIn (2.97–3.28 Å; Iandelli, 1964), $SrIn_2$ and $BaIn_2$ (2.98 and 2.95–3.11 Å, respectively; Bruzzone & Bonino, 1970), and $BaIn_4$ (2.92 Å; Bruzzone, 1965). Almost regular tetrahedra of the $[In_4]^{8-}$ Zintl polyanion were found in Na_2In. The number of Ba atoms around the In atoms is eight for In1 and nine for In2 and In3. The In—Ba distances are in the range 3.6639 (10)–4.3063 (14) Å, which are comparable with the Ba—In distances reported for $BaIn_2$ (3.54–3.88 Å) and $BaIn_4$ (3.76–4.55 Å).

As discussed previously (DiSalvo et al., 1997; Niewa & DiSalvo, 1998; Yamane et al., 2002), the formal valence of Cu in $^0[CuN_2]$ is considered to be I and the formal charge of $^0[CuN_2]$ is −5. If the formal charge of the Ba atom in site Ba12 is zero, $Ba_{14}Cu_2In_4N_7$ can be represented as $(Ba^0)(Ba^{2+})_{27}\cdot(N^{3-})_6(^0[CuN_2]^{5-})_4(^0[In_4]^{8-})_2$.

The electrical resistivity of $Ba_{14}Cu_2In_4N_7$ is about 0.09 Ω cm at room temperature and decreases with increasing temperature.

Experimental

All manipulations were carried out in an argon-filled glove-box. Ba (99.99%), Cu (99.99%), In (99.999%) and Na (99%) were used as the starting materials. Ba (0.412 mg), In (0.057 mg), Cu (0.032 mg) and Na (0.069 mg), in a Ba:Cu:In:Na molar ratio of 6:1:1:6, were weighed and placed in a BN crucible (inside diameter 7 mm, height 37.5 mm). The crucible was placed in a stainless steel container and sealed in the glove-box. The container was connected to an N_2 gas feed line. After heating to 1023 K in an electric furnace, N_2 gas (99.9999%) was introduced into the container and the pressure was maintained at 7 MPa of N_2 with a pressure regulator. The sample was heated at this temperature for 1 h and then cooled from 1023 to 823 K at a rate of 2 K h^{-1} under 7 MPa of N_2. Below 823 K, the sample was cooled to room temperature by shutting off the electric power to the furnace. The products in the crucible were washed with liquid NH_3 (99.999%) to dissolve the Na flux. Part of the melt surface was covered with a crust of fine granular crystals. Behind the crust and at the side of the melt, single platelet crystals of $Ba_{14}Cu_2In_4N_7$ with a black metallic lustre were obtained (maximum size $2.0 \times 0.5 \times 0.2$ mm). Fine grains of intermetallic compounds were deposited at the bottom of the crucible. The single crystals of $Ba_{14}Cu_2In_4N_7$ (about 1 mg) were dissolved in 1.3 M sulfuric acid and the Ba:Cu:In molar ratio of 7:2:1 was confirmed by inductively coupled plasma (ICP) atomic emission spectrometry. Since the single crystals were not stable in air, the crystals for X-ray diffraction were sealed in glass capillaries. Precession photographs were taken using Mo $K\alpha$ radiation to check the symmetry and space group.

Table 1
Selected geometric parameters (Å, °).

Ba1—N4	2.810 (9)	Ba10—N6	3.074 (11)
Ba1—N2	2.901 (9)	Ba10—N6^{vi}	3.074 (11)
Ba1—N5	2.993 (10)	Ba11—N2	2.762 (10)
Ba2—N6	2.662 (9)	Ba11—N2^i	2.762 (10)
Ba2—N5	2.805 (9)	Ba12—Ba3^{viii}	3.7654 (8)
Ba2—N3	2.869 (10)	Ba12—Ba3	3.7654 (8)
Ba3—N2^i	2.701 (8)	Ba12—Ba3^{ix}	3.7654 (8)
Ba3—N4^{ii}	2.768 (8)	Ba12—Ba3^v	3.7654 (8)
Ba4—N3	2.750 (12)	Ba12—Ba9^{viii}	3.8978 (13)
Ba4—N1^{iii}	2.773 (8)	Ba12—Ba9	3.8978 (13)
Ba4—N1	2.773 (8)	Ba12—Ba1^{viii}	3.9894 (8)
Ba5—N3^{iv}	2.719 (13)	Ba12—Ba1^{ix}	3.9894 (8)
Ba5—N1	2.773 (8)	Ba12—Ba1	3.9894 (8)
Ba5—N1^{iii}	2.773 (8)	Ba12—Ba1^v	3.9894 (8)
Ba6—N4	2.582 (12)	Ba12—Ba11	4.0045 (8)
Ba6—N5	2.586 (11)	Ba12—Ba11^x	4.0045 (8)
Ba7—N1	2.715 (8)	In1—In3^{iv}	2.9548 (14)
Ba7—N1^v	2.715 (8)	In1—In2^{xi}	2.9632 (12)
Ba7—N6	2.792 (15)	In1—In1^{iii}	3.3009 (16)
Ba8—N6^{vi}	2.762 (15)	In2—In3^{xii}	3.7310 (17)
Ba8—N1^v	2.787 (8)	Cu1—N1^{xiii}	1.890 (7)
Ba8—N1	2.787 (8)	Cu1—N1	1.890 (7)
Ba9—N5	2.466 (11)	Cu2—N2^{xiv}	1.906 (10)
Ba10—N1^{vii}	2.775 (7)	Cu2—N2	1.906 (10)
Ba10—N1	2.775 (7)	Cu3—N4^{xv}	1.886 (12)
Ba10—N3^{iv}	3.026 (11)	Cu3—N4	1.886 (12)
Ba10—N3	3.026 (10)		
N1^{xiii}—Cu1—N1	179.0 (5)	N4^{xv}—Cu3—N4	180.0
N2^{xiv}—Cu2—N2	180.0		

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

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Crystal data

$Ba_{14}Cu_2In_4N_7$
$M_r = 2607.19$
Monoclinic, $P2/m$
$a = 9.3225\ (19)$ Å
$b = 8.0089\ (17)$ Å
$c = 21.651\ (5)$ Å
$\beta = 102.263\ (5)°$
$V = 1579.7\ (6)$ Å^3
$Z = 2$

$D_x = 5.481$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 892
 reflections
$\theta = 1.0$–$31.1°$
$\mu = 21.29$ mm^{-1}
$T = 293\ (2)$ K
Plate, black
$0.25 \times 0.12 \times 0.06$ mm

Data collection

Bruker SMART CCD area-detector
 diffractometer
ω scans
Absorption correction: analytical
 face-indexed (*XRPEP*; Bruker,
 1997)
 $T_{min} = 0.051$, $T_{max} = 0.330$
15 245 measured reflections

5370 independent reflections
3463 reflections with $I > 2\sigma(I)$
$R_{int} = 0.098$
$\theta_{max} = 31.1°$
$h = -13 \rightarrow 10$
$k = -10 \rightarrow 11$
$l = -31 \rightarrow 31$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.112$
$S = 0.95$
5370 reflections
151 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 3.67$ e Å^{-3}
$\Delta\rho_{min} = -4.01$ e Å^{-3}
Extinction correction: *SHELXL*97
 (Sheldrick, 1997)
Extinction coefficient: 0.00084 (5)

Data collection: *SMART* and *SAINT* (Bruker, 1999); cell refinement: *SMART* and *SAINT*; data reduction: *XPREP* (Bruker, 1997); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL*97.

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