

RbBa<sub>2</sub>(N<sub>3</sub>)<sub>5</sub>: a new ternary azide

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Rubidium dibarium pentaazide, RbBa<sub>2</sub>(N<sub>3</sub>)<sub>5</sub>, was prepared from an aqueous solution of the binary azides at room temperature. It crystallizes in the monoclinic system (space group *P2<sub>1</sub>/n*). Two central atoms of azide groups occupy the 2*c* ( $\bar{1}$ ) and 2*b* ( $\bar{1}$ ) positions, another azide group lies completely on a twofold axis (2*f*), while Rb atoms are situated in 2*e* (2) positions. The crystal structure of RbBa<sub>2</sub>(N<sub>3</sub>)<sub>5</sub> can be regarded as a distorted AIB<sub>2</sub>-type arrangement of the metal atoms, with the azide groups occupying the voids between the cations. This results in coordination numbers of 8 (Rb) and 10 (Ba). The N–N distances are in the range 1.169 (8)–1.190 (5) Å, typical for the azide group.

## Comment

The chemistry of metal azides has been developing fast recently, exemplified by syntheses and characterization of new binaries *M*(N<sub>3</sub>)<sub>6</sub> (*M* = Mo or W) for the *d* metals (Haiges *et al.*, 2005) and U(N<sub>3</sub>)<sub>7</sub><sup>3-</sup> for the *f* elements (Crawford *et al.*, 2005) just in the past year.

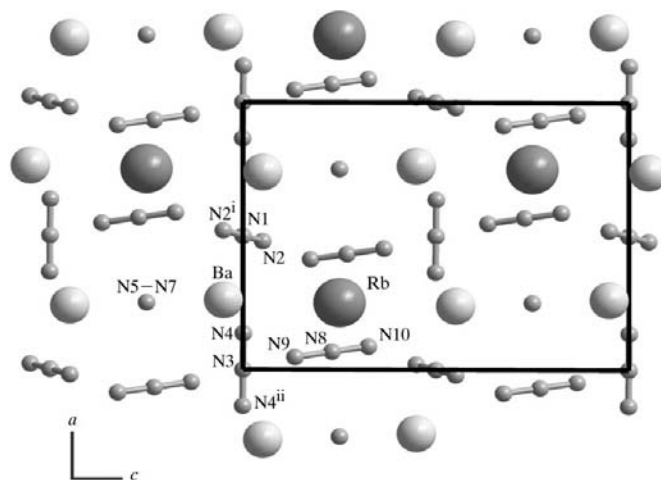
Conversely, more stable azides of the *s* metals have been known for a long time. Alkali metal azides, especially NaN<sub>3</sub>, are classical sources of pure metals and/or nitrogen. Alkaline earth metal azides have not been used as extensively for this purpose owing to their somewhat more violent thermal decomposition and the greater effort needed to obtain solvent-free azides. Anhydrous barium azide can be relatively easily obtained because of the large cation size; its crystallization (Manno, 1965; Marinkas, 1966) and crystal structure (Choi, 1969; Walitzi & Krischner, 1970) attracted some attention previously because of its potential as a high-energy material. Recently, it was shown that Ba(N<sub>3</sub>)<sub>2</sub> can be employed as a valuable precursor, *e.g.* for the preparation of barium pernitride BaN<sub>2</sub> by controlled thermal decomposition (Vajenine *et al.*, 2001). Moreover, anhydrous barium azide can also be used as a barium and nitrogen source in the syntheses of new intermetallic (Smetana *et al.*, 2006*a*) and subnitride (Smetana *et al.*, 2006*b*) phases.

Therefore, the search for new complex azides is important for the development of nitride chemistry. Especially numerous

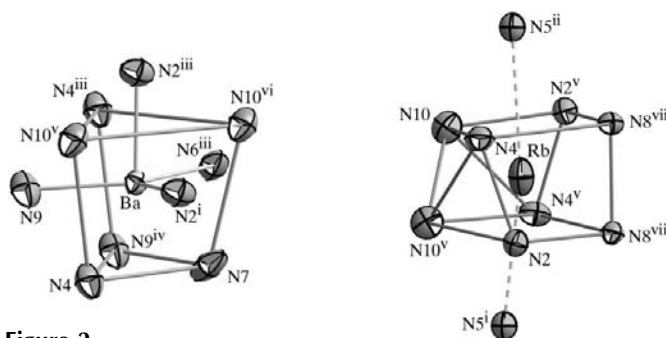
are the mixed azides of alkali and alkaline earth metals. Anhydrous compounds with compositions Cs<sub>7</sub>Ca<sub>4</sub>(N<sub>3</sub>)<sub>15</sub> (Krischner *et al.*, 1984), CsSr(N<sub>3</sub>)<sub>3</sub> (Krischner *et al.*, 1981*a*), Cs<sub>2</sub>Sr(N<sub>3</sub>)<sub>4</sub> (Krischner *et al.*, 1981*b*) and CsBa<sub>2</sub>(N<sub>3</sub>)<sub>5</sub> (Krischner *et al.*, 1982) have been reported so far. Additionally, a number of hydrated azides have been described, *viz.* K<sub>2</sub>Ca(N<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O (Krischner *et al.*, 1980), Rb<sub>2</sub>Ca(N<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O (Mautner & Krischner, 1988), CsCa(N<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O (Krischner, Mautner & Kratky, 1983), Cs<sub>5</sub>Ca<sub>2</sub>(N<sub>3</sub>)<sub>9</sub>·2H<sub>2</sub>O (Saracoglu *et al.*, 1983), Cs<sub>6</sub>Ca(N<sub>3</sub>)<sub>8</sub>·2H<sub>2</sub>O (Krischner, Saracoglu *et al.*, 1983) and K<sub>2.24</sub>Sr<sub>1.34</sub>(N<sub>3</sub>)<sub>4.92</sub>·6.16H<sub>2</sub>O (Walitzi & Krischner, 1978).

In this study, we focused on ternary azides of alkali metals with barium. The synthesis of the hitherto only known azide of this kind, CsBa<sub>2</sub>(N<sub>3</sub>)<sub>5</sub>, was reproduced and a new rubidium compound with the same stoichiometry was obtained. Our attempts to prepare ternary azides of barium with potassium or sodium were unsuccessful.

The crystal structures of orthorhombic CsBa<sub>2</sub>(N<sub>3</sub>)<sub>5</sub> and monoclinic RbBa<sub>2</sub>(N<sub>3</sub>)<sub>5</sub> are similar. The arrangements of the metal ions in both azides can be regarded as distorted variants of the AIB<sub>2</sub>-type structure (Fig. 1); graphite-like sheets of



**Figure 1**  
The crystal structure of RbBa<sub>2</sub>(N<sub>3</sub>)<sub>5</sub> viewed along [010]. [Symmetry codes: (i)  $-x + 1, -y + 1, -z$ ; (ii)  $-x, -y + 1, -z$ .]

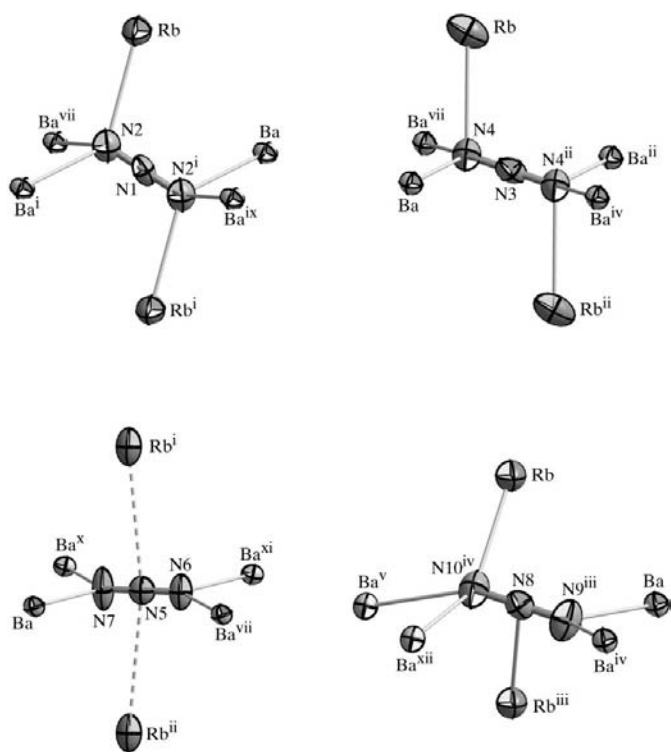


**Figure 2**  
Tenfold coordination of barium (left) and (8+2)-fold coordination of rubidium (right) by N atoms of the azide groups. [Symmetry codes: (iii)  $x, y + 1, z$ ; (iv)  $-x, -y + 2, -z$ ; (v)  $-x + \frac{1}{2}, y, -z + \frac{1}{2}$ ; (vi)  $x + \frac{1}{2}, -y + 2, z - \frac{1}{2}$ ; (vii)  $x, y - 1, z$ ; (viii)  $-x + \frac{1}{2}, y - 1, -z + \frac{1}{2}$ ; other codes as in Fig. 1.]

barium ions are separated by alkali metal cations. Azide anions occupy the voids between the cations, whereby a slight difference in their coordination environment leads to a lower crystal symmetry in the case of  $\text{RbBa}_2(\text{N}_3)_5$ .

The coordination polyhedra of rubidium and barium in  $\text{RbBa}_2(\text{N}_3)_5$  are shown in Fig. 2. The barium cations are surrounded by ten terminal N atoms of azide groups in the form of a trigonal prism with four additional caps. The Ba–N distances range from 2.834 (3) to 3.255 (5) Å, which is comparable to the ranges for ninefold coordinated barium in  $\text{CsBa}_2(\text{N}_3)_5$  [2.816 (6)–3.087 (6) Å] and  $\text{Ba}(\text{N}_3)_2$  [2.883 (3)–2.985 (3) Å]. The rubidium coordination can be described as a polyhedron intermediate between a cube and a square antiprism. Here the distances to the terminal N atoms [3.047 (5)–3.251 (4) Å] are only slightly shorter than the closest contacts to the central atoms of the azide groups [3.165 (4)–3.308 (4) Å]. Two additional capping azide groups lie much farther away at 4.352 (5) Å, favoring the thermal motion of the rubidium cations along the *a* axis. Eightfold coordination of rubidium is also found in  $\text{RbN}_3$ , with Rb–N distances of 3.099 Å (Choi & Prince, 1976), and in  $\text{Rb}_2\text{Ca}(\text{N}_3)_4 \cdot 4\text{H}_2\text{O}$  [six Rb–N contacts of 2.967 (7)–3.133 (7) Å, with two additional water molecules].

The coordination environments of the four crystallographically inequivalent azide groups in  $\text{RbBa}_2(\text{N}_3)_5$  are shown in Fig. 3. The arrangement of the metal cations can be described as distorted octahedra of four barium and two *trans* rubidium cations. These two rubidium positions lie farther



**Figure 3**

The azide groups in  $\text{RbBa}_2(\text{N}_3)_5$ , each surrounded by four Ba atoms in the horizontal plane and two Rb atoms above and below the plane. [Symmetry codes: (ix)  $-x + 1, -y + 2, -z$ ; (x)  $-x + \frac{1}{2}, y, -z - \frac{1}{2}$ ; (xi)  $-x + \frac{1}{2}, y - 1, -z - \frac{1}{2}$ ; (xii)  $x - \frac{1}{2}, -y + 2, z + \frac{1}{2}$ ; other codes as in Figs. 1 and 2.]

away (*cf.* the rubidium environment above) in the case of the N6/N5/N7 azide group, resulting in a (4+2)-coordination. The nearly side-on coordination of the azide group to rubidium is particularly evident for the N9/N8/N10 group. The latter is also the only azide group not restricted to be linear by symmetry, though this anion is almost linear, with a bonding angle of 179.6 (5)°. The N–N distances range from 1.169 (8) to 1.190 (5) Å and are thus in good agreement with the structures of other known azide compounds.

In comparison to  $\text{CsBa}_2(\text{N}_3)_5$ , in which three of four crystallographically inequivalent azide groups are in a fivefold coordination and only one is in a sixfold coordination by metal cations, the average coordination number of the azide groups in  $\text{RbBa}_2(\text{N}_3)_5$  is slightly higher (six for three azide groups and four for one) owing to the smaller size of  $\text{Rb}^+$  compared with  $\text{Cs}^+$ . This minute difference is apparently sufficient to favor the monoclinic structure for the rubidium compound.

An alternative description of the crystal structure of  $\text{RbBa}_2(\text{N}_3)_5$  is instructive. If the positions of the central atoms of the azide groups alone are considered (*i.e.* the centers of mass of the anions) then the ternary azide may be described as a slightly distorted variant of the  $\text{Ga}_3\text{Pt}_5$  structure (Bhan & Schubert, 1960), with the metal cations in the gallium positions and the azide groups in the platinum sites. The latter intermetallic phase is in turn an ordered  $2 \times 2 \times 1$  superstructure of the fcc packing with 16 atoms in the unit cell [ $Z = 2$ , as in  $\text{RbBa}_2(\text{N}_3)_5$ ]. The observed axis ratio of  $a:b:c = 1.54:1:2.08$  for the azide group illustrates the degree of distortion compared with the expected value of 2:1:2 for the ideal fcc lattice. Interestingly, the crystal structure of  $\text{CsBa}_2(\text{N}_3)_5$  can also be reduced to the  $\text{Ga}_3\text{Pt}_5$  structure type.

According to our preliminary results, thermal decomposition of the ternary azides  $\text{RbBa}_2(\text{N}_3)_5$  and  $\text{CsBa}_2(\text{N}_3)_5$  leads to  $\text{BaN}_2$  accompanied by evaporation of the alkali metal.

## Experimental

Barium azide (98.5%, Schuchardt) was recrystallized twice from aqueous solution by adding ethanol.  $\text{RbN}_3$  was obtained by mixing aqueous solutions of  $\text{Ba}(\text{N}_3)_2$  and  $\text{Rb}_2\text{CO}_3$  (99%, Merck) in a 1:1 molar ratio followed by filtration and recrystallization. Transparent colorless single crystals of  $\text{RbBa}_2(\text{N}_3)_5$  were obtained by slowly evaporating concentrated aqueous solutions of  $\text{Ba}(\text{N}_3)_2$  with a sixfold excess of  $\text{RbN}_3$ .

### Crystal data

$\text{Ba}_2\text{N}_{15}\text{Rb}$   
 $M_r = 570.30$   
 Monoclinic,  $P2_1/n$   
 $a = 8.6681$  (10) Å  
 $b = 5.6287$  (4) Å  
 $c = 11.7330$  (14) Å  
 $\beta = 90.199$  (14)°  
 $V = 572.45$  (10) Å<sup>3</sup>

$Z = 2$   
 $D_x = 3.310$  Mg m<sup>-3</sup>  
 Ag  $K\alpha$  radiation  
 $\mu = 5.91$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Ellipsoid, colorless  
 $0.16 \times 0.07 \times 0.05$  mm

### Data collection

Stoe IPDS-I diffractometer  
 $\varphi$  scans  
 Absorption correction: numerical  
 [X-RED (Stoe & Cie, 2001) and  
 X-SHAPE (Stoe & Cie, 1999)]  
 $T_{\min} = 0.663, T_{\max} = 0.815$

16393 measured reflections  
 2812 independent reflections  
 2178 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.075$   
 $\theta_{\text{max}} = 28.0^\circ$

## Refinement

Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.034$  $wR(F^2) = 0.084$  $S = 1.14$ 

2812 reflections

87 parameters

$$w = 1/[\sigma^2(F_o^2) + (0.054P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 1.81 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.25 \text{ e } \text{\AA}^{-3}$$

The slight deviation of the  $\beta$  value from  $90^\circ$  was confirmed by powder X-ray diffraction on a single-phase sample, where splitting of relevant reflections, especially for  $\bar{4}12$  and  $412$ , is evident.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 1998); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Crystal Impact, 2005); software used to prepare material for publication: *publCIF* (Westrip, 2006).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3011). Services for accessing these data are described at the back of the journal.

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