The Last Missing Member of the $AE_2[BN_2]Cl$ Series – Synthesis, Structural and Spectroscopic Characterization of $Ba_2[BN_2]Cl$

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Pale grey-blue, transparent single crystals of $Ba_2[BN_2]Cl$ ($I4_132$ (no. 214), a = 1462.88(1) pm, Z = 24) are obtained by the reaction of Ba, $BaCl_2$, BN and NaN_3 in arc-welded Ta ampoules at 1200 K. The crystal structure was determined by single crystal X-ray structure analysis. The Raman and IR spectra of the title compound show the expected fundamental frequencies (ν_s = 1038; ν_{as} = 1969 and 2087; δ = 616 / 636 cm^{-1}) for a nitridoborate unit with $D_{\infty h}$ symmetry. The [N–B–N] structure obtained by X-ray single crystal structure determination corroborates this finding within the standard deviations of the measurement with d(B–N) = 132.3(8) pm and $\measuredangle$(N–B–N) = 178.5(13)°. Our results compare well to the data reported for cubic and orthorhombic $Ba_3[BN_2]_2$ as well as to the isotypic compound $Ba_2[BN_2]Br$.

Key words: Barium, Chloride, Nitridoborate, Nitride, Structure Elucidation, IR Spectroscopy, Raman Spectroscopy

Introduction

Since quaternary alkaline earth metal halide nitrido borates have been reported for the first time some ten years ago [1], only two different stoichiometries were found to be adopted by those compounds: $AE_2[BN_2]X$ (AE = Mg, Ca, Sr, Ba; X = H, F, Cl, Br, I) [1 – 7] and $AE_8[BN_2]_5X$ [3, 6]. The $AE_2[BN_2]Cl$ series was nearly complete with only the Ba compound missing, and since $Ba_2[BN_2]Br$ [7] was already reported, we thought it would be worth synthesizing $Ba_2[BN_2]Cl$ for comparison. We present here the synthesis and the structural and the spectroscopic characterization of $Ba_2[BN_2]Cl$.

Experimental Section

Synthesis

All manipulations were performed in a glove box under purified argon unless stated otherwise. 415 mg (3.02 mmol) Ba (99.9 %, dendritic, Strem), 210 mg (1.01 mmol) $BaCl_2$ (Alfa Aesar, powder, ultra dry, 99.995 %), 50 mg (2.01 mmol) hexagonal BN (99 %, powder, Aldrich, degassed at 400 K under dynamic vacuum for 2 h) and 45 mg (0.69 mmol) NaN_3 (99 %, powder, Aldrich, degassed at 400 K under dynamic vacuum for 2 h) were intimately ground in an agate mortar and arc-welded into a clean Ta container. The metal container was sealed into an evacuated silica tube. The tube was placed upright in a box furnace and heated to 1200 K within 12 h. After 3 d reaction time the furnace was switched off and allowed to cool to r. t. The product contained as the main product transparent, pale-blue chunky crystals of $Ba_2[BN_2]Cl$ as well as some cube-shaped NaCl crystals. Crystals of $Ba_2[BN_2]Cl$ are moderately air and moisture sensitive.

Crystallographic studies

Samples of the reaction mixture were removed from the glove box in polybutene oil (Aldrich, $M_n \sim 320$, isobutylene > 90 %) for single-crystal selection. A suitable single crystal of $Ba_2[BN_2]Cl$ was selected under a polarization microscope, mounted in a drop of polybutene sustained in a plastic loop, and placed onto the goniometer. A cold stream of nitrogen (T = 173(2) K) froze the polybutene oil, thus keeping the crystal stationary and protected from oxygen and moisture from the air. Preliminary examination and subsequent data collection were performed on a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and graphite-monochromatized MoK_α radiation (λ = 71.073 pm). The orientation matrix and the respective lattice parameters were obtained by using APEX2 [8]. The program SAINT [9] was used to integrate the data. An empirical absorption correc-

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Table 1. Summary of X-ray single crystal structure determination data on $Ba_2[BN_2]Cl$.

Compound	$Ba_2[BN_2]Cl$
Space group (No.), Z	$I4_132$ (214), 24
CSD number	418947
Lattice parameters: a, pm	1462.88(1)
Calculated density, g cm^{-3}	4.44
Crystal color	transparent pale blue
Crystal shape	irregular plate
Crystal size, mm^3	$0.20 \times 0.20 \times 0.04$
Diffractometer	Bruker X8 Apex II equipped with a 4 K. CCD
Radiation; monochromator	MoK_α (λ = 71.073 pm); graphite
Temperature, K	173(2)
Ranges, $2\theta_{max}$	56.37°
h,k,l	±19, $-18 \rightarrow 13$, $-11 \rightarrow 13$
Distance detector-crystal, mm	40
Number of frames	224
Exposure time, sec	10
Data correction	LP, SADABS [10]
Transmission ratio min. / max.	0.634
μ, mm^{-1}	15.4
Reflections: measured / unique	3756 / 659
Unique refls. [$F_o \geq 4\sigma(F_o)$]	621
R_{int}	0.095
Refined parameters	31
Flack parameter x [25]	0.02(12)
Weight factors x / y	0.0296 / 6.22
$R1^a$ / $wR2^b$ / GooF^c (all refls.)	0.035 / 0.074 / 1.074
Max. shift / esd, last refinement cycle	< 0.0005
Res. electron density: max. / min., e Å^{-3}	1.35, 68 pm to Ba3 / -1.20, 74 pm to Ba2

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP$ with $P = [(F_o^2) + 2F_c^2]/3$; [c] GooF: $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, with n being the number of reflections and p being the number of parameters.

Table 2. Atomic coordinates and isotropic thermal parameters[a] (pm^2) of $Ba_2[BN_2]Cl$.

Atom	W.-Site	x	y	z	U_{eq}
Ba1	8b	7/8	7/8	7/8	287(3)
Ba2	24f	0.40895(5)	0	1/4	281(3)
Ba3	16e	0.03162(3)	x	x	308(3)
Cl	24h	1/8	0.7651(2)	0.4849(2)	620(15)
N	48i	0.5606(5)	0.6365(5)	0.0427(5)	308(18)
B	24h	1/8	0.5862(6)	0.6638(6)	211(27)

[a] U_{eq} is defined as a third of the orthogonalized U_{ij} tensors.

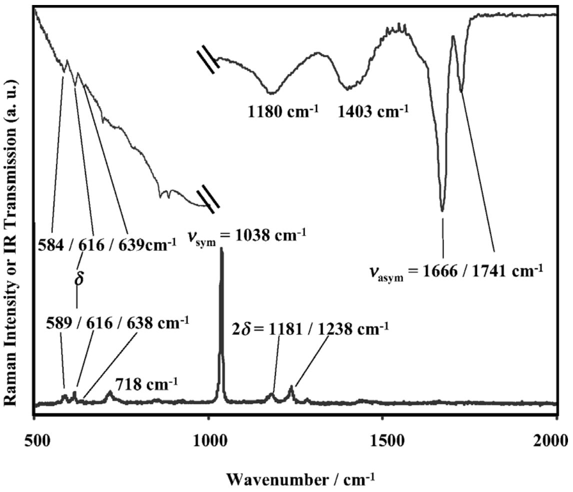

Fig. 1. Raman and IR spectra of $Ba_2[BN_2]Cl$.

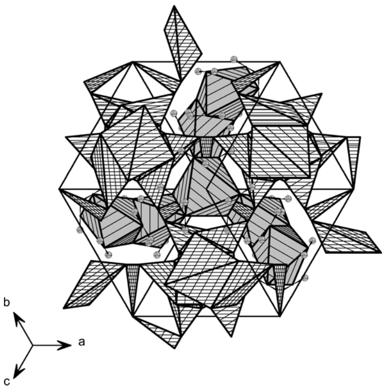

Fig. 2. View of the unit cell of $Ba_2[BN_2]Cl$ parallel to [111]. $(Ba1)[BN2]_6$ are shown as light grey hatched polyhedra, the coordination around the Cl atom in $Cl(Ba2)_2(Ba3)_2$ is displayed as a creased white hatched plane.

tion was applied using SADABS [10]. The initial input file for solving the crystal structure was prepared by XPREP [11]. This program found the space group $I4_132$ (no. 214) to be the only possible one. The initial Ba and Cl positions were obtained by Direct Methods with SHELXS-97 [12], the B and N positions were apparent from the positions of highest electron density in the difference Fourier map resulting from the first refinement cycle by full-matrix least-squares techniques with SHELXL-97 [13]. Doing further refinement cycles, the refinement converged and resulted in a stable model for the crystal structure. Additional crystallographic details are summarized in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 2, and Table 3 displays the anisotropic displacement parameters. Selected bond lengths and angles are listed in Table 4.

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the deposition number CSD-418947.

Vibrational spectra

Raman investigations [microscope laser Raman spectrometer (Jobin Yvon, 1 mW, excitation line at λ = 632.817 nm (HeNe laser), grating: 1800 lines mm^{-1}, 20 × magnification, samples in glass capillaries, 3 × 150 s accumulation time]

Table 3. Anisotropic displacement parameters[a] (pm^2) of $Ba_2[BN_2]Cl$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba1	287(3)	U_{11}	U_{11}	−114(3)	U_{23}	U_{23}
Ba2	220(4)	83(3)	540(9)	33(3)	0	0
Ba3	308(3)	U_{11}	U_{11}	−122(2)	−122(2)	U_{13}
Cl	393(20)	733(20)	U_{22}	326(25)	338(18)	U_{13}
N	177(35)	394(45)	352(46)	−73(34)	−61(33)	125(33)
B	367(75)	132(33)	U_{22}	−12(44)	97(39)	U_{13}

[a] The anisotropic displacement factor takes the form: $U_{ij} = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

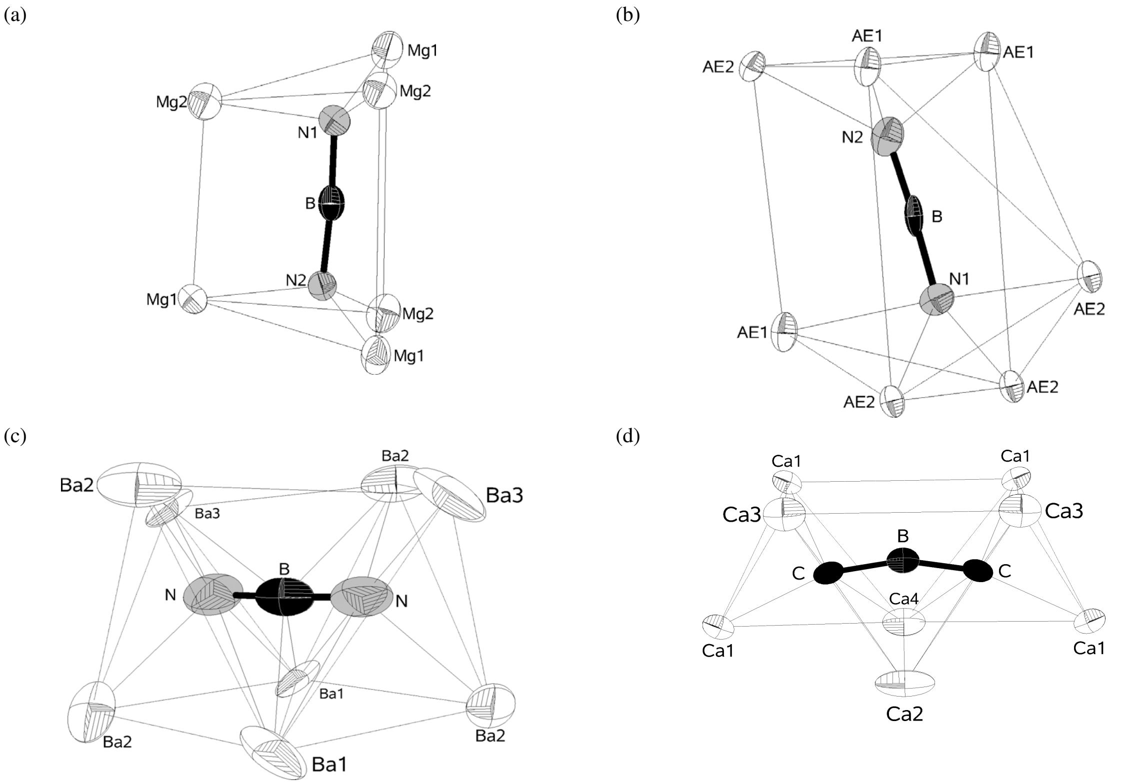

Fig. 3. The coordination environment of triatomic units in $Mg_2[BN_2]Cl$ (a), $AE_2[BN_2]Cl$ (AE = Ca or Sr) (b), $Ba_2[BN_2]Cl$ (c) and, for comparison, in $Ca_9Cl_8[BC_2]_2$(d). The alkaline earth atoms are displayed as white, N as light grey-hatched, B as black hatched, and C as solid black ellipsoids at the 95 % probability level.

Table 4. Selected atomic distances (pm) and angles (deg) in $Ba_2[BN_2]Cl$.

Atoms			Distance	Atoms			Distance
Ba1–	N	6×	297.5(7)	Cl–	Ba2	2×	314.3(3)
	B	6×	314.2(7)		Ba3	2×	328.1(3)
Ba2–	N	2×	271.5(7)	N–	B	1×	132.3(8)
	N	2×	285.9(7)		Ba2	1×	271.5(7)
	B	2×	301.7(7)		Ba3	1×	272.2(8)
	Cl	2×	314.3(3)		Ba2	1×	285.9(7)
					Ba1	1×	297.5(7)
Ba3–	N	3×	272.2(8)	B–	N	2×	132.3(8)
	Cl	3×	328.1(3)		Ba2	2×	301.5(7)
					Ba1	2×	314.2(7)
				∡(N–B–N)		1×	178.5(13)

performed on the same specimen used for single crystal measurements showed ν_{sym} = 1038 and δ = 582/617/639 cm^{-1} (Fig. 1). Unfortunately, the IR investigations could not be done under strictly inert conditions due to the setting of the IR spectrometer. Since some of the CO_2 vibrations are in the region we expected for $\nu_{as}([BN_2]^{3-})$, we used different techniques to obtain all the information about the fundamental frequencies. Thus, IR spectra were obtained either with a Bruker AFS 66 FT-IR spectrometer (KBr pellet technique for the region 500 – 1000 cm^{-1}) or with a Thermo Nicolet instrument with ATR attachment. The IR measurements yielded the deformation modes δ = 582/617/639 cm^{-1} and the asymmetric stretching modes ν_{asym} = 1666/1741 cm^{-1}. The results are displayed in Fig. 1 and summarized in Table 5.

	ν_{sym}	ν_{asym} (^{11}B)	ν_{asym} (^{10}B)	δ (^{11}B)	δ (^{11}B)	δ (^{10}B)	δ (^{10}B)		Ref.
$Mg_2[BN_2]Cl$		1716	1791	604	638		667	IR	[3]
	1080							Raman	
$Ca_2[BN_2]H$	1064	1703	1758	606	625		630	IR	[4]
	1064	1692		603	622			Raman	
$Ca_2[BN_2]F$	1066	1711	1766	605	625		646	IR	[7]
	1066	1690		603	622			Raman	
$Ca_2[BN_2]Cl$	1058	1683	1743	586	628	616	647	IR	[7]
	1055				623			Raman	
$Sr_2[BN_2]F$	1044	1670	1725	600	616		633	IR	[7]
$Sr_2[BN_2]Cl$	1036	1620	1708	582	617			IR	[7]
$Sr_2[BN_2]I$	1023	1659		440	510		673	IR	[7]
$Ba_2[BN_2]Cl$	1038	1666	1741	582	617		639	IR	This
		1663		589	616		638	Raman	work
$Ba_4[BN_2]_2O$		1630	1720		608	625		IR	[14]
	1026							Raman	
c-$Ba_3[BN_2]_2$		1637	1711	585	606	625		IR	[15]
	1028							Raman	
o-$Ba_3[BN_2]_2$	1026	1614/1625	1691/1712	585/590	611/627	635	652	IR	[15]
	1029							Raman	

Table 5. Fundamental frequencies (cm^{-1}) of the $[BN_2]^{3-}$ moiety in alkaline earth metal containing quaternary compounds.

Results and Discussion

Crystal structure

The crystal structure of $Ba_2[BN_2]Cl$ is isotypic to that of $Ba_2[BN_2]Br$ [7]. In this intricate structure (Fig. 2), some complex, four-fold interpenetration of Ba-centered prisms is observed, whereas the prisms are best described as $(Ba1)[BN_2]_6$, $(Ba2)[BN_2]_4Cl_2$ and $(Ba3)[BN_2]_3Cl_3$ (Fig. 3). Due to the size of the Ba^{2+} cation the $[BN_2]^{3-}$ units are coordinating side-on, which is not observed for $AE_2[BN_2]Cl$ (AE = Mg [3], Ca or Sr [1 – 2]) (Fig. 3). For the nitridoborate unit we have found a very similar coordination environment as in the ionic compound $Ca_9Cl_8[BC_2]_2$ [16], which contains $[BC_2]^{5-}$ units. In both cases, the triatomic moieties are surrounded by a bicapped trigonal prism formed by Ca^{2+} cations, but for the title compound we have found the prism to be distorted (Fig. 3).

While the coordination pattern of the $[BN_2]^{3-}$ anions is thus familiar, the one of the Cl^- ions is quite unusual. The halide ions are located inside the channels created by the Ba^{2+} centered rows of prisms (Fig. 2), with a low coordination number and a rather flat coordination polyhedron (Fig. 4).

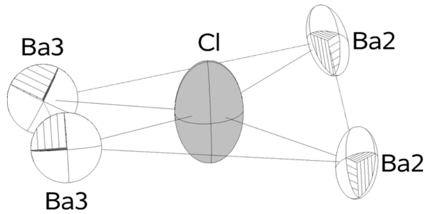

Fig. 4. The coordination environment of the Cl atom. Ba atoms are displayed as white hatched and Cl atoms as light grey crossed ellipsoids at the 95 % probability level.

Conclusion

The family of quaternary alkaline earth metal nitrido borates of the stoichiometry $AE_2[BN_2]Cl$ has been completed by adding the so far missing Ba compound – if one neglects Be. The structure of the title compound is a complex 3D structure which is completely different from the 2D structure adopted by $Ca_2[BN_2]Cl$ and $Sr_2[BN_2]Cl$. Nevertheless, the vibrational spectra are in the range expected for this class of compounds.

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