

# Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F: A Barium Fluoride Compound with Isolated BN<sub>2</sub><sup>3-</sup> Units

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The compound Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F was synthesized from a mixture of the binary components Ba<sub>3</sub>N<sub>2</sub>, BaF<sub>2</sub>, and BN in sealed steel ampoules at 1273 K. The structure was refined from single crystal data. Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F crystallizes with the triclinic symmetry *P* $\bar{1}$  (No. 2) with  $a = 4.204(3)$  Å,  $b = 20.92(2)$  Å,  $c = 20.95(2)$  Å,  $\alpha = 91.74(6)^\circ$ ,  $\beta = 90.03(6)^\circ$ ,  $\gamma = 93.12(7)^\circ$ ,  $Z = 4$ , and  $V = 1839(2)$  Å<sup>3</sup>. The structure is built from isolated BN<sub>2</sub><sup>3-</sup> anions, barium cations, and [Ba<sub>2</sub>Ba<sub>2</sub>F]<sup>5+</sup> units. © 1999 Academic Press

## INTRODUCTION

Since the work of Goubeau and Anselmet [1] in 1961 the linear nitridoborate anion BN<sub>2</sub><sup>3-</sup>, which is isoelectronic and isostructural to CO<sub>2</sub>, has been known. Recently, we reported on four new halogenide compounds containing such anions, M<sub>2</sub>BN<sub>2</sub>X, with  $M = \text{Ca, Sr}$  and  $X = \text{F, Cl}$  [2]. Trying to synthesize the analogous barium compounds, we did not succeed but found different structures of other compositions [3]. We report here on the compound Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F.

## EXPERIMENTAL

The compound is synthesized from stoichiometric amounts of the nitride Ba<sub>3</sub>N<sub>2</sub>, the fluoride BaF<sub>2</sub>, and boron nitride. Several experiments using different compositions to obtain pure Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F failed. The best samples were yielded according to the following synthesis procedure. The basic educts are well mixed and heated in stainless steel ampoules to 1273 K. The temperature is kept for 10 h and then lowered to room temperature by 50 K/h. The product is a mixture of yellow needles which are intergrown and light yellow crystals of rod-like shape. The comparison of the X-ray powder patterns of the product and the calculated diagram (cf. Fig. 1) shows that the main product is Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F with an impurity of BaF<sub>2</sub>. The latter must be used as a flux.

We measured three different single crystals of three different syntheses. All of them showed the same lattice parameters and crystal structure. The crystal structure was

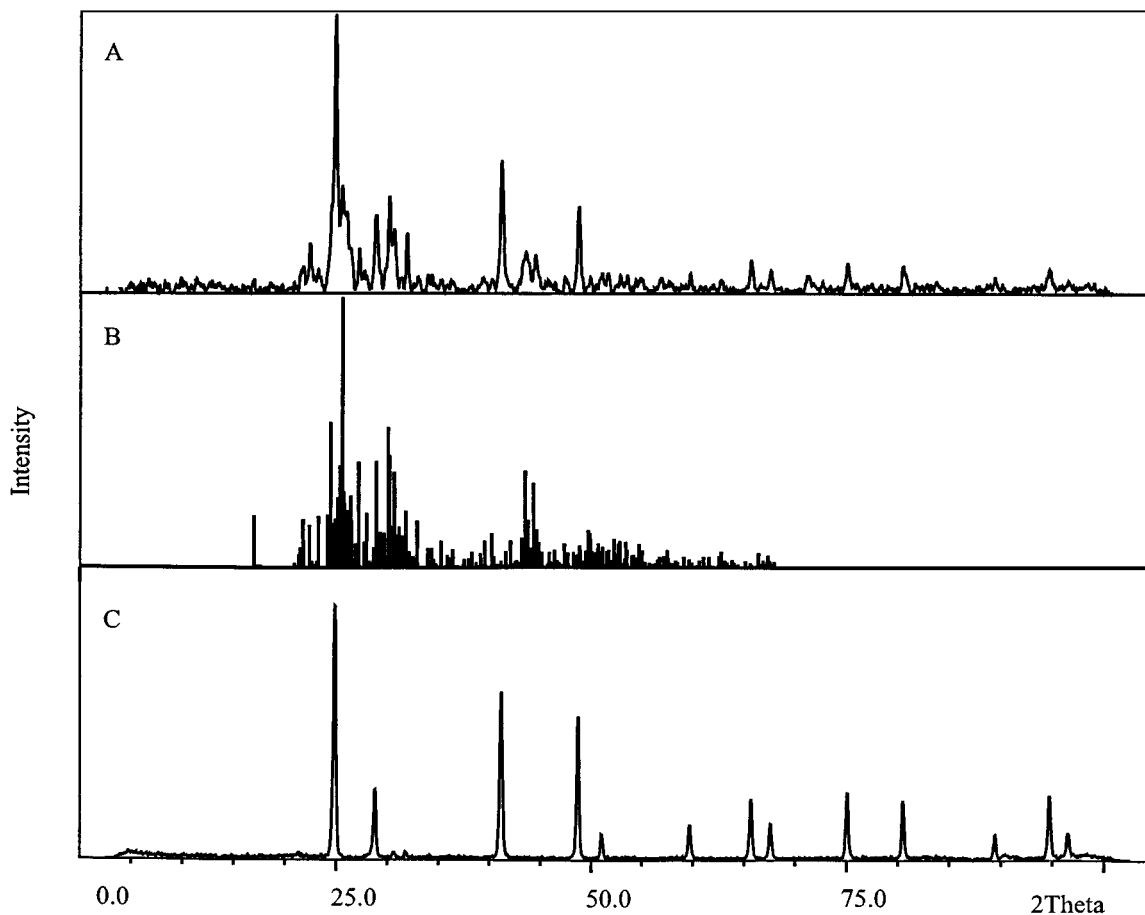
determined by single crystal X-ray diffraction. Table 1 contains the crystal data and the results of the X-ray structure determination for the single crystal of the best quality. The systematic absences belong to the space group *P* $\bar{1}$  or *P*1. No higher symmetry pattern could be found. The structure was solved by direct methods and refined by the full-matrix least-squares procedure [4]. The residual difference electron density did not give any indications of further atoms. During the anisotropic refinement B1, B2, and B4–B6 were not positively refined. A refinement in *P*1 lead to very large correlation matrix elements. We thus believe that *P* $\bar{1}$  is the correct space group, but the boron atom parameters are suffering from data errors because they are the weakest scatterers. That is why we kept the displacement parameters for the B atoms isotropic.

Atomic coordinates and displacement parameters are listed in Table 2. Bond lengths and angles are in Table 3. Structure factor tables and further information may be obtained upon request.

## CRYSTAL STRUCTURE

The crystal structure is influenced not only by the different anion types but by their varying coordination geometries, as shown in Fig. 3. The fluoride anions are surrounded by four barium cations just as in the two compounds M<sub>2</sub>BN<sub>2</sub>F with  $M = \text{Ca, Sr}$  [2]. The tetrahedron around F1 is quite regular, but the one around F2 relatively irregular with Ba–F distances of 265, 2 × 267, and 274 pm. The large difference, about 10 pm, is a result of the size differences of the three types of ions and the different local coordinations in the structure. The edge-sharing Ba<sub>4</sub>F tetrahedra form a one-dimensional strand along the short *a*-axis (cf. Fig. 2b).

The M<sub>2</sub>BN<sub>2</sub>X compounds ( $M = \text{Ca, Sr}$ ;  $X = \text{F, Cl, I}$ ) have been described as double salts [3]. This applies for Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F as well. In contrast to the former compounds the low content of halogenide anions leads to vertex-sharing Ba<sub>4</sub>F tetrahedra which are surrounded by a large number of nitridoborate anions (cf. Fig. 2). In the M<sub>2</sub>BN<sub>2</sub>X phases one-dimensional double chains of tetrahedra ( $X = \text{F}$ ),



**FIG. 1.** X-ray powder diagrams of Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F: (A) measured powder diagram of Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F; (B) calculated powder diagram of Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F; (C) measured powder diagram of BaF<sub>2</sub>.

square pyramids ( $X = \text{Cl}$ ), triple chains of square pyramids and octahedra ( $M = \text{Eu}$ ;  $X = \text{Cl}$ ), and two-dimensional monolayers of octahedra ( $M = \text{Sr}$ ;  $X = \text{I}$ ) have been found. In all cases the polyhedra are linked via edge-sharing. This series clearly shows that the relative sizes of cations and anions and of  $M_nX$  polyhedra and  $\text{BN}_2^{3-}$  anions have a pronounced influence on the actual structure. In this respect, it is interesting to note that obviously there is no preferred structural solution for the hypothetical compound  $\text{Ba}_2\text{BN}_2\text{F}$ .

## DISCUSSION

### Lattice Energy Calculation

The lattice energy, Madelung factors, and point potentials were calculated using the program MADKUG [5] which utilizes an Ewald procedure (Table 4). For the calculation of all the Madelung factors the same reference

distance of  $2.5 \text{ \AA}$  was used. The calculation of the Madelung parts of lattice energy (MAPLE) under assumption of the formal charges shows that the energy per unit charge is fairly high compared to rocksalt.

The differences of the point potentials in the nitrogen pairs in the  $\text{BN}_2^{3-}$  units hint at a quite large polarization. All the nitrogen atoms with a higher point potential are situated towards the outside of the double layers shown in Fig. 1a, which means that a certain modulation of the lattice potential is generated not only by the different anions but also by the packing requirements.

Just as for all known nitridoborate compounds the anisotropy of the  $\text{BN}_2^{3-}$  group has a marked influence on the overall packing in Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F. In [100] projection the  $\text{BN}_2^{3-}$  units form layers perpendicular to [010] of fairly well aligned rods with two sets of Ba<sup>2+</sup> cations (cf. Fig. 2b). The Ba atoms of one set alternate with  $\text{BN}_2^{3-}$  groups along [001] while those of the other set are shifted to the periphery. This distribution combines with a consecutive tilting of

**TABLE 1**  
**Crystallographic Data for Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F**

Formula	Ba <sub>8</sub> (BN <sub>2</sub> ) <sub>5</sub> F
Molecular weight [g/mol]	1311.9
Space group	<i>P</i> $\bar{1}$ (No. 2)
Volume [Å <sup>3</sup> ]	1839(2)
Lattice constants	<i>a</i> = 4.204(3) Å; $\alpha$ = 91.74(6)° <i>b</i> = 20.92(2) Å; $\beta$ = 90.03(6)° <i>c</i> = 20.95(2) Å; $\gamma$ = 93.12(7)°
Formula units	4
Density g/cm <sup>3</sup>	4.739
Absorption coef. $\mu$ [mm <sup>-1</sup> ]	16.854
Crystal size [mm]	0.4 × 0.1 × 0.1
Data collection	STOE IPDS
Radiation	MoK $\alpha$
Measuring method	$\omega$ - $\theta$ scan
$2\theta_{\max}$	56.29
Measured reflections	22122
Unique reflections	8299 ( <i>R</i> <sub>int.</sub> = 0.0736)
Data used $F^2 > 3\sigma(F^2)$	7749
Solution	Direct methods
Refinement method	SHELXL93
Parameters, restrictions	412, 0
<i>R</i> -value [ $I > 2\sigma(I)$ ]	<i>R</i> <sub>1</sub> = 0.0490, <sup>a</sup> <i>wR</i> <sub>2</sub> = 0.1247 <sup>b,c</sup>
<i>R</i> -value for all data	<i>R</i> <sub>1</sub> = 0.0703, <sup>a</sup> <i>wR</i> <sub>2</sub> = 0.1378 <sup>b,c</sup>

Note.  $\text{Goof} = \sqrt{\frac{\sum(w(F_o^2 - F_c^2)^2)}{(n - p)}}$ ;  $R_{\text{int}} = \frac{\sum F_o^2 - F_c^2}{\sum F_o^2}$ ; *n* = no. of reflections, *p* = no. of parameters.

$${}^a R_1 = \frac{\sum(F_o - F_c)}{\sum F_o}$$

$${}^b wR_2 = \sqrt{\frac{\sum(w(F_o^2 - F_c^2)^2)}{\sum w(F_o^2)^2}}$$

$${}^c w = \frac{1}{\sigma^2(F_o^2) + (g \cdot P)^2 + k \cdot P}; P = \frac{\text{Max}(F_o^2, 0) + 2 \cdot F_c^2}{3};$$

*k*, *g* = weighting factors.

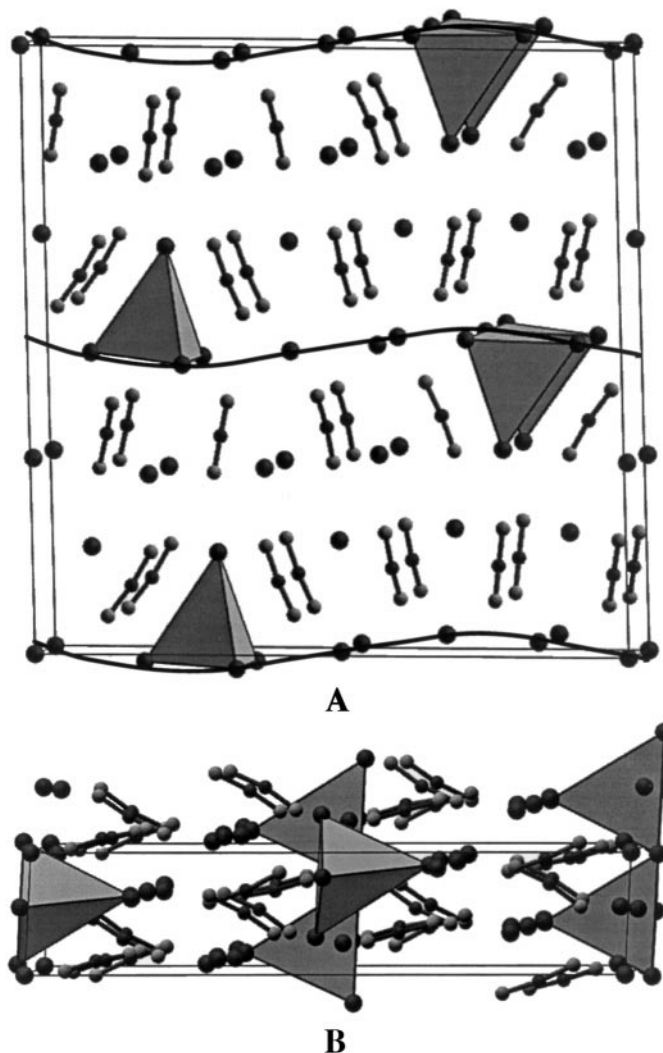
the rods which after five BN<sub>2</sub><sup>3-</sup> periods generates enough space to fit in a tetrahedron which cancels the resulting curvature in the layer (cf. Fig. 2a). The unit cell contains four of such layers which are shifted against each other by approximately [00½]. These mutual shifts are responsible for the low symmetry despite the fact that lattice constants are fairly close to a tetragonal situation.

#### Geometry of BN<sub>2</sub><sup>3-</sup> Anions

The cumulated double bonds in the 16e systems impose a strong linear component onto the conformation of such units. Still, packing requirements and cation-anion interactions induce distortion which may be taken to be significant. The B-N distances in Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F vary only slightly

between 129 and 138 pm, which may be traced back to the different coordinations. Though, quite small compared to their standard deviations we think that these differences are significant. This is supported by the electrostatic point potentials, calculated for the nitrogen atoms. The angles vary between 169° and 173° and are, compared to other novel BN<sub>2</sub><sup>3-</sup> containing phases, fairly small [2, 3].

Comparing the local environments of the 17 barium positions four different types of coordinates exist (cf. Fig. 3). For Ba1 to Ba4 a neighborhood according to the formulation [BaF(BN<sub>2</sub>)<sub>5</sub>] is found; the only difference occurs in the spatial distribution of the coordinated BN<sub>2</sub><sup>3-</sup> units: Ba5 and Ba6 have each two fluoride neighbors and four BN<sub>2</sub><sup>3-</sup> units ([BaF<sub>2</sub>(BN<sub>2</sub>)<sub>4</sub>]), while Ba7, Ba8, and Ba9 have six BN<sub>2</sub><sup>3-</sup>



**FIG. 2.** Structure of Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F: barium atoms are isolated or form tetrahedra around F<sup>-</sup> anions. The BN<sub>2</sub><sup>3-</sup> units show pronounced deviations from linearity. (A) skew view along the *a*-axis of Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F; (B) skew view along the *b*-axis of Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F [8].

TABLE 2  
Atomic Coordinates and Equivalent Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F

Atom	Site	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>	U <sub>eq</sub>
Ba1	2i	0.4561(2)	0.9815(1)	0.1655(1)	16(1)	18(1)	18(1)	0(1)	0(1)	1(1)	18(1)
Ba2	2i	0.2097(2)	0.4859(1)	0.0796(1)	17(1)	18(1)	17(1)	1(1)	0(1)	2(1)	18(1)
Ba3	2i	0.6233(2)	0.8401(1)	0.7091(1)	17(1)	17(1)	19(1)	0(1)	-1(1)	2(1)	18(1)
Ba4	2i	0.1210(2)	0.6596(1)	0.2063(1)	17(1)	18(1)	18(1)	0(1)	0(1)	1(1)	18(1)
Ba5	2i	0.9370(2)	0.9768(1)	0.3362(1)	16(1)	19(1)	20(1)	0(1)	0(1)	0(1)	18(1)
Ba6	2i	0.7102(2)	0.4737(1)	0.2497(1)	16(1)	20(1)	19(1)	0(1)	1(1)	0(1)	18(1)
Ba7	1f	0	0	0	19(1)	23(1)	19(1)	-2(1)	-2(1)	4(1)	20(1)
Ba8	1f	1/2	0	1/2	17(1)	17(1)	20(1)	1(1)	1(1)	0(1)	18(1)
Ba9	2i	0.2155(2)	0.4906(1)	0.4164(1)	17(1)	18(1)	19(1)	0(1)	-1(1)	1(1)	18(1)
Ba10	2i	0.6350(2)	0.7979(1)	0.3079(1)	16(1)	19(1)	17(1)	0(1)	0(1)	1(1)	18(1)
Ba11	2i	0.6438(2)	0.8192(1)	0.5040(1)	16(1)	18(1)	18(1)	1(1)	-1(1)	1(1)	18(1)
Ba12	2i	0.0945(2)	0.6695(1)	0.4142(1)	18(1)	18(1)	18(1)	0(1)	-2(1)	0(1)	18(1)
Ba13	2i	0.6222(2)	0.8318(1)	0.9216(1)	18(1)	19(1)	19(1)	2(1)	1(1)	-1(1)	18(1)
Ba14	2i	0.0762(2)	0.7045(1)	0.8041(1)	17(1)	20(1)	17(1)	1(1)	-1(1)	2(1)	18(1)
Ba15	2i	0.1302(2)	0.6798(1)	0.9991(1)	17(1)	20(1)	18(1)	1(1)	1(1)	-1(1)	18(1)
Ba16	2i	0.1175(2)	0.6935(1)	0.6095(1)	16(1)	20(1)	17(1)	1(1)	1(1)	0(1)	18(1)
Ba17	2i	0.6670(2)	0.8033(1)	0.1161(1)	18(1)	20(1)	18(1)	0(1)	0(1)	1(1)	18(1)
F1	2i	0.5538(20)	0.9657(4)	0.7164(4)	20(4)	20(4)	28(4)	-1(3)	2(3)	-3(3)	23(2)
F2	2i	0.2158(21)	0.5348(4)	0.1978(4)	28(4)	14(4)	30(4)	-5(3)	0(3)	0(3)	24(2)
N1	2i	0.2668(30)	0.4316(6)	0.9569(6)	25(6)	19(6)	22(6)	1(5)	4(5)	4(5)	22(2)
N2	2i	0.4088(27)	0.3270(7)	0.8893(6)	10(5)	39(8)	26(6)	-6(5)	1(4)	2(5)	25(3)
N3	2i	0.9392(27)	0.9072(6)	0.2191(6)	15(5)	17(6)	28(6)	-3(5)	-6(4)	5(4)	20(2)
N4	2i	0.1720(26)	0.7917(6)	0.2114(5)	15(5)	24(6)	15(5)	-1(4)	-1(4)	0(4)	18(2)
N5	2i	0.8777(28)	0.1914(6)	0.9837(5)	22(6)	21(6)	16(5)	7(5)	13(4)	4(5)	20(2)
N6	2i	0.5502(26)	0.0805(6)	0.9543(6)	11(5)	27(7)	24(6)	7(5)	5(4)	9(4)	20(2)
N7	2i	0.3264(28)	0.5920(5)	0.8712(6)	22(6)	7(6)	27(6)	-5(4)	-5(5)	-3(4)	19(2)
N8	2i	0.6405(27)	0.7020(6)	0.9064(6)	12(5)	31(7)	24(6)	1(5)	0(4)	5(5)	22(2)
N9	2i	0.5719(28)	0.7075(6)	0.7110(5)	19(5)	27(7)	11(5)	4(4)	-4(4)	0(4)	19(2)
N10	2i	0.8101(28)	0.5938(6)	0.6937(6)	19(6)	18(6)	24(6)	7(5)	8(4)	3(4)	20(2)
N11	2i	0.4187(25)	0.9111(6)	0.3955(6)	8(5)	24(6)	23(6)	4(5)	2(4)	0(4)	18(2)
N12	2i	0.1079(31)	0.7990(6)	0.4079(6)	26(6)	16(6)	30(7)	-2(5)	-7(5)	-3(5)	24(3)
N13	2i	0.5884(30)	0.6693(6)	0.3039(6)	24(6)	21(7)	26(6)	2(5)	-11(5)	-2(5)	24(3)
N14	2i	0.7215(28)	0.5582(6)	0.3543(6)	16(6)	26(7)	26(6)	10(5)	-6(5)	-1(4)	22(3)
N15	2i	0.6239(27)	0.6902(6)	0.5104(5)	16(5)	29(7)	13(5)	4(5)	2(4)	0(4)	19(2)
N16	2i	0.3109(30)	0.5768(6)	0.5236(6)	23(6)	18(6)	29(7)	-2(5)	2(5)	3(5)	24(3)
N17	2i	0.1534(30)	0.8338(7)	0.8066(6)	23(6)	30(7)	20(6)	1(5)	5(5)	-2(5)	24(3)
N18	2i	0.0215(30)	0.9376(6)	0.8770(6)	25(6)	20(6)	18(5)	0(5)	12(5)	4(5)	21(2)
N19	2i	0.1629(32)	0.8234(6)	0.6121(6)	34(7)	16(6)	21(6)	1(5)	-6(5)	-1(5)	24(3)
N20	2i	0.0042(31)	0.0665(6)	0.4381(6)	35(7)	11(6)	19(6)	6(5)	-8(5)	-5(5)	22(2)
B1	2i	0.3358(31)	0.3822(7)	0.9203(6)							11(2)
B2	2i	0.0728(34)	0.8513(7)	0.2166(7)							14(3)
B3	2i	0.7411(32)	0.1333(8)	0.9688(6)	8(6)	30(8)	6(5)	-2(5)	-1(4)	10(5)	14(3)
B4	2i	0.4974(33)	0.6433(7)	0.8877(7)							13(3)
B5	2i	0.6650(38)	0.6485(8)	0.7018(8)							20(3)
B6	2i	0.2494(34)	0.8587(7)	0.4027(7)							15(3)
B7	2i	0.6394(38)	0.6119(9)	0.3258(8)	15(7)	33(10)	22(8)	-3(7)	1(6)	-8(6)	24(3)
B8	2i	0.4970(35)	0.6305(8)	0.5156(6)	16(6)	26(8)	4(5)	-2(5)	-6(5)	7(5)	15(3)
B9	2i	0.1007(31)	0.8882(8)	0.8385(7)	6(6)	22(8)	17(6)	4(6)	0(5)	-2(5)	15(3)
B10	2i	0.9112(36)	0.1200(8)	0.4096(7)							17(3)

Note.  $U_{(eq)}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. The components of the anisotropic displacement tensor take the form  $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$ . All the positions are fully occupied.

ligands ([Ba(BN<sub>2</sub>)<sub>6</sub>]). In all these barium surroundings (Ba1 to Ba9) the BN<sub>2</sub><sup>3-</sup> units are exclusively *end-on* coordinated. The local environments of the other barium atoms (Ba10 to Ba17) show three *end-on* and in addition two *side-on* coordinated BN<sub>2</sub><sup>3-</sup> units according to

[Ba(BN<sub>2</sub>)<sub>5</sub>]. In the first case chemical bonding between barium and the boron or the second nitrogen cation can be excluded; in the second interaction of barium with all three atoms of the BN<sub>2</sub><sup>3-</sup> group is quite likely (cf. Fig. 3, Ba10).

**TABLE 3**  
**Bond Lengths [pm] and Angles [°] for Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F**

Atom-pair	<i>d</i>	<i>n</i>	Atom-pair	<i>d</i>	Atom-pair	<i>d</i>	Atom-pair	<i>d</i>	Atom-pair	<i>d</i>
Ba1-F1	268.0(9)		Ba11-N15	270(1)	N2-B1	136(2)	N9-B5	132(2)	N17-B9	133(2)
-N6	279(1)		-B10	283(2)	-N1	267(2)	-N10	264(2)	-N18	267(2)
-N18	286(1)		-N12	284(1)	-Ba17	273(1)	-Ba3	277(1)	-Ba14	271(1)
-N3	285(1)		-B6	286(1)	-Ba4	282(1)	-Ba14	286(1)	-Ba3	284(1)
-N18	286(1)		-N20	297(1)	-Ba4	303(1)	-Ba16	286(1)	-Ba3	303(1)
-N3	287(1)				-Ba15	305(1)	-Ba14	289(1)	-Ba13	311(1)
Ba2-F2	265.0(9)		Ba12-N12	271(1)	-Ba15	326(1)	-Ba16	315(1)	-Ba13	329(1)
-N1	279(1)		-B7	285(2)			N10-B5	133(2)	N18-B9	135(2)
-N7	282(1)		-N15	287(1)	N3-B2	132(2)	-N9	264(2)	-N17	267(2)
-N1	283(1)		-B8	288(1)	-N4	266(2)	-Ba6	281(1)	-Ba1	286(1)
-N1	284(1)		-N14	298(1)	-Ba5	282(1)	-Ba6	282(1)	-Ba7	286(1)
-N7	292(1)				-Ba1	285(1)	-Ba9	286(1)	-Ba1	286(1)
Ba3-F1	266.0(9)		Ba13-N8	273(1)	-Ba1	287(1)	-Ba16	301(1)	-Ba13	288(1)
-N9	277(1)		-B3	286(1)	-Ba17	318(1)	-Ba14	337(1)	-Ba13	359(1)
-N19	281(1)		-N18	288(1)	-Ba10	320(1)				
-N17	284(1)		-B9	289(1)			N11-B6	129(2)	N19-B10	133(2)
-N17	303(1)		-N5	292(1)	N4-B2	134(2)	-N12	264(2)	-N20	269(2)
-N19	307(1)				-N3	266(2)	-Ba5	282(1)	-Ba16	271(1)
Ba4-F2	266.5(8)		Ba14-N17	271(1)	-Ba4	276(1)	-Ba8	284(1)	-Ba3	281(1)
-N4	276(1)		-N8	282(1)	-Ba10	280(1)	-Ba10	313(1)	-Ba11	304(1)
-N2	282(1)		-N9	286(1)	-Ba17	289(1)	-Ba11	320(1)	-Ba3	307(1)
-N13	283(1)		-B4	287(1)	-Ba17	294(1)			-Ba11	314(1)
-N2	303(1)		-N9	289(1)	-Ba10	304(1)	N12-B6	136(2)	N20-B10	136(2)
-N13	305(1)						-N12	264(2)	-N19	269(2)
Ba5-F1	265.4(8)		Ba15-N5	271(1)	N5-B3	134(2)	-Ba12	271(1)	-Ba5	280(1)
-F1	269.5(9)		-B1	287(1)	-N6	269(2)	-Ba11	284(1)	-Ba8	281(1)
-N20	280(1)		-N8	290(1)	-Ba15	271(1)	-Ba10	289(1)	-Ba8	290(1)
-N11	282(1)		-B4	290(1)	-Ba17	284(1)	-Ba11	302(1)	-Ba11	297(1)
-N3	282(1)		-N1	296(1)	-Ba13	292(1)	-Ba10	305(1)	-F1	379(2)
-N11	282(1)				-Ba13	296(1)				
Ba6-F2	266.9(9)		Ba16-N19	271(1)	-Ba17	311(1)	N13-B7	133(2)	B1-N1	132(2)
-F2	273.9(9)		-N9	286(1)			-N14	267(2)	-N2	136(2)
-N14	277(1)		-B5	286(2)	N6-B3	136(2)	-Ba10	269(1)	B2-N3	132(2)
-N10	281(1)		-B8	287(1)	-N5	269(2)	-Ba4	283(1)	-N4	134(2)
-N10	282(1)		-N15	293(1)	-Ba7	279(1)	-Ba4	305(1)	B3-N5	134(2)
-N7	285(1)				-Ba1	279(1)	-Ba12	311(1)	-N6	136(2)
Ba7-N6	279(1)	2	Ba17-N2	273(1)	-Ba7	296(1)	-Ba12	314(1)	B4-N7	130(2)
-N18	286(1)	2	-B2	283(2)	-Ba17	306(1)	N14-B7	135(2)	-N8	138(2)
-N6	296(1)	2	-N5	283(1)	-Ba13	324(1)	-N13	267(2)	B5-N9	132(2)
Ba8-N20	281(1)	2	-B3	287(1)			-Ba6	277(1)	-N10	133(2)
-N11	284(1)	2	-N4	289(1)	N7-B4	130(2)	-Ba9	283(1)	B6-N11	129(2)
-N20	290(1)	2			-N8	267(2)	-Ba12	298(1)	-N12	136(2)
Ba9-N16	282(1)		F1-Ba5	265.4(8)	-Ba2	282(1)	-Ba12	380(1)	B7-N13	133(2)
-N14	283(1)		-Ba3	266.0(9)	-Ba6	285(1)	N15-B8	134(2)	-N14	135(2)
-N16	285(1)		-Ba1	268.0(9)	-Ba2	292(1)	-N16	267(2)	B8-N15	134(2)
-N10	286(1)		-Ba5	269.5(9)	-Ba14	302(1)	-Ba11	270(1)	-N16	135(2)
-N16	287(1)				-Ba15	333(1)	-Ba12	287(1)	B9-N17	133(2)
-N14	290(1)		F2-Ba2	265.0(9)	-Ba15	320(1)	-Ba16	293(1)	-N18	135(2)
Ba10-N13	269(1)		-Ba4	266.5(8)	N8-B4	138(2)	-Ba16	298(1)	B10-N19	133(2)
-N4	280(1)		-Ba6	266.9(9)	-N7	267(2)	-Ba12	301(1)	-N20	136(2)
-B2	287(1)		-Ba6	273.9(9)	-N7	267(2)	N16-B8	135(2)		
-B6	287(2)				-Ba13	273(1)	-N15	267(2)		
-N12	289(1)		N1-B1	132(2)	-Ba14	282(1)	-Ba9	282(1)		
			-N2	267(2)	-Ba15	289(1)	-Ba9	285(1)		
			-Ba2	279(1)	-Ba15	292(1)	-Ba16	313(1)		
			-Ba2	283(1)	-Ba14	320(1)	-Ba12	321(1)		
			-Ba2	284(1)						
			-Ba15	296(1)						
			-Ba15	367(1)						

TABLE 3—Continued  
Bond angles

Atoms	Angle
N1–B1–N2	173(1)°
N3–B2–N4	172(1)°
N5–B3–N6	169(1)°
N7–B4–N8	172(1)°
N9–B5–N10	170(2)°
N11–B6–N12	172(2)°
N13–B7–N14	171(2)°
N15–B8–N16	168(1)°
N17–B9–N18	171(1)°
N19–B10–N20	173(2)°

The one-dimensional [Ba<sub>2</sub>Ba<sub>2/2</sub>F]<sup>5+</sup> strand not only may only be a geometrically separated moiety but can be understood as a complex polymeric cation which is surrounded by the rod-shaped nitridoborate anions and additional barium cations for charge compensation. Complex cations of related types have been found in other compound types such as the alkali metalsuboxides Cs<sub>11</sub>O<sub>3</sub> [6] and Zintl phases such as Ca<sub>4</sub>Sb<sub>2</sub>O ([Ca<sub>6</sub>O]<sup>10+</sup> [7], just to mention a few examples. Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F provides another example of the large variability which is seen in the rather new class of nitridoborate double salts.

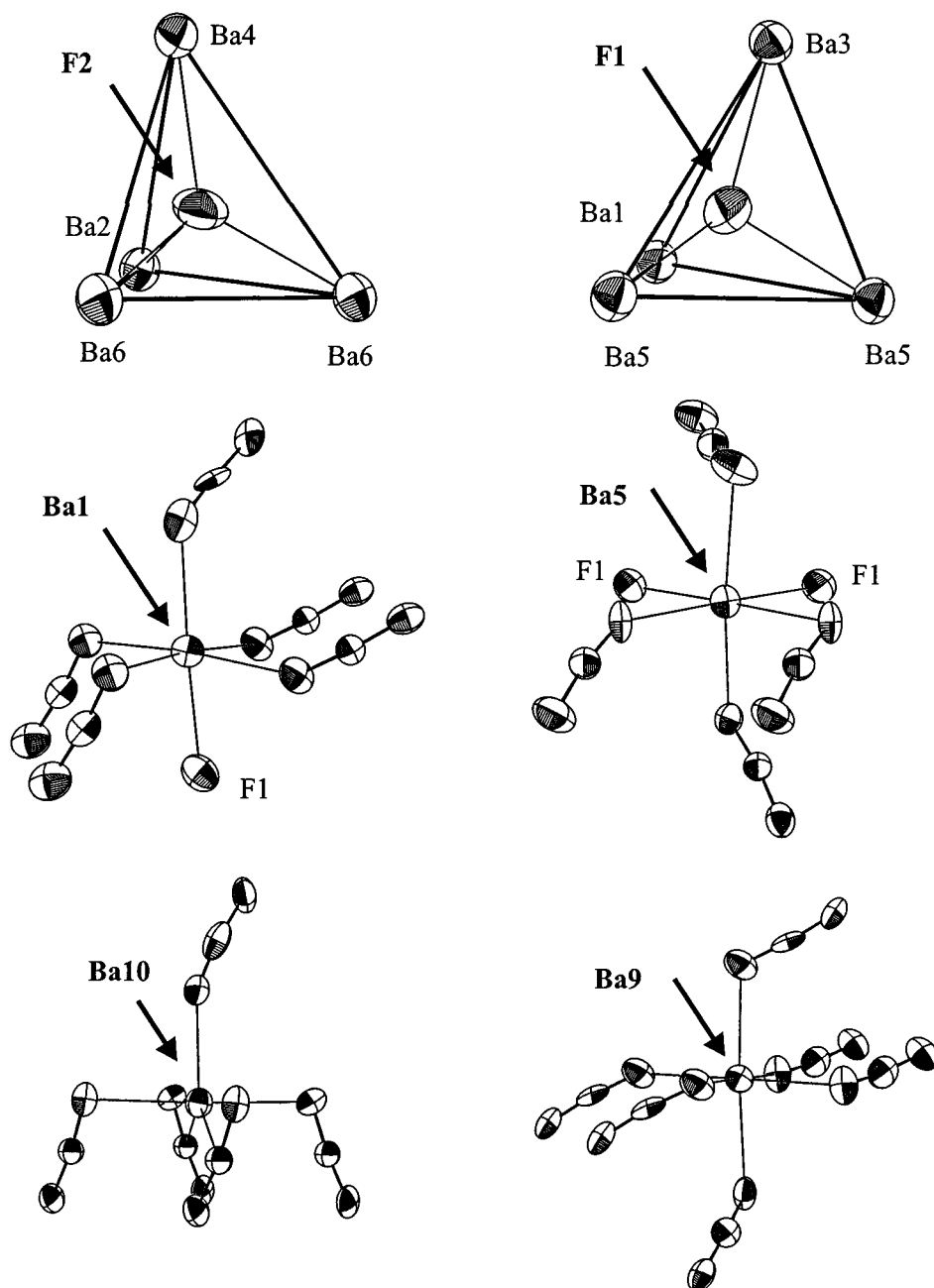


FIG. 3. Local coordinations in Ba<sub>8</sub>(BN<sub>2</sub>)<sub>5</sub>F (ortep plots, 90% probability ellipsoids) [9].

TABLE 4

Results of Lattice Energy Calculation (MADKUG) for  $\text{Ba}_8(\text{BN}_2)_5\text{F}$  [5]: Electrostatic Point Potentials  $P$  [a.u.], First Coordination Numbers (CN), Mean Coordination Distances  $\bar{d}$  [pm], and Lattice Energy MAPLE [ $\text{kJ C}^{-2}\text{mol}^{-1}$ ]

Atom	$P$	CN/ $\bar{d}$	Atom	$P$	CN/ $\bar{d}$
Ba1	-1.120	6/281.8	N7	0.247	4/290.0
Ba2	-1.109	6/281.0	N8	0.389	4/284.2
Ba3	-1.070	6/286.5	N9	0.351	4/284.2
Ba4	-1.068	6/285.8	N10	0.257	4/287.5
Ba5	-1.136	6/276.7	N11	0.238	4/290.0
Ba6	-1.149	6/277.6	N12	0.352	4/286.7
Ba7	-1.059	6/286.9	N13	0.330	4/292.8
Ba8	-1.089	6/284.8	N14	0.255	4/287.2
Ba9	-1.103	6/285.6	N15	0.343	4/286.9
Ba10	-1.133	5/282.2	N16	0.269	4/291.8
Ba11	-1.157	5/284.1	N17	0.331	4/292.4
Ba12	-1.153	5/285.8	N18	0.299	4/286.3
Ba13	-1.124	5/285.6	N19	0.338	4/290.8
Ba14	-1.132	5/282.6	N20	0.269	4/287.0
Ba15	-1.109	5/286.8	B1	-0.071	2/134
Ba16	-1.151	5/284.5	B2	-0.059	2/133
Ba17	-1.120	5/283.1	B3	-0.017	2/135
F1	0.736	4/267.2	B4	-0.048	2/134
F2	0.724	4/268.1	B5	-0.072	2/132.5
N1	0.291	4/285.8	B6	-0.086	2/132.5
N2	0.361	4/290.5	B7	-0.103	2/134
N3	0.252	4/293.1	B8	-0.071	2/134.5
N4	0.379	4/284.7	B9	-0.077	2/134
N5	0.379	4/285.7	B10	-0.081	2/134.5
N6	0.324	4/290.1	MAPLE		320

Note. Formal charges according to  $\text{Ba}^{2+}$ ,  $\text{F}^-$ ,  $\text{N}^-$ ,  $\text{B}^-$  have been applied.

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