Orthoborate Halides with the Formula $(M^{+II})_5(BO_3)_3X$: Syntheses, Crystal Structures and Raman Spectra of $Eu_5(BO_3)_3Cl$ and $Ba_5(BO_3)_3X$ (X = Cl, Br)

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Single crystals of $Eu_5(BO_3)_3Cl$ were obtained by serendipity by reacting Eu_2O_3 and Mg with B_2O_3 at 1300 K in the presence of an NaCl melt for 13 h in silica-jacketed Nb ampoules. $Ba_5(BO_3)_3X$ (X = Cl, Br) crystals were formed by direct synthesis from appropriate amounts of $Ba(OH)_2$, H_3BO_3 and the respective barium halide (hydrate) in alumina crucibles kept in the open atmosphere at 1300 K for 13 h. The crystal structures of the title compounds were determined with single-crystal X-ray diffraction. All compounds crystallize isotypically to $Sr_5(BO_3)_3Cl$ in the orthorhombic space group $C222_1$ (no. 20, Z = 4) with the lattice parameters a = 1000.34(7), b = 1419.00(9), c = 739.48(5) pm for $Eu_5(BO_3)_3Cl$, a = 1045.49(5), b = 1487.89(8), c = 787.01(4) pm for $Ba_5(BO_3)_3Cl$, and a = 1048.76(7), b = 1481.13(9) and c = 801.22(5) pm for $Ba_5(BO_3)_3Br$. The Raman spectra of all compounds were acquired and are presented and compared to literature data. The incremental volume of the orthoborate $(BO_3)^{3-}$ anion has been determined and is compared to the Biltz volume.

Key words: Incremental Volume, Barium, Europium, Chloride, Bromide, Orthoborate, Raman Spectra

Introduction

Orthoborates with the general stoichiometry $(M^{+II})_5(BO_3)_3X$ (M = divalent metal; X = halide or cyanide) [1 – 6] have been found to crystallize with at least four different crystal structures (Table 1). It is interesting to note that except for the pseudo-halide $Ba_5(BO_3)_3(CN)$ [7] no barium orthoborate of this general formula has been reported as yet. Triggered by the discovery of this pseudo-halide compound, and after obtaining single crystals of $Eu_5(BO_3)_3Cl$, we wanted to find out if a Ba analog could be synthesized.

We report the syntheses, the structural characterization by X-ray single-crystal methods and the Raman spectra of $Ba_5(BO_3)_3Cl$, $Ba_5(BO_3)_3Br$ and $Eu_5(BO_3)_3Cl$. From these results and from literature data, we calculated with the help of Biltz volumes of the monoatomic cations and anions the incremental volume of the $(BO_3)^{3-}$ orthoborate anion which is considerably smaller than the one expected just from the sum of the Biltz volumes for B^{3+} and O^{2-}.

Experimental Section

Syntheses

All manipulations were carried out under normal atmosphere. All reaction mixtures were placed in a box furnace and heated over 13 h from r. t. to 1300 K. This temperature was held for 13 h, then the furnace was shut off and allowed to cool to r. t. $Eu_5(BO_3)_3Cl$ was obtained while attempting to synthesize EuB_4 by reacting 360 mg (1.02 mmol) Eu_2O_3 (Ventron, powder, 99.99 %), 85 mg (7.86 mmol) B (Strem, crystalline, 99.5 %), and 75 mg (3.09 mmol) Mg (Aldrich, chips, 99.98 %) in 200 mg (3.42 mmol) NaCl (Fisher Scientific, powder, 99.9 %) which was intended to serve as a

M	F	Cl	Br	CN
Mg	*Pna*2_1 [1]	–	–	–
Ca	*Cm* (8) [2, 3]	–	–	–
Sr	*Pnma* (62) [4]	$C222_1$ (20) [5]	$C222_1$ (20) [4]	–
Eu	*Pnma* (62) [6]	**$C222_1$ (20)**	–	–
Ba	–	**$C222_1$ (20)**	**$C222_1$ (20)**	$C222_1$ (20) [7]

Table 1. Space group symmetry of $(M^{+II})_5(BO_3)_3X$ compounds. In this table, identical symmetry is indicating isotypical structures. Symbols given in bold are results obtained in this work.

molten flux. This reaction took place in silica-jacketed, cleaned and arc-welded Nb ampoules.

The barium compounds were obtained in a different way. 300 mg (1.75 mmol) $Ba(OH)_2$ (Fisher Scientific, Analytical Grade), 75 mg (1.21 mmol) H_3BO_3 (Fisher Scientific, Analytical Grade) and 100 mg (0.48 mmol) $BaCl_2$ (Alfa Aesar, powder, ultra dry, 99.995 %) or 150 mg (0.45 mmol) $BaBr_2 \cdot 2\ H_2O$ (Fisher Scientific, Analytical Grade) were ground intimately in an agate mortar, the mixture placed in an alumina boat and subjected to the same temperature program as described above under normal atmosphere. In the case of $Eu_5(BO_3)_3Cl$, the main product (about 50 % as estimated by the color and habit of the crystals) consisted of red-orange transparent crystals and amorphous black material with some NaCl. Regarding the barium compounds, in both cases a transparent, colorless layer of the respective crystalline compound was found of which only a few crystals were secured by extracting them with force from the sintered mass. In the case of the reaction of the chloride only $Ba_5(BO_3)_3Cl$ crystals were obeserved; in the case of the reaction with the bromide about four out of five crystals showed lattice parameters of $Ba_5(BO_3)_3Br$, while the other crystals showed hexagonal symmetry (see below).

$Eu_5(BO_3)_3Cl$, $Ba_5(BO_3)_3Cl$ and $Ba_5(BO_3)_3Br$ react with air and/or moisture after a few days and yield either X-ray-amorphous products or $BaCO_3$.

Raman spectroscopy

Single crystals of the title compounds were sealed under a protective argon atmosphere inside pyrex capillaries and used for the Raman investigations (microscope laser Raman spectrometer: Jobin Yvon, 1 mW, excitation line at λ = 632.817 nm (HeNe laser), 20× magnification, 3600 s accumulation time; Fig. 1). The crystals were taken out of the pyrex capillaries and measured again after a few days. $Eu_5(BO_3)_3Cl$ crystals then exhibited no Raman peaks, while the spectrum of $Ba_5(BO_3)_3Cl$ showed the same spectrum as obtained before with considerably lower intensities, but at 1059 cm^{-1} a vibration typical for $BaCO_3$ was observed. For $Ba_5(BO_3)_3Br$, the carbonate signal was even more pronounced.

Crystallographic studies

Samples of the reaction mixtures were removed from the glove box in polybutene oil (Aldrich, $M_n \sim 320$, isobutylene > 90 %). Suitable single crystals were 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. Preliminary examination and subsequent data collection were performed

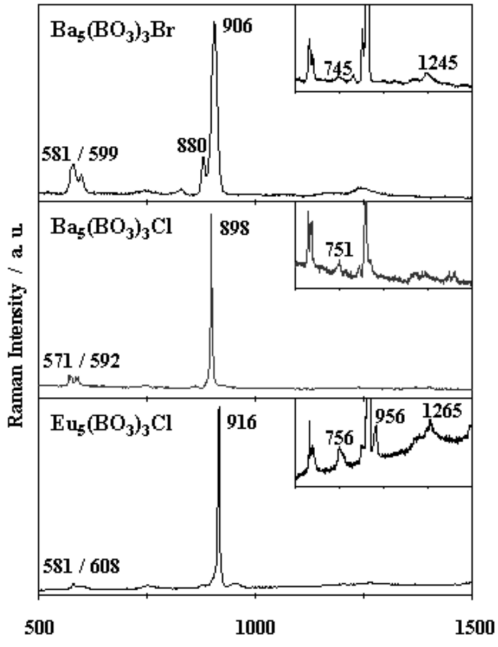

Fig. 1. Raman spectra of $Eu_5(BO_3)_3Cl$, $Ba_5(BO_3)_3Cl$ and $Ba_5(BO_3)_3Br$ (bottom to top). Raman intensity is displayed on the vertical axis in arbitrary units. In the top right corner of each spectrum, an inset from 500 to 1500 cm^{-1} is shown with different scaling of the Raman intensity (scaled up 10 times) to emphasize observed Raman modes with low intensities.

on a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and using 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 correction was applied using SADABS [10]. The initial input files were prepared by XPREP [11]. The atomic positions known for $Sr_5(BO_3)_3Cl$ [5] were used as a starting model. These positions were refined by full-matrix least-squares techniques with SHELXL-97 [12]. For $Ba_5(BO_3)_3Br$, the coordinates had to be inverted since the Flack parameter [13] was unusually high. After this operation, the Flack parameter was considerably lower, but since the refined value of 0.13(2) deviated significantly from zero, we applied the refinement as an inversion twin which resulted in no improved R values and a twin ratio of 0.86 : 0.14 nearly equalling the previously observed Flack parameter.

Additional crystallographic details are given in Table 2. Atomic coordinates and anisotropic and equivalent isotropic displacement coefficients are shown in Table 3. Table 4 displays selected bond lengths and angles.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karls-

Table 2. Details of the X-ray single-crystal structure determinations on $Eu_5(BO_3)_3Cl$, $Ba_5(BO_3)_3Cl$ and $Ba_5(BO_3)_3Br$.

Compound	$Eu_5(BO_3)_3Cl$	$Ba_5(BO_3)_3Cl$	$Ba_5(BO_3)_3Br$
Crystal color	transparent red	transparent colorless	transparent colorless
Crystal shape	irregular polyhedron	block	block
Crystal size, mm^3	$0.04 \times 0.04 \times 0.04$	$0.08 \times 0.10 \times 0.15$	$0.08 \times 0.10 \times 0.12$
Crystal system		— orthorhombic —	
Space group (no.), Z	$C222_1$ (20), 4	$C222_1$ (20), 4	$C222_1$ (20), 4
a, pm	1000.34(7)	1045.49(5)	1048.76(7)
b, pm	1419.00(9)	1487.89(8)	1481.13(9)
c, pm	739.48(5)	787.01(4)	801.22(5)
M_r	971.68	3594.32	3772.16
V, $Å^3$	1049.7(1)	1224.3(1)	1244.6(1)
D_{calcd}, g cm^{-3}	6.15	4.88	5.03
F(000), e	1676	1536	1608
T, K		173(2)	
Diffractometer		— Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector —	
Radiation, monochromator		— MoK_α (λ = 71,073 pm), graphite —	
Scan mode		— φ- and ω-scans —	
$2\theta_{max}$, deg	72.87	68.2	66.41
hkl range	$\pm 16, -18 \rightarrow 23, -12 \rightarrow 9$	$-16 \rightarrow 12, -23 \rightarrow 19, -6 \rightarrow 12$	$-13 \rightarrow 16, -22 \rightarrow 16, -10 \rightarrow 12$
μ(MoK_α), mm^{-1}	29.7	16.1	18.8
Data correction		— Lp, SADABS [10] —	
Transmission: min. / max.	0.584 / 0.747	0.517 / 0.747	0.528 / 0.747
Reflections: measured / unique	5968 / 2561	5538 / 2469	5092 / 2391
R_{int}	0.044	0.032	0.025
$\lvert E^2 - 1 \rvert$	0.772	0.732	0.763
Unique refls. with $F_o \geq 4\,\sigma(F_o)$	2229	2297	2285
Refined parameters	80	85	86
$R1$[a] / $wR2$[b] / GoF[c] (all refl.)	0.0426 / 0.0671 / 1.052	0.0307 / 0.0588 / 1.037	0.0263 / 0.0467 / 1.044
Max. shift / esd	< 0.001	< 0.001	< 0.001
Weighting factors x / y[b]	0.0193 / 0	0.0226 / 0	0.0152 / 0
Extinction coefficient	0.00159(6)	–	–
Flack parameter [13]	−0.07(5)	−0.03(4)	0.00(3)
Twin ratio	–	–	0.86 : 0.14
$\Delta\rho_{fin}$ (max, min), $e^- Å^{-3}$	3.24 (72 pm to Eu2), −2.03 (68 pm to Eu3)	1.41 (76 pm to Ba1), −2.90 (71 pm to Ba2)	1.53 (71 pm to Ba2), −1.37 (144 pm to O4)
CSD number	422555	422556	422557

[a] $R1 = \Sigma\|\|F_o| - |F_c\|| / \Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})]^{1/2}$.

ruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-422555 for $Eu_5(BO_3)_3Cl$, CSD-422556 for $Ba_5(BO_3)_3Cl$, and CSD-422557 for $Ba_5(BO_3)_3Br$.

Calculating the incremental volume of the $(BO_3)^{3-}$ anion with Biltz volume increments

The molar volumes of several compounds containing the $(BO_3)^{3-}$ anion were used to determine the incremental volume of this anion by subtracting the Biltz volume increments for the respective monoatomic cations and anions [14 – 16] from the respective molar volume determined experimentally by X-ray methods. The obtained values (Table 5) were averaged to yield $V((BO_3)^{3-})$ = 28.3(12) $cm^3\,mol^{-1}$ which is considerably smaller than expected from the sum of the Biltz volume increments for V = $V(B^{3+}) + 3\times V(O^{2-})$ = 33.0 $cm^3\,mol^{-1}$.

Results and Discussion

Raman spectra of $M_5(BO_3)_3X$ (M = Eu or Ba, X = Cl or Br)

The Raman spectroscopic data show clearly the presence of the orthoborate $(BO_3)^{3-}$ anion when compared to compounds containing this anion such as $La^{10}BO_3$ [22] and $Eu_5(BO_3)_3F$ [6] (Table 6). The symmetric stretching mode is clearly detectable in the Raman spectra of the title compounds, and the data are comparable to the frequencies known for $La^{10}BO_3$ [22] and $Eu_5(BO_3)_3F$ [6].

Table 3. Atomic coordinates, anisotropic[a] and equivalent isotropic[b] displacement parameters (pm^2) of $Eu_5(BO_3)_3Cl$, $Ba_5(BO_3)_3Cl$ and $Ba_5(BO_3)_3Br$.

Atom	Wyck. site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Eu1	4*a*	0.76147(5)	0	0	58(2)	60(2)	40(2)	−5(2)	0	0	53(1)
Eu2	8*c*	0.13207(4)	0.87270(3)	0.93957(5)	62(2)	60(2)	69(2)	3(2)	−1(1)	2(2)	64(1)
Eu3	4*b*	1/2	0.86474(4)	3/4	66(2)	47(2)	30(2)	0	3(2)	0	48(1)
Eu4	4*b*	1/2	0.13836(4)	3/4	66(2)	59(3)	32(2)	0	−2(2)	0	52(1)
Cl	4*b*	0	0.0516(2)	3/4	95(12)	122(12)	74(10)	0	−7(10)	0	97(5)
O1	4*a*	0.5076(8)	0	0	–	–	–	–	–	–	66(13)
O2	8*c*	0.6693(6)	0.8096(4)	0.0076(10)	67(23)	93(25)	82(22)	−7(26)	−22(25)	36(19)	81(10)
O3	8*c*	0.3538(6)	0.8008(4)	0.9857(9)	95(26)	89(24)	57(23)	−3(22)	−3(23)	−58(20)	81(10)
O4	8*c*	0.6967(6)	0.0000(5)	0.3378(7)	132(27)	127(27)	48(21)	−28(27)	21(19)	−39(28)	102(11)
O5	8*c*	0.8814(6)	0.8534(4)	0.8820(8)	78(27)	47(26)	117(24)	25(21)	−16(22)	15(21)	81(11)
B1	8*c*	0.8010(9)	0.7887(7)	0.9664(11)	37(32)	58(35)	45(37)	1(28)	−17(24)	5(28)	47(15)
B2	4*a*	0.3689(12)	0	0	–	–	–	–	–	–	25(16)
Ba1	4*a*	0.76097(4)	0	0	50(2)	70(2)	74(2)	−4(2)	0	0	65(1)
Ba2	8*c*	0.13403(3)	0.87042(2)	0.94355(4)	63(1)	75(1)	81(1)	−2(1)	2(1)	3(1)	73(1)
Ba3	4*b*	1/2	0.86305(3)	3/4	65(2)	67(2)	56(2)	0	6(2)	0	53(1)
Ba4	4*b*	1/2	0.14132(3)	3/4	64(2)	78(3)	56(2)	0	−5(2)	0	66(1)
Cl	4*b*	0	0.0470(1)	3/4	87(8)	129(9)	93(7)	0	−14(7)	0	103(3)
O1	4*a*	0.5062(5)	0	0	56(22)	112(24)	91(21)	−24(24)	0	0	86(10)
O2	8*c*	0.6783(4)	0.8118(3)	0.0080(6)	73(17)	82(17)	123(18)	−23(18)	−9(17)	8(14)	93(7)
O3	8*c*	0.3573(4)	0.7921(3)	0.9851(6)	106(18)	99(17)	117(19)	−13(16)	7(17)	−23(15)	107(8)
O4	8*c*	0.6915(4)	−0.0015(3)	0.3465(5)	95(17)	116(18)	98(16)	−2(18)	40(14)	16(19)	103(7)
O5	8*c*	0.8797(4)	0.8507(3)	0.8801(6)	88(19)	130(20)	99(17)	7(15)	53(15)	−14(17)	105(8)
B1	8*c*	0.8059(6)	0.7905(4)	0.9680(7)	68(24)	67(25)	58(29)	9(19)	5(19)	10(21)	64(11)
B2	4*a*	0.3722(9)	0	0	91(33)	50(31)	57(29)	−10(30)	0	0	67(13)
Ba1	4*a*	0.24154(4)	0	0	57(2)	57(2)	83(1)	0(2)	0	0	66(1)
Ba2	8*c*	0.86195(3)	0.13112(2)	0.06496(4)	71(1)	62(1)	90(1)	5(1)	−1(1)	3(1)	74(1)
Ba3	4*b*	1/2	0.13847(3)	1/4	74(2)	62(2)	50(2)	0	7(2)	0	62(1)
Ba4	4*b*	1/2	0.85966(3)	1/4	75(2)	65(2)	48(2)	0	−2(2)	0	63(1)
Br	4*b*	0	0.94443(5)	1/4	110(3)	133(3)	88(3)	0	−4(3)	0	110(1)
O1	4*a*	0.4936(5)	0	0	86(22)	69(18)	100(21)	2(23)	0	0	85(9)
O2	8*c*	0.3188(3)	0.1875(2)	0.9898(6)	64(16)	88(13)	124(17)	−4(17)	22(17)	17(12)	92(7)
O3	8*c*	0.6405(4)	0.2079(2)	0.0147(5)	101(16)	66(13)	103(17)	−14(15)	7(17)	−28(12)	90(7)
O4	8*c*	0.3120(3)	0.0000(3)	0.6507(4)	141(18)	85(14)	70(15)	−3(17)	46(13)	−19(16)	99(7)
O5	8*c*	0.1191(4)	0.1485(2)	0.1205(5)	97(19)	104(15)	104(16)	16(14)	31(15)	10(14)	102(7)
B1	8*c*	0.1925(6)	0.2091(4)	0.0306(7)	68(24)	60(20)	84(29)	−21(20)	16(19)	−20(18)	70(11)
B2	4*a*	0.6243(8)	0	0	85(34)	3(23)	100(31)	−15(31)	0	0	63(12)

[a] The anisotropic displacement factor takes the form: $U_{ij} = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$; [b] U_{eq} is defined as one third of the orthogonalized U_{ij} tensor, $U_{23} = U_{13} = 0$.

The crystal structure of $M_5(BO_3)_3X$ (M = Eu or Ba, X = Cl or Br)

As can already be deduced from their transparency, all $M_5(BO_3)_3X$ compounds are ionic, electroneutral compounds, therefore consisting of M^{2+} cations, trigonal-planar $(BO_3)^{3-}$ orthoborate anions and X^- anions. The crystal structure itself can be described by focussing on the halides which are coordinated by the divalent metal cations in a distorted octahedral fashion. These $[M_6X]$ octahedra form face-sharing $^1_\infty[M_{6/2}X]$ columns running parallel to the crystallographic *c* axis. The columns are linked to each other *via* the $((B2)O_3)^{3-}$ anions which are oriented perpendicular to the crystallographic *b* axis to form planes. The plane at $b = 1/2$ is shifted by $1/2$ *a* and $1/4$ *c* relative to the planes at $b = 0$ and 1 (Fig. 2). The layers are held together by metal cations surrounding the ortho-borate ions coplanar to the *bc* plane and the second type of ortho-borate species $((B1)O_3)^{3-}$. The orthoborate moieties are coordinated differently by M^{2+} cations. $((B1)O_3)^{3-}$ anions are located in a tetragonally distorted antiprism (Fig. 3a) while the $((B2)O_3)^{3-}$ anions orientated perpendicular to the *b* axis have a distorted tricapped trigonal prismatic coordination (Fig. 3b) which is also known for BN_3^{6-} anions [23].

It is noteworthy that the *b* axis of the unit cell of $Ba_5(BO_3)_3Cl$ is by nearly 7 pm shorter than the

Table 4. Selected atomic distances (pm) and bond angles (deg) for $Eu_5(BO_3)_3Cl$ (1), $Ba_5(BO_3)_3Cl$ (2) and $Ba_5(BO_3)_3Br$ (3). If not indicated otherwise, the multiplicity is one.

		*M*1	*M*2		*M*3		*M*4	B1		B2
Cl(1)	2×	310.59(8)	285.8(1)		–		–	–		–
			318.6(2)							
Cl(2)	2×	325.66(5)	304.80(9)		–		–	–		–
			334.5(2)							
Br(3)	2×	333.27(4)	311.71(4)		–		–	–		–
			345.53(7)							
O1(1)		253.9(8)	–	2×	266.6(1)	2×	269.8(1)	–		138.9(14)
O1(2)		266.4(5)	–	2×	283.32(4)	2×	288.04(4)	–		140.1(10)
O1(3)		264.4(5)	–	2×	286.75(3)	2×	288.75(3)	–		137.0(9)
O2(1)	2×	285.6(6)	264.2(6)	2×	266.6(6)	2×	257.(7)	138.4(11)		–
O2(2)	2×	293.1(4)	277.7(4)	2×	285.9(5)	2×	275.5(5)	140.8(8)		–
O2(3)	2×	289.4(4)	276.0(4)	2×	291.3(4)	2×	279.1(4)	140.1(7)		–
O3(1)		–	246.5(6)	2×	245.0(6)	2×	258.9(6)	142.1(11)		–
O3(2)		–	262.9(4)	2×	260.1(4)	2×	274.9(4)	139.1(7)		–
O3(3)		–	261.8(4)	2×	260.5(4)	2×	277.0(4)	139.3(6)		–
O4(1)	2×	258.7(5)	260.1(7)	2×	282.5(7)	2×	285.5(6)	–	2×	136.7(8)
			298.4(7)							
O4(2)	2×	282.2(4)	277.7(4)	2×	297.2(5)	2×	298.6(5)	–	2×	138.0(6)
			311.3(5)							
O4(3)	2×	289.5(3)	275.1(4)	2×	295.3(4)	2×	297.4(4)	–	2×	138.0(5)
			317.7(4)							
O5(1)	2×	255.5(6)	239.8(6)		–		–	137.0(11)		–
			255.8(6)							
O5(2)	2×	271.3(4)	256.8(8)		–		–	137.0(8)		–
			272.2(4)							
O5(3)	2×	272.4(4)	254.1(4)		–		–	138.4(7)		–
			274.5(4)							

Table 5. Experimental volumes of compounds containing the $(BO_3)^{3-}$ anions and calculated incremental volumes of $(BO_3)^{3-}$ anions determined using the Biltz volumes [16 – 18] of monoatomic cations and anions.

Compound	*Z*	V_{exp} in Å^3 of the unit cell	V_{exp} in Å^3 $Z = 1$	V_{exp} in cm^3 mol^{-1} $Z = 1$	ΣV_{Biltz} in cm^3 mol^{-1} of M^{+II} and X^{-I}	$V(BO_3{}^{3-}) = (V_{exp} - \Sigma V_{Biltz})/n(BO_3{}^{3-})$	Ref.
$Mg_3(BO_3)_2$	2	204.3	102.15	61.5	6.0	27.75	[17]
$Ca_3(BO_3)_2$	6	765.6	127.6	76.84	19.5	28.67	[18]
$Sr_3(BO_3)_2$	6	889.8	148.3	89.31	33.0	28.16	[19]
$Eu_3(BO_3)_2$	6	893.34	148.89	89.66	32.4	28.63	[20]
$Mg_5(BO_3)_3F$	4	678.39	169.6	102.13	19.5	27.54	[1]
$Ca_2(BO_3)Cl$	4	418.81	104.7	63.05	33.0	30.05	[21]
$Ca_5(BO_3)_3F$	2	453.4	226.7	136.52	42.0	31.51	[2, 3]
$Sr_5(BO_3)_3F$	4	998.1	249.53	150.26	64.5	28.59	[4]
$Sr_5(BO_3)_3Cl$	4	1053.9	263.48	158.66	75.0	27.89	[5]
$Sr_5(BO_3)_3Br$	4	1059.0	264.75	159.4	80.0	26.47	[4]
$Eu_5(BO_3)_3F$	4	1006.1	251.53	151.47	63.5	29.32	[6]
$Eu_5(BO_3)_3Cl$	4	1049.7	262.43	158.03	74.0	28.01	this work
$Ba_5(BO_3)_3Cl$	4	1224.3	306.08	184.32	100.0	28.11	this work
$Ba_5(BO_3)_3Br$	4	1244.6	311.15	187.37	105.0	27.46	this work

corresponding value for $Ba_5(BO_3)_3Br$ despite the increase in the ionic radius of the halide anion. An analogous observation can be made for $Sr_5(BO_3)_3Cl$ [5] and $Sr_5(BO_3)_3Br$ [4], but here the decrease of the *b* axis of the unit cell is only 0.5 pm. The $[BrBa_6]$ octahedra are larger than the $[ClBa_6]$ octahedra which causes a rotation of the $((B1)O_3)^{3-}$ anions of the bromide compounds around their threefold axis. This happens in such a way that the coordination of the $((B1)O_3)^{3-}$ anions stays nearly identical, but the packing in the *b* direction is more dense resulting in the decrease of the *b* unit cell parameter.

	$La^{10}BO_3$ [22]	$Eu_5(BO_3)_3F$ [6]	$Eu_5(BO_3)_3Cl$	$Ba_5(BO_3)_3Cl$	$Ba_5(BO_3)_3Br$
ν_{sym}	*939*	**917**	**916**	**898**	**906**
		952			
ν_{asym}	*1330*	**1362**	–	–	–
		1272 / 1381			
δ	*741*	*769*	**756**	**751**	**745**
γ	*606*	*591*	**581/608**	**571/592**	**581/599**

Table 6. Optical frequencies (given in cm^{-1}) for selected compounds containing the $(BO_3)^{3-}$ orthoborate anion. Frequencies obtained by Raman measurements are printed bold, IR results are given in italics.

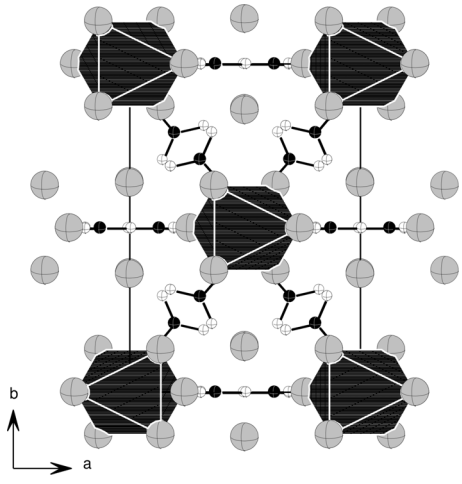

Fig. 2. Non-perspective view of the unit cell of $(M^{+II})_5(BO_3)_3X$ compounds with $C222_1$ symmetry. Black $[XM_6]$ octahedra are displayed white-hatched. *M* are shown as light grey, B as black and O as white crossed octands. No displacement ellipsoids are used for clarity.

The incremental volume of the $(BO_3)^{3-}$ anion

The incremental volume of the orthoborate anion calculated with the help of the Biltz volumes of the monoatomic cations and anions unexpectedly is by more than 14 % smaller than that calculated with the incremental Biltz volumes. This difference is due to the covalent bonding between boron and oxygen in this polyatomic anion. Nevertheless, the obtained average value seems to be a good estimate for the molar volume of the $(BO_3)^{3-}$ anion, since the distribution around the calculated average is rather narrow.

Conclusion

The Raman spectra and the structures of $Eu_5(BO_3)_3Cl$, $Ba_5(BO_3)_3Cl$ and $Ba_5(BO_3)_3Br$ have been determined. The results match quite well the already reported data for compounds with the same or similar stoichiometry and structure containing the orthoborate $(BO_3)^{3-}$ anion. The incremental volume of this anion was determined to be 28.3(12) $cm^3\ mol^{-1}$ or 47.0(7) $Å^3$ per anion.

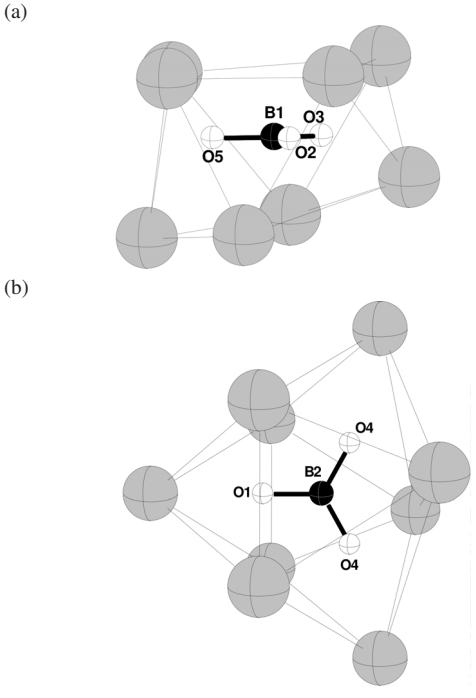

Fig. 3. Coordination polyhedra around the $(BO_3)^{3-}$ anions. Fig. 3a shows the coordination of $((B1)O_3)^{3-}$, while Fig. 3b displays the coordination of $((B2)O_3)^{3-}$. The same color code as for Fig. 2 is used.

Final Remark

While pursuing this work, we encountered two more compounds crystallizing in the space group $P6_3mc$ (no. 186). The general formulae were confirmed to be $Ba_7(BO_3)_3F(Y)_4$ (a = 1117.5(2) and c = 723.7(2) pm) and $Ba_7(BO_3)_3Br(Z)_4$ (a = 1118.1(1) and c = 723.9(2) pm), but neither by X-ray nor by spectroscopic methods the nature of the missing moieties *Y* and *Z* could be determined. Considering the educts and the experimental conditions, *Y* and *Z* are expected to be either F^-, O^{2-} and OH^-, or O^{2-} and OH^-, respectively. $Ba_7(BO_3)F_5$ [24] was reported to crystallize in the space group $P31c$ (no. 161) with a = 1120.8(5) and c = 725.0(2) pm, but the crystallographic coordinates of this compound have not been given.

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