M_2BN_2X (M = Ca, Sr; X = F, Cl): New Halogenide Compounds with Isolated BN_2^{3-} Units

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The compounds M_2BN_2X (M = Ca, Sr; X = F, Cl) were synthesized from stoichiometric mixtures of the binary components M_3N_2, MX_2, and BN in sealed steel ampoules at 1273 K. All four structures were refined from single crystal data. The isotypic fluorides crystallize in the orthorhombic space group *Pnma* (No. 62) with $a = 9.182(2)$ Å, $b = 3.649(1)$ Å, $c = 9.966(2)$ Å, $Z = 4$, and $V = 333.9(1)$ Å^3 for Ca_2BN_2F and $a = 9.891(2)$ Å, $b = 3.904(1)$ Å, $c = 10.193(2)$ Å, $Z = 4$, and $V = 393.6(2)$ Å^3 for Sr_2BN_2F. The structures are built from isolated BN_2^{3-} anions and $[MM_{3/3}F]$ units. The chlorides, which are related but not isotypic, crystallize in the space group *Pnma* (No. 62) with $a = 11.657(1)$ Å, $b = 3.891(1)$ Å, $c = 8.965(1)$ Å, $Z = 4$, and $V = 406.6(1)$ Å^3 for Ca_2BN_2Cl and $a = 12.408(1)$ Å, $b = 4.161(1)$ Å, $c = 9.170(1)$ Å, $Z = 4$, and $V = 473.4(1)$ Å^3 for Sr_2BN_2Cl. The structures are built from isolated BN_2^{3-} anions and $[M_{3/3}M_{2/2}Cl]$ units. Calculations of the Madelung parts of lattice energy (MAPLE) and vibration spectra of the compounds are reported. © 1998 Academic Press

INTRODUCTION

The linear nitridoborate anion BN_2^{3-} which is isoelectronic and isostructural to CO_2 is known since the work of Goubeau and Anselmet (1) in 1961. During the past 10 years a series of new salt-like compounds with BN_2^{3-} anions has been synthesized and characterized, most of which contain alkali or alkaline earth metal cations or combinations thereof. Primer ones like Li_3BN_2 (2) and Na_3BN_2 (3) crystallize with monoclinic symmetry while the latter prefer primitive cubic arrangements $Sr_3(BN_2)_2$ (4). Compounds with different cations like $LiM_4(BN_2)_3$ (M = Ca, Sr, Ba, Eu) and $NaBa_4(BN_2)_3$ have cubic crystal structures, as well, but show body centering like $Ca_3(BN_2)_2$ (5–10). $LiMgBN_2$, however, has a tetragonal unit cell (11, 12). The different structures may be taken as indicators for a large structural variability in such phases. A few examples with the isosteric CBN^{4-} anions are known, as well, namely Ca_3CBNCl_2, Sr_3CBNCl_2, and Ca_3CBNBr_2 (13, 14) which constitute the first double salts of 16 electron and halogen anions. They

have orthorhombic symmetry. Recently, combinations like $Ba_4(BN_2)O$ (12, 15) and even $Ca_{15}(CBN)_6(C_2)O$ (16) have been synthesized and characterized. The latter is a triple salt containing CBN_2^{4-}, C_2^{2-}, and O^{2-} anions in a complex cubic structure which is related to the garnet structure type (17). We wanted to investigate whether double or triple salts of such kind can in general be obtained by reacting the nitridoborate compounds with halogenide salts. Such reactions seem to open a vast field of novel compounds with a large variety of structural arrangements and of quite different properties. We report here on new double salts of the type M_2BN_2X (M = Ca, Sr; X = F, Cl) (18, 19).

EXPERIMENTAL

The compounds are synthesized from stochiometric amounts of the nitrides M_3N_2, halogenides MX_2, and boron nitride. The basic educts are well mixed and heated in stainless steel ampoules to 1273 K. The temperature is kept for 30 h and then lowered to room temperature by 100 K/h. The products are white fine powders which all react with water and diluted mineral acids. Ca_2BN_2F is the only compound which is stable on exposure to air and moisture.

Synthesis at 1423 K (M_2BN_2F) and 1123 K (M_2BN_2Cl) yields transparent colorless single crystals of rod-like shape. According to the X-ray powder pattern, phase impurities were not detected. Observed and calculated powder patterns are given in Fig. 1.

The crystal structures were determined by single crystal X-ray diffraction. For all four compounds the systematic absences belong to space groups *Pnma* or *Pna*2. The structure solution did not give any indication for the noncentrosymmetric space group. Table 1 contains the crystal data and the results of the X-ray measurements. The structures were solved by direct methods and refined by the full-matrix least-squares procedure (20). The residual difference electron density did not give indications for further atoms, for split positions, or for statistical occupations. A test for larger voids gave negative results because the smallest distances of the largest voids were too small and the coordination of
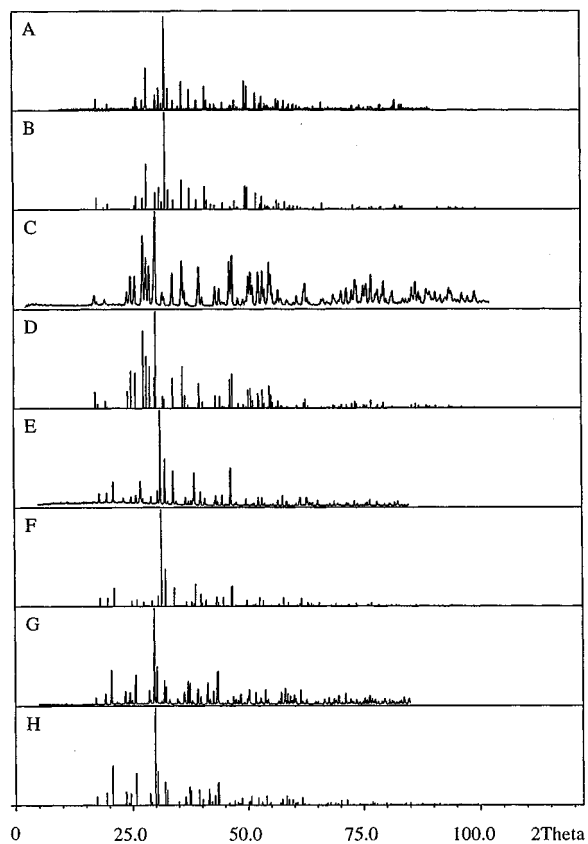
FIG. 1. Powder diagrams of M_2BN_2X compounds: (A,B) measured and calculated powder diagrams of Ca_2BN_2F; (C,D) measured and calculated powder diagrams of Sr_2BN_2F; (E,F) measured and calculated powder diagrams of Ca_2BN_2Cl; (G,H) measured and calculated powder diagrams of Sr_2BN_2Cl.

such voids was too heterogeneous to make chemical sense $(d_{max}(\text{void}) = 2.01\,Å$ (Ca_2BN_2F), $2.28\,Å$ (Sr_2BN_2F), $2.25\,Å$ (Ca_2BN_2Cl), and $2.41\,Å$ (Sr_2BN_2Cl) (21)). Atomic coordinates and displacement parameters are listed in Table 2. Structure factor tables and further information may be obtained upon request.[1]

CRYSTAL STRUCTURES AND DISCUSSION

The Fluorides M_2BN_2F

The crystal structures can best be understood by consideration of the anion coordinations. Basically there is a

relatively clear separation between tetrahedra of the kind $CaCa_{3/3}F$ which have three vertices in common to form one-dimensional strands along the short orthorhombic b axis. One of the calcium atoms (Ca2) connects three tetrahedra, two of which are shifted by $1/2\,b$ and $1b$ against the other and form a syndiotactic chain of tetrahedra (Fig. 2). The calcium atoms have eight principal neighbors with quite varying distances between 234–302 pm. The cal-

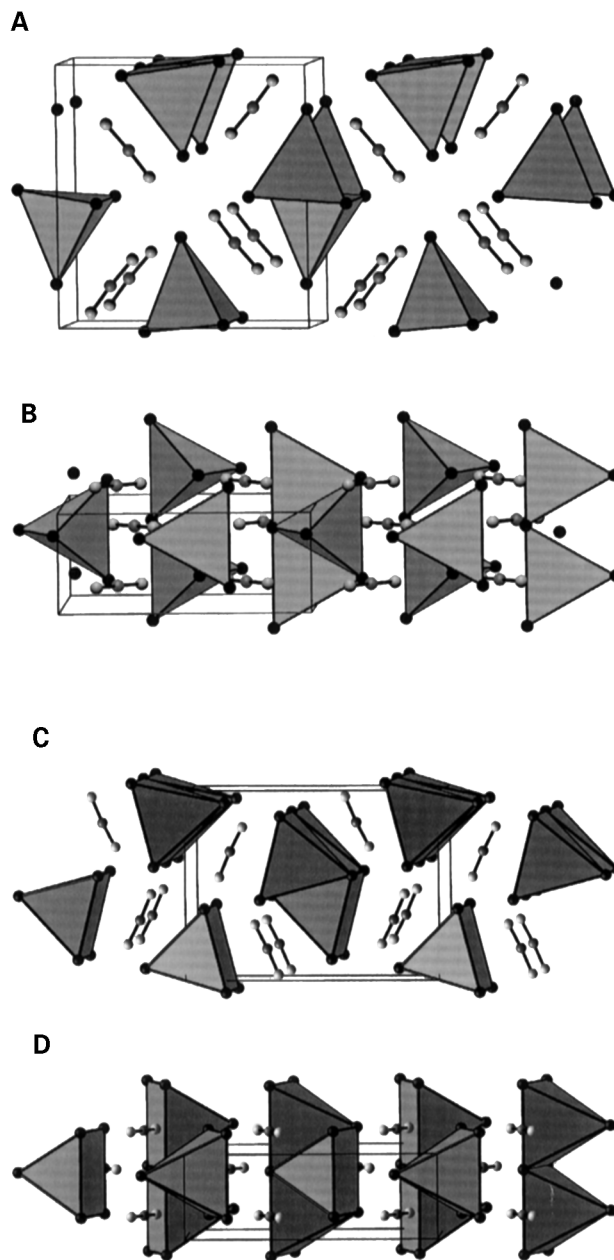**FIG. 2.** Structures of M_2BN_2X (23); (A) skew view along b axis of M_2BN_2F, $M = Ca, Sr$; (B) skew view along c axis of M_2BN_2F, $M = Ca, Sr$; (C) skew view along b axis of M_2BN_2Cl, $M = Ca, Sr$; (D) skew view along c axis of M_2BN_2Cl, $M = Ca, Sr$.

TABLE 1
Crystallographic Data for Ca_2BN_2F, Sr_2BN_2F, Ca_2BN_2Cl, and Sr_2BN_2Cl

Formula	Ca_2BN_2F	Sr_2BN_2F	Ca_2BN_2Cl	Sr_2BN_2Cl
Molecular weight (g/mol)	137.98	233.12	154.43	249.52
Space group	$Pnma$, (No.62)	$Pnma$, (No.62)	$Pnma$, (No.62)	$Pnma$, (No.62)
Volume	333.9(1)	393.6(2)	406.6(1)	473.4(1)
Lattice constants	$a = 9.182(2)$	$a = 9.891(2)$	$a = 11.657(1)$	$a = 12.408(1)$
	$b = 3.649(1)$	$b = 3.904(1)$	$b = 3.891(1)$	$b = 4.161(1)$
	$c = 9.966(2)$	$c = 10.193(2)$	$c = 8.965(1)$	$c = 9.170(1)$
Formula units	4	4	4	4
Density	2.745	3.933	2.523	3.501
Absorption coef. μ [mm^{-1}]	3.207	26.928	3.250	22.916
Crystal size [mm]	$0.4 \times 0.2 \times 0.15$	$0.3 \times 0.08 \times 0.1$	$0.3 \times 0.1 \times 0.1$	$0.35 \times 0.12 \times 0.1$
Data collection	STOE IPDS	STOE IPDS	STOE IPDS	STOE IPDS
Radiation	$MoK\alpha$	$MoK\alpha$	$MoK\alpha$	$MoK\alpha$
Measuring method	ω-θ-scan	ω-θ-scan	ω-θ-scan	ω-θ-scan
$2\theta_{max}$	56.36	48.4	48.58	48.57
Measured reflexions	2693	2149	3438	2633
Unique reflexions	440	355	365	420
	$R_{int.} = 4.88$	$R_{int.} = 10.59$	$R_{int.} = 10.51$	$R_{int.} = 6.48$
Data used $F^2 > 3\sigma(F^2)$	363	350	362	416
Solution	Direct methods	Direct methods	Direct methods	Direct methods
Refinement method	SHELXL93	SHELXL93	SHELXL93	SHELXL9
Parameters, restrictions	37, 0	34, 0	37, 0	38, 0
R value [$I > 2\sigma(I)$]	$R1 = 3.26^a$	$R1 = 5.16^a$	$R1 = 4.26^a$	$R1 = 2.88^a$
	$wR2 = 9.37^{b,c}$	$wR2 = 14.08^{b,c}$	$wR2 = 11.61^{b,c}$	$wR2 = 7.10^{b,c}$
R value for all data	$R1 = 3.26^a$	$R1 = 5.43^a$	$R1 = 4.46^a$	$R1 = 3.20^a$
	$wR2 = 9.37^{b,c}$	$wR2 = 14.46^{b,c}$	$wR2 = 11.98^{b,c}$	$wR2 = 7.35^{b,c}$

$^a R_1 = 100x\dfrac{\sum(F_o - F_c)}{\sum F_o}.$

$^b wR_2 = 100x\sqrt{\dfrac{\sum(w(F_o^2 - F_c^2)^2)}{\sum w(F_o^2)^2}}.$

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

$^d GooF = \sqrt{\dfrac{\sum(w(F_o^2 - F_c^2)^2)}{(n - p)}};$ n, no. of reflections, p, no. of parameters.

$^e R_{int} = 100x\dfrac{\sum F_o^2 - \bar{F}_o^2}{\sum F_o^2}.$

culations of the effective coordination numbers (21) yield $CN(Ca1) = 5.80$ and $CN(Ca2) = 6.02$. The local coordinations are displayed in Fig. 3. They can be classified as distorted octahedra of F and N atoms and a varying secondary coordination of the boron atoms. The boron atoms, though significantly coordinated, have only calcium atoms at larger distances (Table 3).

The coordination of the nitrogen atoms of the BN_2^{3-} group, however, is quite different due to the highly anisotropic and unflexible form of this moiety. Qualitatively, the observed differences seem to be reasonable. The less coordinated N1 atom shows a significantly shorter N–B distance than the other. The Ca_4F tetrahedra are relatively irregular because of the discrimination of the calcium ligands into connecting and terminal ones, with Ca–F distances of

245 pm as well as 2×234 and 237 pm, respectively. The large difference of about 10 pm is obviously a result of the size differences of the three types of ions in the structure, which becomes clearer by comparison with the strontium compound with Sr–F distances of 2×247 pm and 2×253 pm which more or less shows the same general arrangement and coordination numbers. The distortion of the Sr_4F tetrahedron is markedly smaller, but the different nitrogen coordinations are still observed. This is a consequence of the way the BN_2^{3-} rod coordinates the M_4 polyhedra: One end points to a vertex and the other is surrounded by three vertices of three different tetrahedra. This seems to be a prefered structural solution close to the compositions $M_m(BN_2)X_n$ with $m = 2, 3$ and $n = 1, 2$ because the same type of anisotropic coordination is found not only in the

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TABLE 2

Atomic Coordinates and Equivalent Anisotropic Displacement Parameters ($\mathring{A}^2 \times 10^3$) for Ca_2BN_2F, Sr_2BN_2F, Ca_2BN_2Cl, and Sr_2BN_2Cl

</div>

| Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
Ca1	4c	0.0250(1)	1/4	0.1568(1)	15(1)	12(1)	12(1)	0	0(1)	0	13(1)
Ca2	4c	0.6752(1)	1/4	0.9742(1)	12(1)	14(1)	14(1)	0	0(1)	0	14(1)
F1	4c	0.4591(2)	1/4	0.1048(2)	17(1)	15(1)	16(1)	0	− 1(1)	0	22(1)
N1	4c	0.8220(3)	1/4	0.7813(2)	18(1)	13(1)	16(1)	0	0(1)	0	16(1)
N2	4c	0.1532(2)	1/4	0.9538(2)	17(1)	15(1)	15(1)	0	− 2(1)	0	16(1)
B1	4c	0.1532(2)	1/4	0.8240(3)	17(1)	7(2)	15(1)	0	− 5(1)	0	13(1)
Sr1	4c	0.0261(1)	1/4	0.1617(1)	16(1)	11(1)	5(1)	0	0(1)	0	11(1)
Sr2	4c	0.6763(1)	1/4	0.9804(1)	15(1)	11(1)	9(1)	0	− 1(1)	0	12(1)
F1	4c	0.4525(7)	1/4	0.1002(6)	19(4)	11(4)	8(3)	0	5(3)	0	13(2)
N1	4c	0.8180(12)	1/4	0.7689(10)	15(6)	17(6)	17(6)	0	− 4(5)	0	16(3)
N2	4c	0.1482(11)	1/4	0.9335(9)	18(6)	12(6)	7(5)	0	3(5)	0	12(2)
B1	4c	0.2279(16)	1/4	0.8298(14)							14(3)
Ca1	4c	0.0896(1)	1/4	0.6090(1)	18(1)	17(1)	21(1)	0	− 2(1)	0	19(1)
Ca2	4c	0.6697(1)	1/4	0.4503(1)	19(1)	17(1)	24(1)	0	1(1)	0	20(1)
Cl1	4c	0.4388(1)	1/4	0.3474(1)	22(1)	22(1)	22(1)	0	− 1(1)	0	22(1)
N1	4c	0.2865(5)	1/4	0.6846(5)	19(2)	18(3)	23(2)	0	− 3(2)	0	20(1)
N2	4c	0.8776(4)	1/4	0.5434(4)	22(2)	18(3)	17(2)	0	− 2(2)	0	19(1)
B1	4c	0.3353(5)	1/4	0.8189(6)	19(2)	10(3)	24(3)	0	2(2)	0	18(1)
Sr1	4c	0.0874(1)	1/4	0.6177(1)	19(1)	34(1)	29(1)	0	− 1(1)	0	27(1)
Sr2	4c	0.6701(1)	1/4	0.4417(1)	19(1)	35(1)	43(1)	0	0(1)	0	29(1)
Cl1	4c	0.4381(2)	1/4	0.3552(2)	23(1)	40(1)	31(1)	0	− 1(1)	0	32(1)
N1	4c	0.2856(5)	1/4	0.6982(7)	23(4)	35(4)	36(4)	0	− 3(3)	0	31(2)
N2	4c	0.8776(5)	1/4	0.5376(7)	28(4)	39(4)	26(4)	0	− 1(3)	0	31(2)
B1	4c	0.3336(7)	1/4	0.8278(11)	16(4)	40(5)	34(5)	0	11(4)	0	30(2)

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

chlorides M_2BN_2Cl which will be discussed in the next section but also in the compounds M_3CBNX_2 ($X = Cl, Br$) which have been reported earlier (13, 14). For the latter case it was the polar CBN unit found to have a threefold M coordination at the nitrogen site and a $1 + 4$ coordination of M around carbon. However, no indication was given by the authors of how they discriminated between carbon and nitrogen in the CBN unit and this is even more problematic if one considers the somewhat unusual displacements given. To check whether there is a distinct difference between the two terminal sites in the rod group we have analyzed the corresponding point potentials on the basis of lattice energy calculations. The results will be discussed in a later section.

In the [010] projection each of the tetrahedra strands has the shape of a rhomb and its four Ca–Ca vertices are coordinated by four of the linear BN_2^{3-} anions. This gives rise to a nearly tetragonal pattern which is distorted to orthorhombic symmetry by the shape of the rhombs (Fig. 2). A similar building principle is found for the chlorides of the same nominal composition M_2BN_2Cl, which, however, are distinct by the Cl coordination.

The Chlorides M_2BN_2Cl

The structures of the Ca and the Sr compounds are isotypic like those of the fluorides and only minor differences do occur on changing the cations. The main distinction between fluorides and chlorides is the quadratic pyramidal coordination of the chlorine atoms giving rise to $CN = 5$ instead of $CN = 4$. In addition, the relative difference of the distances leads to a more pronounced orthorhombic distortion than for the fluorides. The local coordinations shown in Fig. 3 reveal the distorted octahedral coordinations of the cations of the types $Cl_2(BN_2)_4M$ and $Cl_3(BN_2)_3M$, respectively (Table 4). The different structures found so far seem to indicate that rod-like anions similar to BN_2^{3-} are quite versatile structural entities which allow for a large variety of different arrangements. This is found to be true not only for double salts with halogens of different kinds (4) but also for more complicated triple salts like $Ca_{15}(CBN)_6(C_2)_2O$ (16) and there may be even more complex ones to be found in the future.
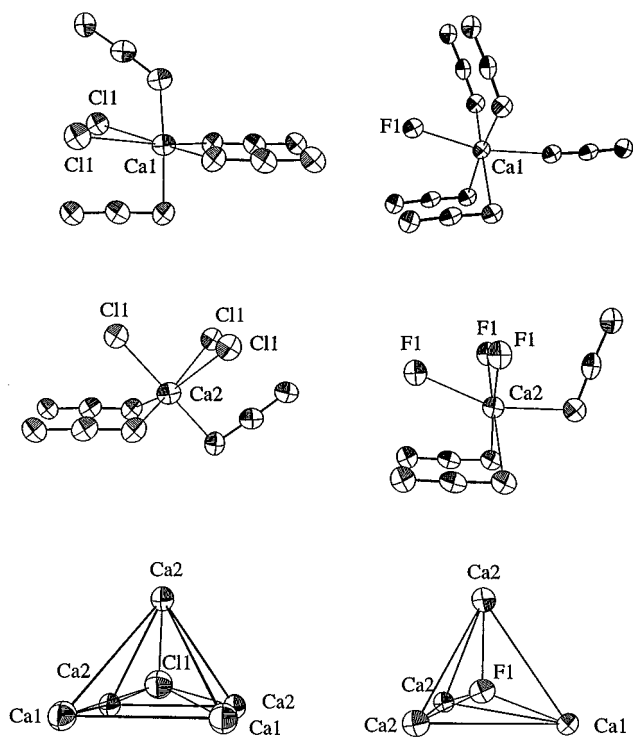
FIG. 3. Local coordinations in Ca_2BN_2X ($X = F, Cl$) (24).

TABLE 4
Bond Lengths [pm] for Ca_2BN_2Cl and Sr_2BN_2Cl

Atom – Paar		d	n	Atom – Paar		d	n
Ca1	– N1	239.3(4)		Sr1	– N2	255.8(4)	2
	– N2	240.8(2)	2		– N1	256.8(4)	
	– N2	254.0(4)			– N2	270.5(7)	
	– Cl1	290.9(1)	2		– Cl1	302.9(2)	2
Ca2	– N1	234.7(2)	2	Sr2	– N1	250.5(4)	2
	– N2	256.3(4)			– N2	272.1(7)	
	– B1	283.0(6)			– B1	293.0(9)	
	– Cl1	284.5(2)			– Cl1	298.6(2)	
	– Cl1	294.6(1)	2		– Cl1	309.8(2)	2
Cl1	– Ca2	284.5(1)		Cl1	– Sr2	298.6(2)	
	– Ca1	290.9(1)	2		– Sr1	302.9(2)	2
	– Ca2	294.6(1)	2		– Sr2	309.9(2)	2
N1	– B1	133.2(7)		N1	– B1	133(1)	
	– Ca2	234.7(2)	2		– Sr2	250.5(4)	2
	– Ca1	239.3(4)			– Sr1	256.7(7)	
N2	– B1	132.9(6)		N2	– B1	135(1)	
	– Ca1	240.8(2)	2		– Sr1	255.8(4)	2
	– Ca1	254.0(4)			– Sr1	270.5(7)	
	– Ca1	256.3(4)			– Sr1	272.3(7)	
B1	– N2	132.9(7)		B1	– N1	133(1)	
	– N1	133.2(7)			– N2	135(1)	
	– Ca2	283.0(6)			– Sr2	293.0(8)	
	– Ca1	303.4(6)			– Sr1	318.9(9)	
	– Ca2	310.1(5)	2		– Sr2	323.0(7)	2

TABLE 3
Bond Lengths [pm] for Ca_2BN_2F and Sr_2BN_2F

Atom – Paar		d	n	Atom – Paar		d	n
Ca1	– N1	238.4(2)	2	Sr1	– F1	253.4(6)	
	– F1	245.2(2)			– N1	258.6(7)	2
	– N2	249.7(3)			– N2	262.1(9)	
	– N2	261.8(2)	2		– N2	277.7(7)	2
Ca2	– F1	233.8(1)	2	Sr2	– F1	247.2(4)	2
	– N1	234.8(2)			– F1	252.6(7)	
	– F1	237.3(2)			– N1	257(1)	
	– N2	257.3(2)	2		– N2	275.8(7)	2
F1	– Ca2	233.8(1)	2	F1	– Sr2	247.2(4)	2
	– Ca2	237.3(2)			– Sr2	252.6(7)	
	– Ca1	245.2(2)			– Sr1	253.4(6)	
N1	– B1	131.6(4)		N1	– B1	134(2)	
	– Ca2	234.8(2)			– Sr2	257(1)	
	– Ca1	238.4(2)	2		– Sr1	258.6(7)	2
	– N2	266.2(3)			– N2	266(1)	
	– F1	323.5(2)	2		– F1	345(1)	2
N2	– B1	134.7(4)		N2	– B1	132(2)	
	– Ca1	249.7(3)			– Sr1	262.1(9)	
	– Ca2	257.3(2)	2		– Sr2	275.8(7)	2
	– Ca1	261.8(2)	2		– Sr1	277.7(7)	2
B1	– N1	131.6(4)		B1	– N2	132(1)	
	– N2	134.7(4)			– N1	134(1)	
	– Ca2	283.7(2)	2		– Sr2	291(1)	2
	– Ca1	301.5(3)	2		– Sr1	318(1)	2
	– Ca2	302.2(3)			– Sr2	320(1)	

Geometry of BN_2^{3-} 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 some distortion which may be taken to be significant. The geometric variations of the hitherto known compounds with such linear anions have been discussed in a recent work of von Schnering *et al.* (12). The variations that we find for the four compounds presented here are in the medium range of distortions. The B–N distances vary between 131.6 and 135.0 pm. According to Pauling's bond-length–bond-strength relation this corresponds to a change

TABLE 5
Angles [deg] for M_2BN_2X

	Atoms	Angles
Ca_2BN_2F	N2–B1–N1	177.0(3)
Sr_2BN_2F	N2–B1–N1	175(1)
Ca_2BN_2Cl	N1–B1–N2	176.5(3)
Sr_2BN_2Cl	N1–B1–N2	177.2(8)
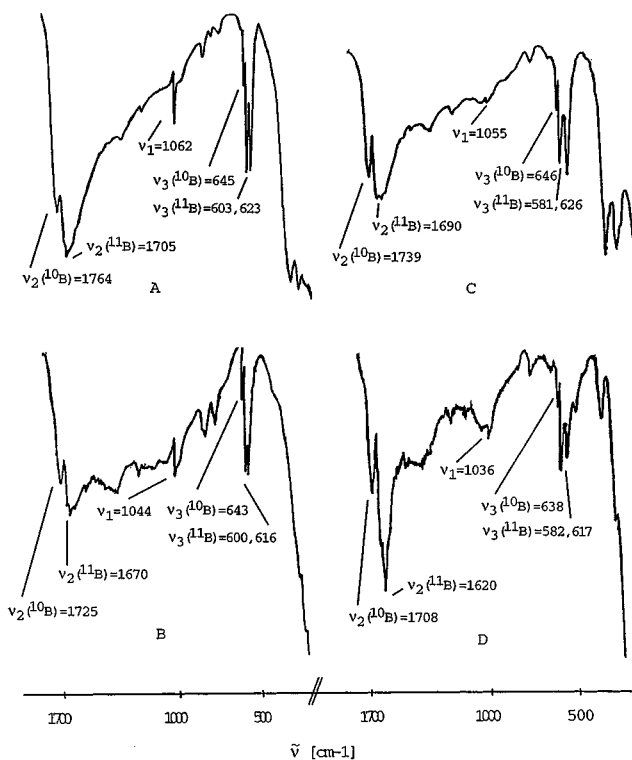
FIG. 4. Measured infrared absorption spectra of M_2BN_2X: (A) spectrum of Ca_2BN_2F; (B) spectrum of Sr_2BN_2F; (C) spectrum of Ca_2BN_2Cl; (D) spectrum of Sr_2BN_2Cl.

of about 11% in strength. The angles vary between 177.2° and 175° and the deviations are fairly small compared to other novel BN_2^{3-} containing phases (4) (Table 5).

The infrared absorption spectra of the four compounds are displayed in Fig. 4. Compounds containing BN_2^{3-} units show the following Raman (R) and Infrared (IR) absorption bands according to the symmetry representations:

$$\Gamma_{vib}\ (D_{\infty h}) = \Sigma_g(R) + \Sigma_u(IR) + \Pi_u(IR)$$

$$\Gamma_{vib}\ (C_{2v}) = 2A_1(R, IR) + B_2(R, IR).$$

The v_1 absorption was somewhat controversial, as discussed in (12), for the compounds $LiMgBN_2$ and $Ba_4(BN_2)_2O$. The

TABLE 6
Vibration Frequences from M_2BN_2X (M = Ca, Sr; X = F, Cl)

Compound	$v_3(^{11}B)$	$v_3(^{11}B)$	$v_3(^{10}B)$	v_1	$v_2(^{11}B)$	$v_2(^{10}B)$
Ca_2BN_2F	603	623	645	1062	1705	1764
Sr_2BN_2F	600	616	638	1044	1670	1725
Ca_2BN_2Cl	581	626	646	1055	1690	1739
Sr_2BN_2Cl	582	617	638	1036	1620	1708

measured infrared absorption bands v_1 (Table 6) for our compounds clearly reveal a symmetry reduction from $D_{\infty h}$ to C_{2v}.

Lattice Energy Calculations

BN_2^{3-}-containing compounds may be understood as typical ionic compounds. The lattice energies, Madelung factors, and point potentials were calculated using the program MADKUG (22) which utilizes an Ewald procedure (Table 7). For the calculation of all the Madelung factors a reference distance of 2.5 Å 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 high compared to rocksalt, the most favorable structure for a binary salt. A polarization can be found by comparing the point potentials (Table 8) for the different N positions. The point potentials of N2 are significantly higher than for N1, showing that the coordination of the nitrogen atoms generates polar BN_2^{3-} groups. The difference of the nitrogen-point potentials for the two different nitrogen atoms in the nitridoborate anions indicates that electrostatic and packing effects may well account for significant distortions of the ideally linear $N=B=N^{3-}$ groups. Despite the fact that some coordination environments change markedly on changing from the fluorides to the chlorides, e.g., those of N1 and N2, it is interesting to note that the reduction of the coordination of N2 from six to five does not lower significantly the corresponding point potentials (Table 8), because the change in the number of neighbors is overcompensated by the reduction of mean cation–anion distance. As a consequence the contribution of the BN_2^{3-} groups to the electrostatic energy is higher for the chlorides than for the fluorides. We thus assume chloride salt melts may be better solvents for BN_2^{3-}-containing compounds than corresponding fluoride melts. The point potentials of the boron positions are close to zero because of the two close negatively charged nitrogen neighbors. This does

TABLE 7
Results of Lattice Energy Calculations (MAPLE[1]) for BN_2^{3-}-Containing Compounds and Double Salts (22)

Compound	Madelung factor	Sum of the square charge	MAPLE (kJ/mol)[1]
$Sr_3(BN_2)_2$	10.520	18	325
$LiSr_4(BN_2)_3$	15.576	26	333
Ca_2BN_2F	8.423	12	390
Sr_2BN_2F	7.900	12	359
Ca_2BN_2Cl	7.929	12	367
Sr_2BN_2Cl	7.519	12	348
Ca_3CBNCl_2	12.604	20	350
Sr_3CBNCl_2	11.956	20	332
NaCl	1.96	2	445

[1] MAPLE was divided by the sum of the squares of charges for comparison.

TABLE 8
Electrostatic Point Potentials P (a.u.), First Coordination Numbers (CN), and Mean Coordination Distances $\bar{d}$ (pm)

Compound	$P(M1)$	$CN/\bar{d}(M1)$	$P(M2)$	$CN/\bar{d}(M2)$	$P(X)$	$CN/\bar{d}(X)$	$P(N1)$	$CN/\bar{d}(N1)$	$P(N2)$	$CN/\bar{d}(N2)$	$P(B1)$	$CN/\bar{d}(B1)$
Ca_2BN_2F	−1.202	6/249.2	−1.310	6/242.4	0.778	4/237.5	0.403	4/211.1	0.531	6/237.1	−0.004	5/294.5
Sr_2BN_2F	−1.133	6/264.7	−1.250	6/259.3	0.749	4/250.1	0.327	4/227.1	0.418	6/250.2	−0.059	5/307.6
Ca_2BN_2Cl	−1.138	6/259.5	−1.224	7/268.9	0.655	5/291.1	0.425	4/210.5	0.500	5/225.0	−0.040	4/301.7
Sr_2BN_2Cl	−1.090	6/274.1	−1.173	7/283.5	0.638	5/304.8	0.356	4/222.7	0.425	5/237.9	−0.067	4/314.5

TABLE 9
Electrostatic Point Potentials P for M_3CBNCl_2 ($M = Ca, Sr$)

Compound	$P(M1)$	$P(M2)$	$P(M3)$	$P(Cl1)$	$P(Cl2)$	$P(C)$	$P(B)$	$P(N)$
Ca_3CBNCl_2	−1.212	−1.201	−1.206	0.680	0.714	1.006	−0.223	0.426
	−1.212	−1.201	−1.206	0.680	0.714	0.561	−0.257	0.866
Sr_3CBNCl_2	−1.157	−1.134	−1.203	0.639	0.687	0.889	−0.243	0.373
	−1.157	−1.134	−1.203	0.639	0.687	0.449	−0.275	0.809

not necessarily mean that there is only weak electrostatic interaction between boron atoms and cations but the distance already shows that it must be somewhat weaker than the nitrogen–cation pairs. This is supported by the observation that there is no real side-on coordination of BN_2^{3-} groups to cations in these compounds. For the compounds Ca_3CBNCl_2 and Sr_3CBNCl_2 Meyer *et al.* have given distinct sites for the carbon and nitrogen atoms obviously on the basis of the (C, N)–B distances which are slightly smaller for the B–N contacts (d(B–N) = 138(1) and 139.3(15) pm; d(B–C) = 144(2) and 143.6(15) pm for the two compounds). Because of the anisotropic displacement parameters we applied a riding model to correct the distances (25) (d(B–N) = 139.7 and 138.8 pm; d(B–C) = 144.7 and 144.5 pm, respectively). This means that a small difference in distances still remains after the correction. Furthermore, we have performed lattice energy calculations employing formal charges, e.g., Ca^{2+}, Sr^{2+}, Cl^-, C^{2-}–B^-–N^- (Table 9). Local point potentials and MAPLE (22) reveal that in the electrostatic picture the distribution of nitrogen and carbon atoms given by Meyer *et al.* is slightly more favorable than the inverse distribution. Thus, it seems that the published distribution is correct.

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