Crystal structure of hexabarium mononitride pentaindide, $(\text{Ba}_6\text{N})[\text{In}_5]$

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Abstract

$\text{Ba}_6\text{In}_5\text{N}$, trigonal, $R\bar{3}c$ (no. 167), $a = 8.234(3)$ Å, $c = 44.12(2)$ Å, $V = 2590.6$ Å³, $Z = 6$, $R_{\text{gt}}(F) = 0.028$, $wR_{\text{ref}}(F^2) = 0.060$, $T = 293$ K.

Source of material

Single crystals of $(\text{Ba}_6\text{N})[\text{In}_5]$ with metallic lustre were obtained from reaction of melt beads of the general composition ' Ba_3In ' with nitrogen atmosphere at 973 K next to further ternary phases. Nearly single phase material (according to X-ray powder diffraction) was obtained under the same conditions starting from melt beads with the bulk composition ' Ba_6In_5 ' after two reannealing cycles at 973 K.

Experimental details

Chemical analyses on impurities of H and O were carried out using the carrier gas hot-extraction technique on a LECO analyzer TCH-600. Lattice parameters were obtained from least-squares fittings of reflections taken from a Guinier powder pattern (Cu $K_{\alpha 1}$ radiation, $\lambda = 1.540598$ Å).

Discussion

Indium, when combined with alkaline-earth elements forms a variety of ternary nitrides. The compounds known so far may be described as built from indium clusters and octahedra of alkaline-earth cations surrounding nitride ions. In the latter cationic substructure the polyhedra might be isolated, vertex-, and/or edge-sharing. The variety of In arrangements extends from isolated In species in $(\text{Ca}_7\text{N}_4)\text{In}_{1.04}$ [1], isolated tetrahedral units in $(\text{A}_{19}\text{N}_7)[\text{In}_4]_2$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$) [2,3], trigonal bipyramidal $[\text{In}_5]$ clusters next to $[\text{In}_8]$ ions of more complicated geometry in $(\text{Ba}_{38}\text{N}_{18})[\text{In}_5]_2[\text{In}_8]$ [4], and infinite chains in $(\text{A}_4\text{N})[\text{In}_2]$ ($A = \text{Ca}, \text{Sr}$) [5] and $(\text{Ca}_2\text{N})\text{In}$ [6]. None of these metallic compounds follows Zintl-like counting. The new compound $(\text{Ba}_6\text{N})[\text{In}_5]$ is an isotype of $(\text{A}_6\text{N})[\text{Ga}_5]$ ($A = \text{Sr}, \text{Ba}$) [7].

The crystal structure of $(\text{Ba}_6\text{N})[\text{In}_5]$ is characterized as rocksalt type motif of N-centred octahedra (Ba_6N) and trigonal bipyramidal clusters $[\text{In}_5]$. The trigonal bipyramidal units $[\text{In}_5]$ might be described as $[\text{In}_5]^{7-}$ ions, quite the same according to Zintl-type electronic counting and using the Wade-rules for closo-cluster. The isotypes $(\text{A}_6\text{N})[\text{Ga}_5]$ were previously described by the formula $(\text{A}^{2+})_6(\text{N}^{3-})[\text{Ga}_5]^{7-} \cdot 2e^-$ based on electronic structure calculations. An alternate speculation on unnoticed hydride ion impurities in the sense of ' $(\text{A}_6\text{N})[\text{E}_5]\text{H}_2$ ' ($E = \text{Ga}, \text{In}$) is falsified for the title compound by chemical analyses on hydrogen on a nearly single phase sample: The hydrogen content is below the detection limit of 160 ppm (' $(\text{Ba}_6\text{N})[\text{In}_5]\text{H}_2$ ': 1400 ppm), $w(\text{O}) = 0.10(3)$ wt.%. For the $[\text{In}_5]$ cluster in $(\text{Ba}_{38}\text{N}_{18})[\text{In}_5]_2[\text{In}_8]$ a highly electron deficient situation ($[\text{In}_5]^{5-}$) was derived [4]. Distances within the $[\text{In}_5]$ unit in $(\text{Ba}_6\text{N})[\text{In}_5]$ with $d(\text{In}—\text{In})_{\text{equatorial}} = 3.061(1)$ Å and $d(\text{In}—\text{In})_{\text{axial}} = 3.057(1)$ Å are in the range of the respective distances in $(\text{Ba}_{38}\text{N}_{18})[\text{In}_5]_2[\text{In}_8]$ with $d(\text{In}—\text{In})_{\text{equatorial}} = 3.115(1)$ Å, $3.164(1)$ Å and $d(\text{In}—\text{In})_{\text{axial}} = 2.955(1)$ Å – $3.224(2)$ Å. The distances in the isolated (Ba_6N) octahedra with $d(\text{Ba}—\text{N}) = 2.7827(8)$ Å are similar to those in $(\text{Ba}_6\text{N})[\text{Ga}_5]$ ($d(\text{Ba}—\text{N}) = 2.734(1)$ Å).

Table 1. Data collection and handling.

Crystal:	gray platelet, size $0.035 \times 0.110 \times 0.110$ mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	199.35 cm^{-1}
Diffraction, scan mode:	Rigaku AFC 7 & Mercury CCD, $\chi = 0^\circ$, $\omega = 0^\circ$, $2\theta = -10^\circ$, $\varphi = 0^\circ - 180^\circ$, $\Delta\varphi = 0.5^\circ$, $t = 6$ sec
	$\chi = -90^\circ$, $\varphi = 25^\circ$, $2\theta = -10^\circ$, $\omega = 0^\circ - 60^\circ$, $\Delta\omega = 0.5^\circ$, $t = 6$ sec
$2\theta_{\text{max}}$:	67.1°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	8837, 1079
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1021
$N(\text{param})_{\text{refined}}$:	20
Programs:	SHELXS-97 [8], SHELXL-97 [9]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ba(1)	36c	0.10028(4)	0.31724(4)	0.035077(6)	0.0171(1)	0.0199(1)	0.0195(1)	0.0095(1)	−0.00062(8)	−0.00081(9)
In(1)	18e	0.21465(5)	0	¼	0.0162(1)	0.0248(2)	0.0192(2)	½U ₂₂	−0.00083(8)	2U ₁₃
In(2)	12c	0	0	0.19348(1)	0.0213(2)	U ₁₁	0.0153(2)	½U ₁₁	0	0
N(1)	6b	0	0	0	0.023(3)	U ₁₁	0.025(5)	½U ₁₁	0	0

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