Aluminium and gallium trihalide adducts of 2,4,6-triorganylborazines and the synthesis of triorganylborazinium tetrabromoaluminates [1]

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Dedicated to Prof. Dr. Rosalinda Contreras Theurel on the occasion of her 60th birthday

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Abstract
Borazines of type $R_3B_3N_3H_3$ (R = Me, Et, i-Pr, *t*-Bu, Ph) add $AlBr_3$ and $GaCl_3$ in a 1:1 ratio to one of its N atoms. During this process the planarity of the borazine is lost. The ring system of the adducts show a semi chair conformation. HBr gas reacts with $R_3B_3N_3H_3 \cdot AlBr_3$ in toluene with formation of hitherto unknown borazinium tetrabromo aluminates $(R_3B_3N_3H_4)^+ (AlBr_4)$. The ring system of the cation is almost planar but it shows like the adducts three different B-N bond lengths.

Keywords: 2,4,6-Triorganylborazine EX_3 Adducts, 2,4,6-triorganylborazinium salts, IR, NMR, X-ray structures


Introduction

Borazines are isoelectronic and isolobal with benzenes but their chemical reactivity is grossly different.[2-5] This is due to the inherent B-N bond polarity which places a partial negative charge on the nitrogen atoms and a partial positive charge on the boron atoms. For example: borazine $(HB=NH)_3$ adds 3 equivalents of HBr or HCl to form the cycloborazane $[H(X)B-NH_2]_3$ [6] and HCl adds to $(ClB=NMe)_3$ with formation of $(Cl_2B-NHMe)_3$. [7]

While BCl_3 or BBr_3 give no adducts with borazines of type $(HB=NH)_3$, $(HB=NR)_3$ or $(R'B=NR)_3$ they induce substitution reactions at the boron atoms with formation of B-haloborazines. [8] In contrast, AlX_3 (X = Cl, Br) forms stable 1:1 adducts with $(MeB=NMe)_3$.[9] while $SnCl_4$ reacts with $(HB=NR)_3$ by an H/Cl exchange.[10] One can speculate whether the

addition of HCl to a borazine occurs stepwise with the first step being the formation of a borazinium cation $R_3B_3N_3H_4^{+\cdot}$ So far, this kind of borazinium cation is presently unknown. As we will show here, cations of this type are readily accessible.

Synthesis and characterization of EX$_3$ adducts of borazines

Synthesis. Adducts **1** to **10** can be prepared by reacting equivalent amounts of the respective borazine with either AlBr$_3$ or GaCl$_3$ in toluene as shown in Eq. (1). Yields ranged from 45 % to 100 % (see experimental part):

$$(1)$$
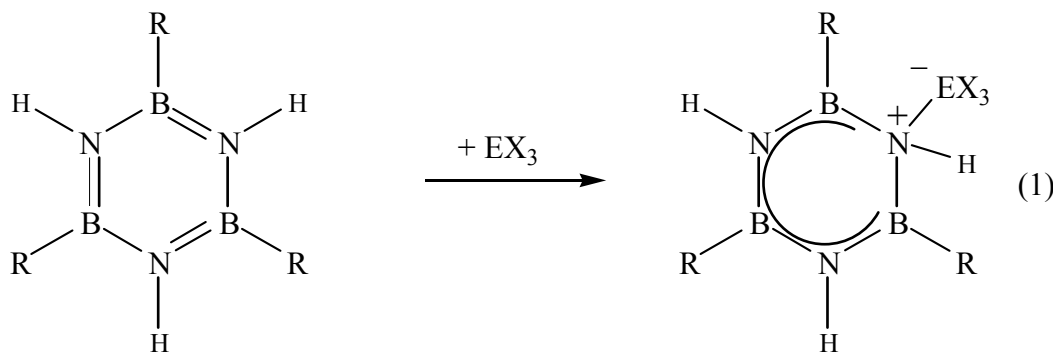
1	R = Me,	EX$_3$ = AlBr$_3$
2	R = Ph,	EX$_3$ = AlBr$_3$
3	R = Et,	EX$_3$ = AlBr$_3$
4	R = i-Pr,	EX$_3$ = AlBr$_3$
5	R = t-Bu,	EX$_3$ = AlBr$_3$
6	R = Me,	EX$_3$ = GaCl$_3$
7	R = Ph,	EX$_3$ = GaCl$_3$
8	R = Et,	EX$_3$ = GaCl$_3$
9	R = i-Pr,	EX$_3$ = GaCl$_3$
10	R = t-Bu,	EX$_3$ = GaCl$_3$

Compounds **2 - 5** and **8** crystallized in tiny needles or very thin plates. These crystals were, however, unsuitable for a crystal structure determination in contrast to well shape crystals of compounds **1**, **6**, **7** and **10**.

NMR spectroscopy. Table 1 contains NMR data of compounds 1 to 10. In all cases the ^{11}B resonances are at lower field than the parent borazines. The ^{11}B nuclei of the AlBr$_3$ adducts are deshielded compared with the GaCl$_3$ adducts indicating that AlBr$_3$ seems to be a stronger Lewis acid than GaCl$_3$. One should note that only a single ^{11}B resonance signal is observed for all these compounds at ambient temperature although two are expected with an intensity ratio of 2:1. This suggests that the EX$_3$ part in these compounds is fluxional at room temperature. This is

supported by the ^{1}H NMR data: only one set of signals for the B-organyl groups is observed instead of the expected two. At –80°C, however, two ^{11}B NMR signals at δ = 38.6 and 42.4 ppm and two ^{1}H NMR signals at δ = 0.18 and 0.36 ppm (intensity ratio1 : 2) are observed for compound 1.

Table 1. Chemical shifts for ^{11}B, ^{27}Al and ^{1}H (in ppm) of the parent borazines and their $AlBr_3$ or $GaCl_3$ 1 : 1 adducts in C_6D_6

Compound	$\delta^{11}B$	$\delta^{27}Al$	δ^1H
MeB=NH)$_3$	36.0		0.23
(MeB=NH)$_3$AlBr$_3$, **1**	38.4	107.8	0.31
(MeB=NH)$_3$GaCl$_3$, **6**	40.5		0.19
(PhB=NH)$_3$	34.8		7.28 – 7.53
(PhB=NH)$_3$AlBr$_3$, **2**	37.6	97.1	6.99 – 7.55
(PhB=NH)$_3$GaCl$_3$. **7**	36.9		7.17 – 7.57
(EtB=NH)$_3$	35.4		0.77 q., 0.94 t
(EtB=NH)$_3$AlBr$_3$, **3**	42.6	96.0	0.85 q, 0.99 t
(EtB=NH)$_3$GaCl$_3$, **8**	41.9		0.78 q, 0.97 t
(iPrB=NH)$_3$	37.4		0.36 sept., 1.25 d
(iPrB=NH)$_3$AlBr$_3$, **4**	43.6	95.9	0.46 sept, 1.19 d
(iPrB=NH)$_3$GaCl$_3$, **9**	40.5		0.38 sept, 1.13 d
(t-BuB=NH)$_3$	37.1		0.98 s
(t-BuB=NH)$_3$AlBr$_3$, **5**	42.4	95.6	1.00 s
(t-BuB=NH)$_3$GaCl$_3$, **10**	40.8		1.01 s

The protons of the alkyl groups are deshielded relative to the parent borazines. This is to be expected because the EX$_3$ group removes electron density from the borazine rings. Except for compounds **1** and **6** the protons of the GaCl$_3$ adducts are less deshielded than the AlBr$_3$ adducts supporting the already mentioned conclusion that AlBr$_3$ is the stronger Lewis acid. However, in case of adducts **1** and **6** this order is reversed. A similar behaviour has been observed for AlBr$_3$ and GaCl$_3$ adducts of aminoboranes. [11]

The Al nuclei of the adducts **1** to **5** are deshielded by 10 to 20 ppm with respect to Al$_2$Br$_6$.. [11] The fairly large difference in the shielding of the ^{27}Al nucleus between (MeB=NH)$_3$.AlBr$_3$ and the other members of the (RB=NH)$_3$AlBr$_3$ series is most likely not a steric effect because in this case the shift difference should increase in the order Et < i-Pr < t-Bu. It may be that the N atoms of trimethylborazine unit are more basic than in the other trialkylborazines. This would fit with the NMR shift for the triphenylborazine-AlBr$_3$ adduct **2**.

IR spectroscopy. The IR spectra of adducts **1** to **10** show many bands. The most intense bands are cited in table 2. Two or three NH stretching bands are expected for the adducts. The NH band of the tetra-coordinated nitrogen atom should be at lower wave number than those of the tri-co-

ordinated N atom. One can note that the positions of these bands are almost unaffected whether $AlBr_3$ or $GaCl_3$ is coordinated. Characteristic IR bands for the BN vibrations of borazines have already been summarized. [2] They are found in the region from 1480 to 1300 cm^{-1}. For each pair of $(RB=NH)_3EX_3$ (EX_3 = $AlBr_3$, $GaCl_3$) compounds the strongest band at highest wave numbers (1562 to 1506 cm^{-1}) stems from a $GaCl_3$ adduct. The largest difference is found for the t-butyl derivatives **5** and **10**. However, we could not find a proper assignment for the B_2N vibrations of the tetra-coordinated N1 atoms. Also, only a tentative assignment is made for the N-E- stretching bands. The difference in the wave number between pairs of $AlBr_3/GaCl_3$ compounds is largest with 99 cm^{-1} while the difference for most others is in the order of 50 to 60 cm^{-1}.

Table 2. Selected IR bands (cm^{-1}) of the $AlBr_3$ and $GaCl_3$ 1: 1 adducts of borazines $(RB=NH)_3$

Compound	νNH	νCH	νBN	νNE	νEX$_3$
$(MeB=NH)_3AlBr_3$, **1**	3447, 3415, 3406	2970, 2945	1509, 1497,1475	496, 486	430. 383
$(MeB=NH)_3GaCl_3$, **6**	3447, 3409	2978, 2950	1511, 1499, 1439	437, 428	404. 375
$(PhB=NH)_3AlBr_3$, **2**	3437, 3420	3076, 3053, 3015	1506, 1473	506, 472	430, 399
$(PhB=NH)_3GaCl_3$, **7**	3432, 2420	3080, 3056, 3015	1509, 1476	447	411 360, 339
$(EtB=NH)_3AlBr_3$, **3**	32442, 2292	2963, 2920, 2877	1521, 1490	495	418, 399, 367,
$(EtB=NH)_3GaCl_3$, **8**	3446, 3393	2963, 2920, 2877	1523, 1489, 1446,	446	394, 377, 343
$(iPrB=NH)_3AlBr_3$, **4**	3445, 3424	2053, 2902, 2877	1519, 1480	500, 476	420, 399
$(iPrB=NH)_3GaCl_3$, **9**	3444, 3424	2953, 2900, 2869	1525m 1491		408, 394, 361
$(tBuB=NH)_3AlBr_3$, **5**	3456, 3416, 3405	2950, 2891, 2865	1533, 1495, 1485	491, 473, 464	414, 365, 336
$(tBuB=NH)_3GaCl_3$, **10**	3542, 3422	2940, 2892, 2863	1562, 1495, 1486	392	392, 380, 367

Structures of the adduct molecules. Single crystals have been obtained for the $AlBr_3$ adduct 1, and of the $GaCl_3$ adducts 6, 7 and 10. Relevant bond lengths and bond angles are listed in Table 3 together with the data for $(MeB=NMe)_3AlBr_3$ [9] although these data are less accurate. Figures 1, 2; 3 and 4 show the molecular structures of these four adducts. It should be noted that the crystals of compound 6 have the composition $(MeB=NH)_3GaCl_3 \cdot MePh$. They contain a site disordered toluene molecule. The addition of $AlBr_3$ or $GaCl_3$ to borazines $(RB=NH)_3$ changes the ring planarity of the borazines into a semichair conformation with the EX_3 coordinated N1 atom

moving above the B1 to B3 five-membered part of the six-membered ring. Particularly noticeable is compound 10 where these 5 atoms are slightly twisted out of the mean plane through B1 to B3 as shown by the respective torsion angles. The interplanar angles between B1N1B3 and B1N2B2N3B3 vary from 22.1° for **6** to 28.0° for **10**. This locates the Al atom or the Ga atoms 0.323 (1), 0.292 (6), 0.353 (7) and 0.375 (10) Å above the B1N2B2N3B3 plane, respectively.
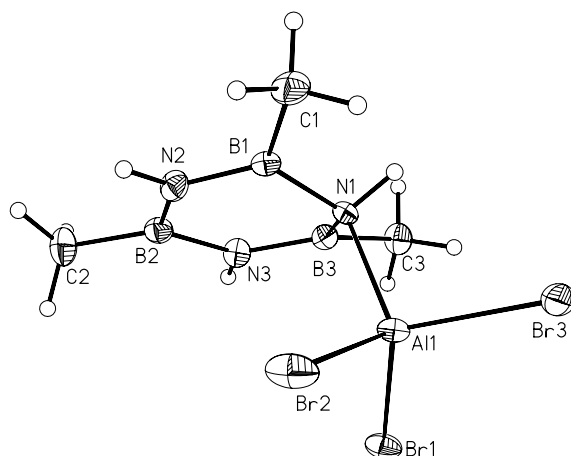

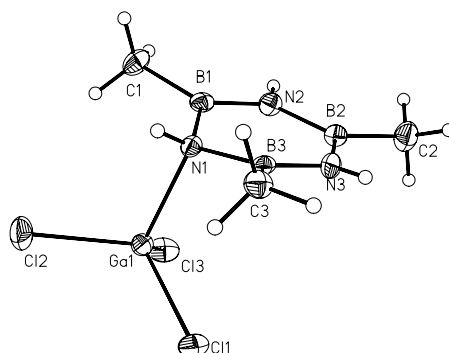**Figure 1a.** ORTEP plot of compound **1.**

Figure 2. ORTEP plot of compound **6.**

Adduct formation at N1 leads to a B-N bond lengthening from 1.504 up to 1.526 Å as expected for tetra-coordinated N atoms. Within the 3σ criterion these bonds can be considered ofalmost equal lengths. This formation of the tetra-coordinated N1 atom induces two different pairs of B-N bond lengths for B1-N2 and B3-N3 on the one hand and N2-B2 and B2-N3 on the other hand. The first pair is significantly shorter than the second pair whose lengths correspond nicely with BN bond lengths determined in borazines (1.41 to 1.43 Å). [13]
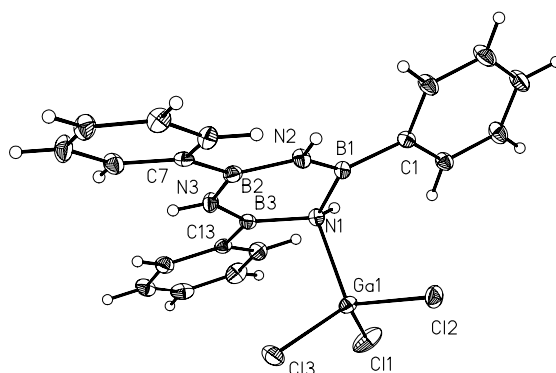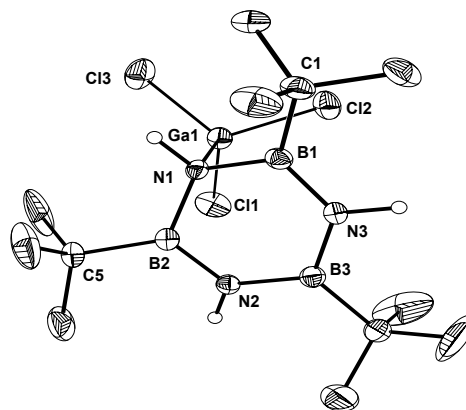
Figure 3. ORTEP plot of compound **7.**

Figure 4. ORTEP plot of compound **10.**

Another feature which is a consequence of the asymmetry induced by atom N1 is that the endocylic bond angles at the boron atoms and atoms N2 and N3 deviate significantly from 120°. The B1-N1-B3 bond angles range from 117.2 to 118.8° which deviate by 7.3 to 8.9° from the ideal tetrahedral bond angles. But more significant are the changes for the N-B-N bond angles at the B atoms which are quite acute with 113.4 to 115.4°. On the other hand, B-N-B bond angles at atoms N2 and N3 are wide with an average close to 126°.

The semichair conformation has still another consequence. The carbon atoms bonded to atoms B1 and B3 are sitting below the B1N2B2N3 plane as shown by the interplanar angle between the planes N3B3C11N1 and N1B1N2B2N3B3 of 7.0° for **1**, 11.0° for **6**, 8.5° for **7** and 17.7 ° for **10**.

Table 3. Selected bond lengths (Å) and bond angles (°) of compounds **1**, **6**, **9** and **10** as well as of (MeB=NMe)$_3$AlBr$_3$

Compound	1	6	7	10	(Me$_3$B$_3$N$_3$Me$_3$)AlBr$_3$ [9]
N1-B1	1.522(6)	1.511(5)	1.522(6)	1.505(5)	1.52(2)
B1-N2	1.403(7)	1.390(5)	1.410(6)	1.401(5)	1.40(2)
N2-B2	1.436(8)	1.447(5)	1.441(6)	1.431(5)	1.44(2)
B2-N3	1.443(7)	1.435(4)	1.437(7)	1.444(4)	1.41(2)
N3-B3	1.397(7)	1.401(5)	1.398(7)	1.401(5)	1.39(1)
B3-N1	1.504(7)	1.520(4)	1.510(5)	1.526(4)	1.54(2)
B1-N1-B3	117.9(4)	118.8(3)	118.1(4)	117.2(2)	109.5(19)
N1-B1-N2	114.5(4)	115.4(3)	113.4(4)	114.5(3)	118(1)
B1-N2-B2	125.7(4)	125.9(3)	125.3(4)	125.4(3)	120(1)
N2-B2-N3	115.4(5)	114.9(3)	115.2(4)	114.9(3)	117(1)
B2-N3-B3	125.5(5)	126.6(3)	125.9(4)	126.3(3)	124(1)
N3-B3-N1	115.0(4)	113.6(3)	114.9(4)	114.3(3)	114(1)
N1-E-X1	108.0(1)	110.2(1)	103.3(1)	108.16(8)	
N1-E-X2	109.6(1)	104.6(1)	108.1(1)	107.68(8)	
N1-E-X3	105.6(1)	113.6(5)	108.0(1)	103.04(9)	
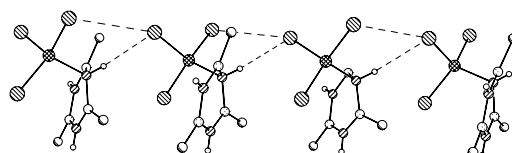
**Figure 1b.** H··Br and Br··Br contacts between molecules **1.**
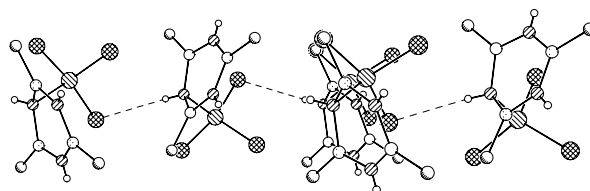
Figure 2b. N-H··Cl hydrogen bonds in between molecules **6.**

In the solid state the molecules of **1** are associated via a N-H···Br bridges to two different AlBr$_3$ molecules forming a chain structure (see Figure 1b) and similar N-H···Cl bridge bonds are found in compound **6** (Figure 2b). There is no hydrogen bond interaction between the NH group

and a Cl atom in $(PhB=NH)_3GaCl_3$, **7**, but there are three in compound **10**. One shows a H·Cl distance of 2.77 Å and an N-H-Cl bond angle of 170.5°, the other H atoms binds to two Cl atoms of the same $GaCl_3$ unit with H·Cl distances of 2.98 and 2.72 Å and N-H·Cl angles of 133.9 and 138.6°.

2,4,6-Triorganylborazinium tetrabromoaluminates

Synthesis. There are several options for generating borazinium salts: i) by replacement of a boron bonded halogen atom as a halide by a strong neutral nucleophile as shown in Eq. (2), -ii) by heterolytic cleavage of a boron halogen bond with a strong halide acceptor as depicted in Eq. (3); and iii) by addition of a proton to an N atom of neutral borazines as indicated in Eq. (4).

R	Et	tBu
E	Al	Al
X	Br	Br
	11	**12**
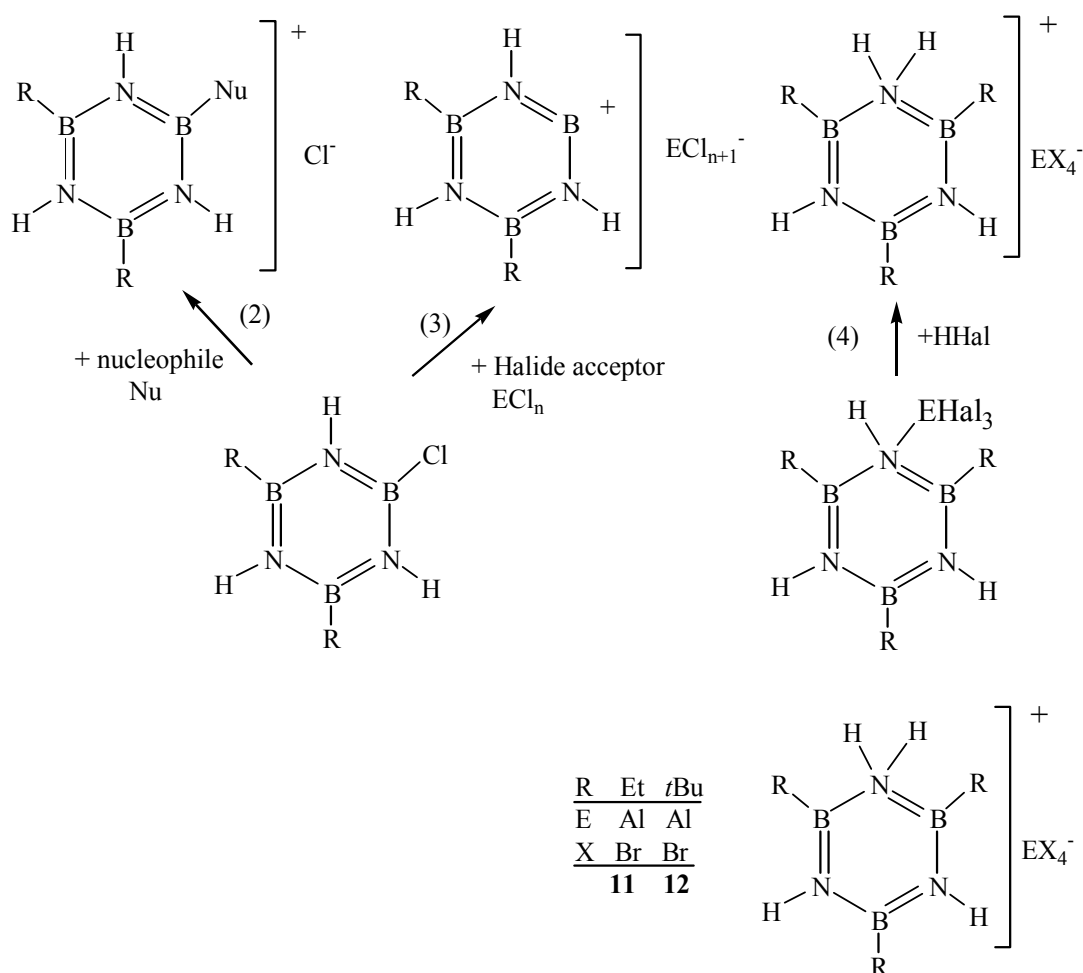
Amongst these reactions (3) is most likely not favored because a borazinium ion with a di-coordinated boron atom would be generated and this will be accompanied by an increased steric strain. A reaction as shown in Equ. (2) has been observed in the reaction of 2,4,6-trichloroborazine with pyridine. Up to 4 molecules of pyridine can add to trichloroborazine $(ClB=NH)_3$. The nature of these adducts have so far not been characterized. [15-17] except for the

1:5 adduct which has been structurally characterized as a penta(pyridine)borazinium^{3+} trichloride. [17] It is also well known that borazines add hydrogen halides up to a 1 : 3 ratio. The latter are cyclotriborazanes [R(Hal)B-NH$_2$]$_3$. [18] Therefore, the formation of borazinium ions is obviously not favored. However, its formation can be expected when the halide anion is replaced by a less nucleophilic and larger anion. From this point of view one may expect that trifluromethylsulfonic acid would be a candidate for borazinium salt formation, as well as HSbF$_6$ or H[Al(Hal)$_4$]. In this study we reacted HBr with the borazine aluminium tribromide adducts **3** and **5** in toluene in order to generate the comparatively large tetrabromoaluminate. We observed a reaction according to Eq. (4). Compounds **11** and **12** were obtained as single crystals suitable for an X-ray structure determination.

NMR and IR spectra. The IR spectra of the borazinium salts **11** and 12 (see table 4) show more bands in the NH and NB region than the EX$_3$ adducts **1 – 10**. In 11 and 12 we have one NH$_2$ group and two NH groups. The former should lead to two IR bands (v_{as} and v_{sym}), the other two may either be degenerate or - if combined – can also lead to two bands at higher wave numbers. Actually, only two bands were located for **11** but four for **12**. In the region of the BN valence bonds four strong band were observed for **11** but only three for **12**. We assign the bands at lower wave numbers to the NB$_2$ vibration of the tetracoordinated N atom, the others to the remaining BN ring atoms. The strongest bands for the parent borazines are 1485 cm^{-1} for (RB=NH)$_3$ (R = Me, Et, Bu) and 1472 cm^{-1} for (PhB=NH)$_3$. [5] So, the high frequency data at 1533, 1520 for **11** and 1518 cm^{-1} for **12** indicates stronger BN bonding for the planar B1 to B3 part of the borazinyl cation. The strong band at 423 cm^{-1} is typical for the AlBr$_4$ anion.

Table 4. Selected IR bands (wave numbers in cm^{-1}) for the borazinium salts **11** and **12** recorded as hostaflon/nujol mulls

Compound	v (NH)	v (CH)	v (BN)	v (AlBr)
[Et$_3$B$_3$N$_3$H$_4$]AlBr$_4$, **11**	3392	2943, 2962, 2928, 2878	1533, 1492, 1463	424 st
[tBu$_3$B$_3$N$_3$H$_4$]AlBr$_4$, **12**	3415 m,3403 st, 2754st	2942, 2891, 2864	1518. 1486, 1459	423 st

Table 5. ^{11}B, ^{1}H and ^{27}Al chemical shifts of the borazinium tetrabromoaluminates (δ in ppm)

Compound	δ ^{11}B	δ ^{1}H	δ ^{27}Al
[Et$_3$B$_3$N$_3$H$_4$]AlBr$_4$, **11**	36.9, 38.0	0.81, 1..03 (q, BC*H*$_2$ 0.94 (t, CH$_2$C*H*$_3$) 4.65 (N*H*)(	84.6
[tBu$_3$B$_3$N$_3$H$_4$]AlBr$_4$, **12**	37.9, 44.2	1.01 C*H*$_3$, 4.58 (N*H*)	84.3

Table 5 summarizes NMR shifts for the two borazinium tetrabromoaluminates. Compared with the δ ^{11}B data for the respective AlBr$_3$ adducts **3** and **5** the boron nuclei of **11** and **12** are

better shielded by 5.7 and 4.7 ppm in **11** and -1.8 and 4.5 ppm for **12**. In contrast, the ^{1}H NMR data reveal two different CH_2B groups in **11** but only one CH_3 group. The intensity ratio for these three signals is 4 : 2 : 9. Obviously the signals for the CH_3 groups show the same chemical shift. On the other hand, only a single ^{1}H NMR signal is found for the *tert*.-butyl groups in **12**. This observation fits with a fluxional behaviour. For both borazinium cations only a single broad proton resonance for the NH groups is observed at 4.65 and 4.38 for **11** and **12** respectively. The tetrabromoaluminate ion is represented by a sharp signal at 84.5 ppm. [13]

Molecular structures. The borazinium salt **11** crystallizes in rectangular platelets. They are orthorhombic, space group $Pca2_1$, Z = 4. The colorless prisms of compound **12** are also orthorhombic, space group $Pna2_1$, Z = 4. Relevant bonding parameters for both compounds are listed in Table 6. Figures 5a and 6a show the molecular units. The six membered borazinium rings are almost planar.
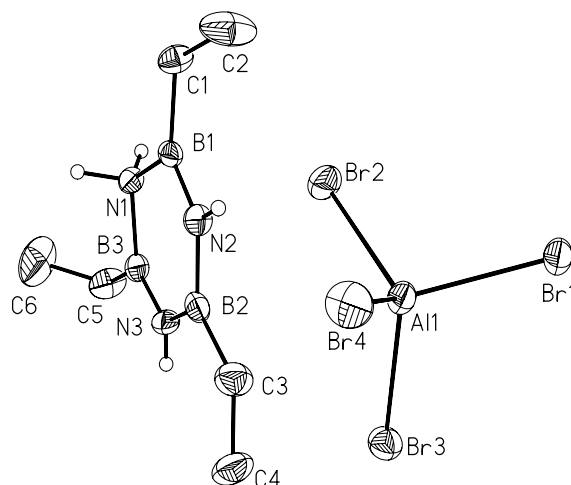

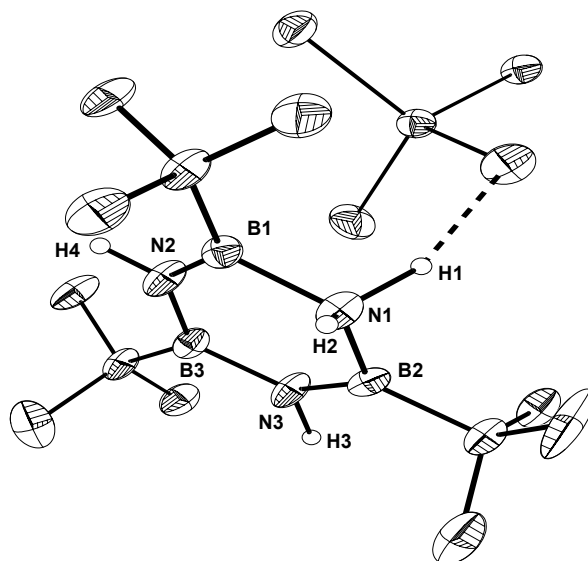**Figure 5a.** ORTEP plot of compound **11** CH atoms omitted.

Figure 6a. ORTEP plot of compound **12** CH atoms omitted.

Table 6. Selected bond lengths and bond angles of the borazinium tetrabromoaluminates **11** and **12**

Compound	11	12		11	12
B1-N1	1.56(1)	1.56(1)	B1-N1-B3	118.4(7)	122.4(6)
B1-N2	1.38(1)	1.37(1))	N1-B1-N2	115.8(7)	112.1(7)
B2-N2	1.44(1)	1.42(1)	B1-N2-B2	124.8(8)	129.9(7)
B2-N3	1.43(1)	1.46(1)	N2-B2-N3	118.8(8)	114.4(7)
B3-N3	1.36(1)	1.39(1)	B2-N3-B3	127.4(8)	127.3(7)
B3-N1	1.56(1)	1.52(1)	N3-B3-N1	114.7(9)	113.7(7)
Al1-Br1	2,299(2)	2.296(3)	Br1-Al1-Br2	106.5(1)	107.9(1)
Al1-Br2	2.295(3)	2.295(3)	Br2-Al1-Br3	110.6(1)	111.0(1)
Al1-Br3	2.292(3)	2.264(3)	Br1-Al1-Br3	107.2(1)	111.9(1)
Al1-Br4	2.270(3)	2.311(2)	Br1-Al1-Br4	106.6(1)	106.5(1)

The B1-N1-B3 plane forms an interplanar angle with the other BN atoms of 8.9° for **11** and 4.2° for **12**. The arrangement of the Et groups in **11** are asymmetric and reduces the point group symmetry to C_1. The angles for N2-B2-C3 and N3-B2-C3 differ by 4.3°, while those of N1-B3-C5 and N3-B3-C5 differ by 11.1° similar to the difference of bond angles for N1-B1-C1 and N2-B1-C1 of 12.2°. While the ethyl group at atoms B1 and B2 are almost coplanar with the ring the torsion angle C6-C5-B3-N1 is 53.5° and the torsion angle C6-C5-B3-N3 122.9°.

The effect of the protonation of the borazine rings is the same as for the addition of EX$_3$ molecules: The N1-B bonds are long (1.56 Å), the adjacent BN bonds are short and the B-N

bond to the *para*-B2 atom is typical for borazines. This indicates that the borazinium cation has lost its pseudoaromatic character. Also the endocyclic ring angles correspond with those of the adducts. The alterations are larger for the 2,4,6-tri(*t*-butyl)borazinium cation than for the ethyl derivative, most likely a steric effect. The N1 atom in **11** lays 0.119Å above the ring plane, and in case of **12** 0.085 Å. All other ring atoms are less than 0.09 Å apart from the mean plane through atoms B1N2B2N3B3.
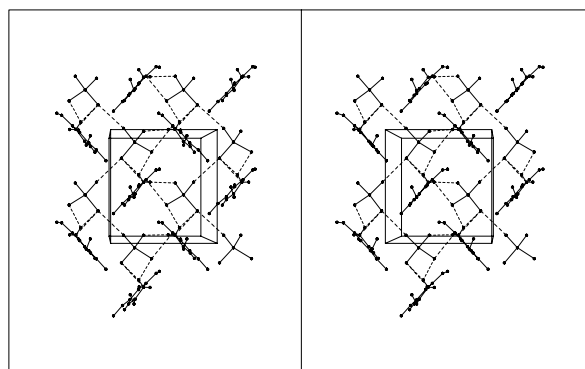

Figure 5b. Stereoplot of the unit cell of compound **11** showing N-H·Br interaction down the b-axis.
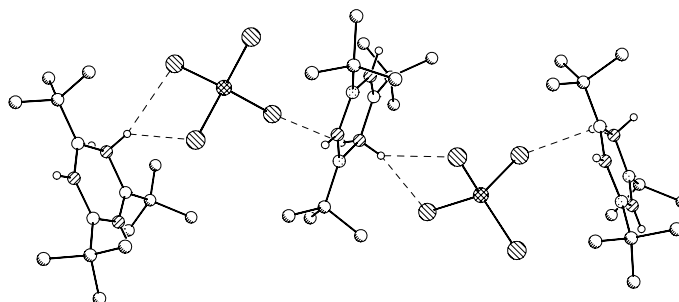
Figure 6b. Part of the chain structure of compound **11**, view down.

Discussion

Borazines of type $(RB=NH)_3$ add readily $AlBr_3$ and $GaCl_3$ in a 1:1 ratio. But even more interesting is the fact that the $AlBr_3$ adducts react with HBr to form the hitherto unknown borazinium salts $[R_3B_3MN_3H_4]AlBr_4$. There is a close structural relationships between the adducts and the borazinium cations. The BN bonds to the tetra-coordinated nitrogen atom N1 are long (aver. 1.56 Å). The adjacent two BN bonds are rather short (aver. 1.38 Å) while the BN

bonds to atom B2 in *para* position resemble those of borazines. [14-19] However, the B_3N_3 rings of the EX_3 adducts possess a semichair conformation while the rings of the two borazinyl cations are almost planar. This corresponds with *ab initio* calculations for the cation $H_3B_3N_3H_4^+$.[20] The N1-B bond lengths of the borazinium cations are about 3% larger than in the adducts and fall already into the range for amine borane adducts (1.58 – 1.64 Å), while those of B1-N2 and B3-N3 are already close to aminoboranes (1.36 Å).

As pointed out, the B1-N1-B3 bond angle is rather wide for a tetracoordinated N atom, but they are close to the calculated value for the parent borazinium cation (118.0°). [20] The molecular parameters of the cation in compound **12** deviate approximately by 3° from the calculated values. This is due to the influence of the rather bulky *t*-butyl group.

A consequence of the semichair conformation of the adducts **1** to **10** is that the boron bonded C atoms are bent in the opposite direction of atom N1. The organyl groups at atoms B1 and B3 in the $AlBr_3$ adducts are more strongly bent backwards than in the $GaCl_3$ adducts. This may be due to the longer Ga-N bonds, although the lengths difference to the Al-N bond is fairly small. The longer B-N bonds to atom N1 and the open B1-N1-B3 bond angle results in an increase of the B1-B3 distance. Consequently the B1-N2 and B3-N3 bonds are no longer parallel to one another.

The ready formation of compounds **11** and **12** suggests that borazinium ions of type $R_3B_3N_3H_4^+$ are readily accessible, provided that a suitable anion is present. Such anions can be $SbCl_6^-$, $O_3SCF_3^-$, or $Al(OC_4F_9)_4^-$. It needs to be shown that also borazines of type $(RB=NR')_3$ can be protonated, maybe not only with formation of $R_3B_3N_3R_3H^+$ but also of $R_3B_3N_3R_3H_2^{2+}$ or even $R_3B_3N_3R_3H_3^{3+}$. This is not an unlikely possibility as triply charged borazinium salts have already been reported. Typical examples are $[Et_3P-N=BH]_3^{3+}$ [21] and $[(HBNPEt_2)_4NPEt_3]^{3+}$ [22].

Experimental Section

General Procedures. All experiments have been performed under anhydrous conditions using the Schlenk technique with dinitrogen as the protecting gas. The borazines have been prepared by procedures described in the literature. [5] Commercial $GaCl_3$ and $AlBr_3$ were sublimed before use. Solvents were dried by conventional methods. NMR spectra were recorded on JEOL 270 and 400 instruments using TMS (^1H, ^{13}C) as an internal standard, and BF_3OEt_2 and a 1M $AlCl_3$ aqueous solution as external standards. C_6D_6 was used as solvent. A Siemens P4 diffractometer equipped with an area detector and a low temperature device was used for data collection. If not otherwise stated data collection was performed at -80 °C with MoKα radiation and a graphite monochromator. The thermal ellipsoids shown in the figures represent a 25 % probability. Elemental analysis was performed at the microanalytical laboratory of the department.

2,4,6-Trimethylborazine-*N*-aluminum tribromide (1). To a stirred solution of $(MeB=NH)_3$ (0.92g, 7.44 mmol) in toluene (50 mL) was added a solution of $AlBr_3$ (2.01 g. 7.44 mmol) in toluene (20 mL) at -78 °C. A white precipitate formed which dissolved on warming to room

temperature. Rectangular platelets separated within a week from the solution which was kept at 4 °C. Yield: 2.98 g (97 %); m. p. 79 – 83 °C. $C_3H_{12}N_3AlB_3Br_3$ (389.72): calc. C 9.26, H 3.11, N 10.79; found C 8.92, H 2.84, N 10.61.

2,4,6-Triphenylborazine-*N*-aluminium tribromide (2). Prepared from (PhB=NH)$_3$ (0.68 g, 2.2 mmol) and AlBr$_3$ (0.64 g, 2.2 mmol) in toluene (50 + 20 mL). A microcrystalline powder formed. No single crystals resulted on crystallization from hexane, hot toluene or CH_2Cl_2. Yield: 1.21 g (91.7 %), m. p. 145° C dec. ^{13}C NMR. δ = 127.4, 128.7, 130.4, 132.5, 133.8, 137.6. $C_{18}H_{18}N_3AlB_3Br_3$ (575.46): calc. C 37.57, H 7.30, N 3.15; found C 37.30, H 7.03, N 3.08.

 2,4,6-Triethylborazine-*N*-aluminium tribromide (3). Prepared as described for **1** from (EtB=NH)$_3$ (0.61 g, 3.7 mmol) in toluene (15 mL) and AlBr$_3$ (0.99 g, 3.66 mmol) in toluene (20 mL) at ambient temperature. A turbid solution formed which was filtered. After reducing the volume of the filtrate to 1/3rd small crystals separated. Attempts to recrystallize from hexane or CH_2Cl_2 gave no crystals suitable for X-ray structure determination. Yield: 1.15 g (72 %):, m. p. 88 – 90° C. $C_6H_{14}N_3AlB_3Br_3$ (431.33): calc. C 16.71, H 4.21, N 9.71, Br 55.57: found: C 16.07, H 4.38, N 9.50, Br 54.34.

2,4,6-Triisopropylborazine-*N*-aluminium tribromide (4). Prepared fro (*i*PrB=NH)$_3$ (0.68 g, 3.3 mmol) in toluene (15 mL) and AlBr$_3$ (0.88 g, 3.3 mmol) in toluene (20 mL). The solution was reduced in vacuo to 1/3rd of its original volume. Small platelets separated at 4 °C but no single crystals were obtained from hexane or CH_2Cl_2. Yield: 1.00 g (65 %). M. p. 95 - 97° C. $C_9H_{24}N_3AlB_3Br_3$ (473.42): calc. C 22.81, H 5.11, N 8.86, Br 50.63; found C 22.48, H 5.25, N 8.94, Br 50.63; found C 21.96, H 5.24, N 8,30, Br 50.25.

 2,4,6-Tri(*tert*-butyl)borazine-*N*-aluminium tribromide (5). Obtained from (*t*BuB=NH)$_3$ (1.45 g, 6.62 mmol) and AlBr$_3$ (1.50 g, 5.62 mmol) in toluene (20 + 20 mL). Colorless needles separated on storing the solution at 4 °C. Yield: 1.30 g (45 %)., m. p. 120 - 121° C. $C_{12}H_{30}N_3AlB_3Br_3$ (515.51): calc. C 27.96, H 5.87, N 8.15, Br 46.50; found C 27.59, H 6.00, N 7.83, Br 45.88.

2,4,6-Trimethylborazine-*N*-gallium trichloride(6). At -78 °C a solution of GaCl$_3$ (1.56 g, 8.88 mmol) in toluene (20 mL) was added while stirring to a solution of (MeB=NH)$_3$ in toluene (1.09 g, 8.88 mmol, 20 mL). At ambient temperature about 60 % of the solvent was removed in vacuo. Single crystals separated at -25 °C within a week. Yield: 2.65 g (99 %); m.p. 109 – 111 °C. $C_3H_{12}N_3B_3Cl_3Ga$ (298.64): Calc. C 12.11, H 3.72, N 14.12; found C 11.91, H 3.76, N 13.89.

2,4,6-Triphenylborazine-*N*-gallium trichloride(7). To stirred toluene solution (30 mL) of (PhB=NH)$_3$ (230 mg, 0.751 mmol) was added at -78 °C slowly a solution of GaCl$_3$ (120 mg, 0.75 mmol) in toluene (10 mL). A white precipitate formed which dissolved at ambient temperature. At 5 °C colorless rhombic crystals separated with in a few days. Yield: 0.36 g (100 %), m. p. 285 °C dec. $C_{18}H_{18}N_3B_3Cl_3Ga$ (484.85): calc. C 44.59, H 3.74, N 8.67; found: C 43.17, H 3.30, N 8.35.

2,4,6-Triethylborazine-N-gallium trichloride(8). To a stirred solution of (EtB=NH)$_3$ (0.58 g, 3.5 mmol) in toluene (10 mL) was added a toluene solution of GaCl$_3$ (0.62 g, 3.5 mmol, 20 mL). A turbid solution formed which was filtered. After about 25 ml of toluene had been removed in

vacuo crystals separated at 4 °C from the slightly green colored solution. Yield: 0.67 g (80 %), m. p. 106° C. $C_6H_{18}N_3B_3Cl_3Ga$ (340.74): calc. C 21.15, H 5.32, N 12.22, Cl 31.21; found: C 20.83, H 5.16, N 11.78, Cl 31.62.

2,4,6-Triisopropylborazine-*N*-gallium trichloride(9).Prepared in analogy to **6** from $(iPrB=NH)_3$ (0.380 g, 2.14 mmol) and $GaCl_3$ (0.441 g, 2.14 mmol) in toluene (20 + 10 mL). Colourless needles separated at 4°C. Yield 0.67 g, (82 %), 61 – 63° C.
$C_9H_{24}N_3B_3Cl_3Ga$ (382.92): calc.: C 28.24, H 6.32, N 10.98, Cl 27.78; found C 28.13, H 6.31, N 10.59, Cl 28.03.

2,4,6-Tri-(tert-butyl)borazine-*N*-gallium trichloride (10). Prepared from $(tBuB=NH)_3$ (0.91 g, 3.53 mmol) and $GaCl_3$ (0.62, 3.53 mmol) in toluene (10 + 20 mL). After removal of 27 ml of toluene in vacuo crystals separated from the solution at 4°C in large needles. Yield: 1.30 g (85 %), m. p. 88 – 90 ° C. $C_{12}H_{30}N_3B_3Cl_3Ga$ (424.90): calc. C 33.92, H 7.11, N 9.89, Cl 25.03; found: C 31.00, H 6.54, N 9.59, Cl 25.76.

2,4,6-Triethylborazinium-tetrabromoaluminate(11). HBr, which was generated form NaBr (100 mg, 1.0 mmol) and 85 % H_3PO_4, was passed via a septum needle into a solution of $(EtB=NH)_3AlBr_3$ (9.44 g, 1.02 mmol) in toluene (10 mL). After all HBr has been swept from the HBr generator into the toluene solution of the $(EtB=NH)_3AlBr_3$ with N_2, stirring was continued for additional 2 h. The slightly turbid solution was cleared by filtration. The filtrate was then kept at 4 °C. Colorless platelets separated within a few days. Yield: 0.25 g (50 %)., m. p. 121 °C dec. $C_6H_{19}N_3AlB_3Br_4$ (512.25): C 14.07, H 3.75, N 8.20, Br 62.39: found; C 14.27, H 3.97, N 8.29, Br 61.11.

2,4,6-Tri(*tert*-butyl)borazinium-tetrabromoaluminate (12). Prepared as **11** from HBr (generated by reacting NaBr (133 mg, 1.3 mmol) with 85 % H_3PO_4) and a toluene solution (30 mL) of $(tBu=NH)_3AlBr_3$ (670 mg, 1.30 mmol). The slightly yellow filtrate was kept at 4 °C for 4 d. Colorless platelets formed. Yield: 470 mg (60 %), m. p. 185 °C. $C_{12}H_{31}N_3AlB_3Br_4$ (596.41): calc.: C 24.61 H 5.24, N 7.05, Br 63.59; found: C 24.23, H 5.27, N 6.98, Br 62.99.

X-Ray structure determinations. Under N_2 cover crystals were placed in a polyfluoro ether oil cooled to -25 °C. The selected crystal was fixed on a glass fibre with this oil and placed on a goniometer head which was flushed with N_2 cooled to -80°C. The unit cell parameters were determined from the reflection on 5 sets of 15 exposures by using the program SMART. Data collection was performed in a the hemisphere mode by changing ω in 0.3 ° intervals and 10 s exposure time.. Data on 1200 frames were reduced with the programme SAINT. Structure solution was performed with SHELXTL after absorption correction (ABSO). Data referring to crystallography and structure solution are listed in Table 6. Additional data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 647 497 to 647 502. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ. UK (Fax int. code+(1223)336-033; e-mail: deposit@ccdc.cam.uk).

Table 6. Crystal data and data related to data collection and structure solution

Compound	1	6	7	10	11	12
Chem. formula	$C_3H_{12}N_3AlB_3$ Br_3	$C_3H_{12}N_3B_3Cl_3G$ a	$C_{18}H_{18}N_3B_3Cl_3$ Ga	$C_{12}H_{30}N_3B_3Cl_3$ Ga	$C_6H_{15}N_3AlB_3B$ r_4	$C_{12}H_{31}N_3Al$ B_3Br_4
Form. wght.	389.30	390.79	484.85	424.89	508.26	596.45
Cry. size [mm]	0.20x0.20x0.30	0.10x0.20x0.30	0.18x0.24x0.28	0.20x0.20x0.30	0.18x0.22x0.32	0.2x0-3x0-3
Cryst. system	Monoclinic	Monoclinic	Orthorhombic	Monoclinc	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$Pna2_1$	$P2_2/n$	**P**ca2(1)	$Pna2_1$
a, [Å]	8.7266(1)	13.9729(2)	13-9729(2)	16.998(1)	16.2301(2)	18.400(2)
b, [Å]	14.8792(1)	15.0518(3)	9.0853(2)	9.8995(8)	10.211(1)	10.400(2)
c, [Å]	10.9407(1)	11.6272(2)	17.9358(3)	13.455(1)	10.974(1)	13.090(2)
α, [°]	90	90	90	90	90	90
β, [°]	107.410(1)	114.008(1)	90	102.353(1)	90	90
γ, [°]	90	90	90	90	90	90
V, [Å^3]	1355.5(3)	1859.12(6)	2162.66(7)	2211.8(3)	1818.8(3)	2504.9(6)
Z	4	4	4	4	4	4
ρ(calcd.), [Mg/m^3]	1.908	1.396	1.489	1.267	1.856	1.582
μ [mm^{-1}]	8.956	1.902	1.652	1.604	8.882	6.462
F(000)	736	792	976	880	960	1168
Index range	$-11 \leq h \leq 11$	$-14 \leq h \leq 14$	$-18 \leq h \leq 18$	$-22 \leq h \leq 15$	$-20 \leq h \leq 20$	$-17 \leq h \leq 17$
	$-19 \leq k \leq 19$	$-18 \leq k \leq 18$	$-10 \leq k \leq 11$	$-12 \leq k \leq 12$	$-13 \leq k \leq 13$	$-13 \leq k \leq 13$
	$-14 \leq l \leq 13$	$-11 \leq l \leq 15$	$-21 \leq l \leq 20$	$-17 \leq l \leq 17$	$-14 \leq l \leq 11$	$-16 \leq l \leq 16$
2 θ [°]	58.86	57.68	28.14	57.22	56.88	55.46
Temp, [K]	183(2)	193(2)	183(2)	193(2)	193(2)	193(2)
Refl. collected	7890	10533	11782	6162	9880	13364
Refl. unique	2671	3245	4340	3395	3624	4749
Refl. obs. (4σ)	2139	2761	3604	3433	2464	2444
R (int.)	0.0314	0.0340	0.0387	0-0199	0.0549	0.0719
No. variables	121	297	262	211	157	217
Wght.[1] x/y	0.0853/1,7218	0.2391/2.5906	0.0556/0.2196	0.0637/0.0707	0.0544/0.00	
GOOF	1.086	1-125	1.086	0.886	0.938	0.881
Final R (4σ)	0.0388	0.0393	0.0429	0.349	0.0460	0.0479
Final wR2	0.1107	0.0844	0-0958	0.996	0.0883	0-0894
Larg. res.[e/Å^3]	1.394	0.590	0.774	0.527	0.636	0.702

[1] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP;\ P = (F_o^2 + 2F_c^2)/3$

Acknowledgements

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