



# A cationic mononuclear and a neutral trinuclear boron compound derived from boric acid and N<sub>2</sub>O<sub>2</sub>-type ligands of the Salan class

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## ABSTRACT

Four different ligands of the Salan class have been prepared and reacted with boric acid. Reaction of saleanH<sub>4</sub> (saleanH<sub>4</sub> = *N,N'*-bis(*o*-hydroxybenzyl)-1,2-diaminoethane) with three equivalents of boric acid gave a neutral trinuclear boron complex containing two four-coordinate and one three-coordinate boron atom involved in a system of four heterocyclic rings of the composition {C<sub>3</sub>BNO}, {C<sub>2</sub>B<sub>2</sub>N<sub>2</sub>O} and {B<sub>3</sub>O<sub>3</sub>}. The salceanH<sub>4</sub> ligand (salceanH<sub>4</sub> = *N,N'*-bis(*o*-hydroxybenzyl)-*trans*-1,2-diaminocyclohexane) gave a so far unknown mononuclear boronium complex of the general formula [(RO)<sub>2</sub>B(NR'R'')<sub>2</sub>]<sup>+</sup>. Both compounds might have applications, the trinuclear species as Lewis acid catalyst and the borocation as positively charged counterion for voluminous anions. With salpanH<sub>4</sub> (salpanH<sub>4</sub> = *N,N'*-bis(*o*-hydroxybenzyl)-1,3-diaminopropane) and salophanH<sub>4</sub> (salophanH<sub>4</sub> = *N,N'*-bis(*o*-hydroxybenzyl)-1,2-diaminobenzene) only unseparable product mixtures of oligo- and/or polymeric boron complexes could be obtained.

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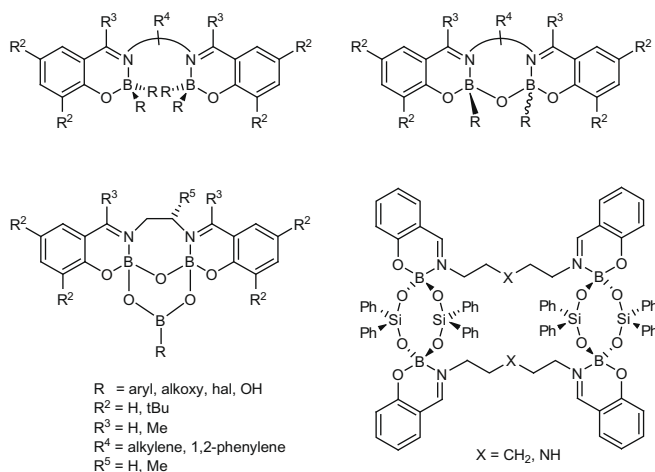
## 1. Introduction

Although boron is located between a metal and a non-metal in the periodic table of the elements, most of its physical and chemical properties and those of the compounds derived from it are typical for nonmetallic species. There are only some features in the chemistry of boron that reflect a relationship to metal compounds, the most prominent perhaps being its capacity to form coordinative bonds with a series of ligands typically used for metal-complexation [1]. The term “boron complex” is commonly used, however, a closer view shows that there are important differences to typical metal complexes. One of the most significant characteristics is that boron does not form easily B<sup>3+</sup> cations, with the consequence that species such as [B(H<sub>2</sub>O)<sub>*x*</sub>]<sup>3+</sup> or [B(NH<sub>3</sub>)<sub>*x*</sub>]<sup>3+</sup> (*X* = 3, 4) are not known yet, although boron shows a high affinity to oxygen and nitrogen donor atoms. While monocationic boronium, borenium and borinium compounds of the composition [X<sub>2</sub>B(D)<sub>2</sub>]<sup>+</sup>, [X<sub>2</sub>BD]<sup>+</sup> and [X<sub>2</sub>B]<sup>+</sup> (*X* = covalently linked group, *D* = donor group) are well-known and have been characterized by spectroscopic methods and X-ray crystallography [2–5], the chemistry of dicationic and tricationic boronium compounds has been established only recently [6–7]. Borocations have attracted

interest due to potential applications as catalysts in polymerization reactions [8], enantioselective Lewis acid activators [5a], electron acceptors for the generation of conjugated π-electron donor–acceptor complexes [9], ionic liquids [3r,w], materials for reversible dihydrogen storage [10], and agents for the sensing of fluoride ions [3x].

The preparative strategy generally applied for the synthesis of boronium cations starts from a boron compound with a labile B–X bond, e.g. B–Cl, B–Br, etc., which can then be substituted by a functional group having a lone-electron pair. For this purpose, frequently bi- and tridentate amine and phosphine ligands are used [3,4]. In the course of our ongoing research on boron compounds derived from Salen- and Salan-type N<sub>2</sub>O<sub>2</sub>-ligands [11], we have now discovered a ligand that is capable to form a monocationic boron complex of the composition [(RO)<sub>2</sub>B(NR'R'')<sub>2</sub>]<sup>+</sup>, using boric acid as starting material. The ligand that is capable to form this complex is saleanH<sub>4</sub>. The resulting complex is also the first mononuclear boron compound that could be prepared from a ligand of the Salen/Salan class [12]; in former studies only dinuclear [8c,11a,b,13], trinuclear [11b,c] and tetranuclear [13g] species had been obtained. Boron is exceptional in this respect, since the heavier group 13 elements aluminum, gallium and indium form monometallic complexes easily, even with the less flexible Salen ligands [12]. With Salan ligands so far only dinuclear boron complexes have been reported [13k]. Furthermore, boronium complexes containing covalent B–O and coordinative N→B bonds are almost unknown so far [14].

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## 2. Experimental

### 2.1. Instrumental

NMR studies were carried out with Bruker 300 and Varian Inova 400 instruments. Standards were TMS (internal, <sup>1</sup>H, <sup>13</sup>C) and BF<sub>3</sub>·OEt<sub>2</sub> (external, <sup>11</sup>B). Chemical shifts are stated in parts per million; they are positive, when the signal is shifted to higher frequencies than the standard. COSY and HMQC experiments have been carried out in order to assign the <sup>1</sup>H and <sup>13</sup>C spectra completely. IR spectra have been recorded on a Bruker Vector 22 FT spectrophotometer. Mass spectra were obtained on HP 5989A and Jeol JMS 700 equipments. Elemental analyses of samples dried in an Abderhalden equipment have been carried out on Perkin Elmer Series II 2400 and Elementar Vario ELIII instruments. It should be mentioned that elemental analyses of boron compounds are frequently complicated by incombustible residues such as boron carbide, and, therefore, not always in the established limits of exactitude, especially with respect to carbon [15]. For this reason only the values for hydrogen and nitrogen are indicated.

### 2.2. Preparative part

Commercial starting materials and solvents have been used. SaleanH<sub>4</sub>, salceanH<sub>4</sub>, salpanH<sub>4</sub> and salophanH<sub>4</sub> have been prepared according to a method reported in the literature [16].

#### 2.2.1. SaleanH<sub>2</sub>{B–O–B}[O<sub>2</sub>BOH] **1**

Compound **1** was prepared from one equivalent of saleanH<sub>4</sub> (0.200 g, 0.74 mmol) and three equivalents of boric acid (0.135 g, 2.20 mmol) in 15 mL of acetonitrile. The mixture was refluxed for 8 h using a Dean-Stark trap, whereupon a colorless precipitate of **1** had formed that was collected by filtration and dried. Recrystallization from DMSO gave crystals suitable for X-ray crystallography. Yield: 0.225 g (68%). Mp 287–288 °C. IR (KBr):  $\tilde{\nu}$  = 3395 (br, m, OH), 3207 (s, NH), 3078 (w), 2950 (w), 1610 (w), 1585 (w), 1494 (m), 1466 (m), 1407 (s), 1284 (m), 1189 (m), 1141 (s), 1072 (m), 1034 (m), 952 (w), 872 (w), 832 (m), 757 (m), 692 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 7.17, 7.14, 7.06, 6.94 (ddd, 4H, H-3, H-3', H-5, H-5'), 6.78, 6.75, 6.67, 6.64 (dd, 4H, H-4, H-4', H-6, H-6'), 6.33 (br, s, 1H, OH), 3.74, 3.54 (m, 4H, H-7), 3.01, 2.91, 2.74 (ABCD, 4H, N-CH<sub>2</sub>CH<sub>2</sub>-N) ppm. <sup>11</sup>B NMR (128 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 20.4, 1.5 ppm. MS (FAB<sup>+</sup>): *m/z* (%) = 307 (25) [M–H<sub>2</sub>BO<sub>3</sub>], 281 (84) [B(saleanH<sub>2</sub>)]<sup>+</sup>, 154 (100), 136 (100).

Anal. Calc. for C<sub>16</sub>H<sub>19</sub>B<sub>3</sub>N<sub>2</sub>O<sub>6</sub>·DMSO (445.89 g mol<sup>-1</sup>): H, 5.60; N, 6.27. Found: H, 5.52; N, 6.30%.

#### 2.2.2. [B(salceanH<sub>2</sub>)]B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub> **2**

Compound **2** was prepared from one equivalent of salceanH<sub>4</sub> (0.500 g, 1.53 mmol) and six equivalents of boric acid (0.565 g, 9.14 mmol) in 15 mL of acetonitrile. The mixture was refluxed for 12 h using a Dean-Stark trap. After two days at room temperature colorless crystals of **2** had formed that were collected by filtration and dried. These crystals were suitable for X-ray diffraction. Yield: 0.440 g (45%). Mp 209–211 °C. IR (KBr):  $\tilde{\nu}$  = 3442 (br, m, OH), 3251 (br, w, NH), 3052 (w), 2946 (w), 1648 (m), 1607 (m), 1505 (w), 1460 (m), 1385 (w), 1279 (w), 1140 (s), 1047 (m), 942 (m), 754 (m), 696 (m), 573 (m), 547 (m), 516 (m), 462 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 7.28 (m, 4H, H-3, H-5), 6.98 (m, 4H, H-4, H-6), 6.38 (s, 4H, OH), 4.22 (AB, 4H, H-7), 2.42 (m, 2H, H-8), 2.20 and 1.36 (m, 4H, H-9), 1.72 and 1.13 (m, 4H, H-10) ppm. <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 157.3 (C-1), 129.5, 128.7 (C-3, C-5), 125.8 (C-2), 119.5, 116.1 (C-4, C-6), 59.9 (C-7), 47.3 (C-8), 30.5 (C-9), 24.9 (C-10) ppm. <sup>11</sup>B NMR (96 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 19.6 (*h*<sub>1/2</sub> = 320 Hz), 3.1 (*h*<sub>1/2</sub> = 160 Hz), 1.4 (*h*<sub>1/2</sub> = 64 Hz) ppm. MS (FAB<sup>+</sup>): *m/z* (%) = 335 ([B(salceanH<sub>2</sub>)]<sup>+</sup>, 6), 333 ([B(salceanH<sub>2</sub>)]-H<sub>2</sub>, 30), 251 (20), 227 (73), 185 (33), 122 (100), 107 (67), 96 (65), 94 (64), 77 (55). Anal. Calc. for C<sub>20</sub>H<sub>28</sub>B<sub>6</sub>N<sub>2</sub>O<sub>12</sub> (553.31 g mol<sup>-1</sup>): H, 5.10; N, 5.06. Found: H, 5.61; N, 4.38%.

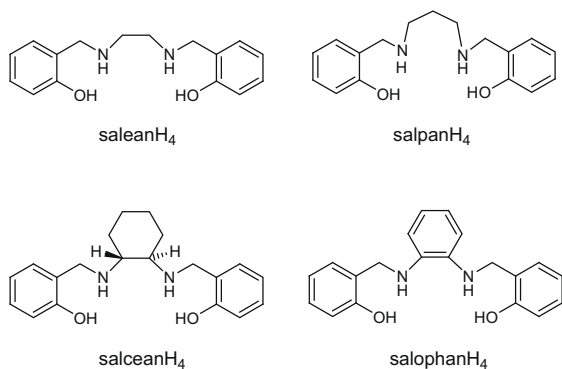
### 2.3. X-ray crystallography

X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector ( $\lambda_{\text{MoK}\alpha}$  = 0.71073 Å, monochromator: graphite). Frames were collected at *T* = 293 K for compound **1** and *T* = 100 K for compound **2** via  $\omega$ - and  $\phi$ -rotation at 10 s per frame (SMART) [17a]. The measured intensities were reduced to *F*<sup>2</sup> and corrected for absorption with SADABS (SAINT-NT) [17b]. Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package [17c,d]. Non hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model. O–H and N–H hydrogen atoms have been localized by difference Fourier maps, whereupon the O–H and N–H distances have been fixed (0.84 and 0.86 Å, respectively). Solvent molecules are present in each of the crystal lattices (DMSO for **1** and acetonitrile for **2**). In compound **1** the DMSO molecules are disordered over two positions (occ = 0.84 and 0.16), and in compound **2** one of the acetonitrile molecules present in the asymmetric unit is located on a crystallographic C<sub>2</sub>-symmetry axis. In compound **2** the asymmetric unit contains two independent boronium ions and their corresponding pentaborate counterions. Molecular structures were illustrated by the SHELXTL-NT software package [17c–d].

## 3. Results and discussion

### 3.1. Preparation and spectroscopic characterization

Four tetradentate ligands have been prepared by reduction of the corresponding salen ligands with NaBH<sub>4</sub>/EtOH: saleanH<sub>4</sub> (saleanH<sub>4</sub> = *N,N'*-bis(*o*-hydroxybenzyl)-1,2-diaminoethane), salceanH<sub>4</sub> (salceanH<sub>4</sub> = *N,N'*-bis(*o*-hydroxybenzyl)-*trans*-1,2-diaminocyclohexane), salpanH<sub>4</sub> (salpanH<sub>4</sub> = *N,N'*-bis(*o*-hydroxybenzyl)-1,3-diaminopropane) and salophanH<sub>4</sub> (salophanH<sub>4</sub> = *N,N'*-bis(*o*-hydroxybenzyl)-1,2-diaminobenzene). In a first approach these



ligands have been reacted with boric acid in a 1:3 stoichiometric relationship, in order to prepare boron complexes analogous to those reported for the corresponding unreduced salen derivatives. For this purpose, the previously established synthetic pathway has been employed. These compounds contain three boron atoms, of which two are four-coordinate and one is three-coordinate [11b,c]. The objective could indeed be achieved with ligand saleanH<sub>4</sub>, giving compound **1** in a yield of 68%, but from the reaction mixture with the ligand derived from salicylaldehyde and *trans*-1,2-cyclohexanediamine (salceanH<sub>4</sub>), crystals containing the boronium complex [B(salceanH<sub>2</sub>)]<sup>+</sup> and the well-known pentaborate [B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sup>-</sup> counterion (compound **2**) were formed (Scheme 1). The remaining two ligands (salpanH<sub>4</sub> and salophanH<sub>4</sub>) gave only unseparable product mixtures that probably contain oligo- and/or polymeric boron complexes, which have not been further studied. In the first case, this can be attributed to the larger separation of the coordinating functions, while in the second case the rigidity of the spacer group probably enhances the ring strain. Similar observations have been made previously for the analogous salen compounds [11c]. The yield of compound **2** could be improved significantly by repeating the reaction using a 1:6 saleanH<sub>4</sub>-to-boric acid stoichiometry (45%). Despite changing the stoichiometry of the reagents in the reaction with saleanH<sub>4</sub> from 1:3 to 1:6, the cationic compound could not be prepared from this ligand, and only compound **1** could be separated from the reaction mixture. This should, however, not be taken as evidence that it is impossible to prepare a cationic species from saleanH<sub>4</sub>, since the reaction conditions may influence the equilibria present in solution, and cause

precipitation of one of the possible products. This statement is supported by the fact that the FAB<sup>+</sup> mass spectrum of compound **1** shows an intense peak for the [B(salceanH<sub>2</sub>)]<sup>+</sup> cation at *m/z* = 281 (84%). The molecular ion for **1** could not be detected in this mass spectrum, but the compound was identified by a peak at *m/z* = 307 (25%) that corresponds to the dinuclear species having the composition [B(salceanH<sub>2</sub>[B–O–B])]<sup>+</sup>. For trinuclear boron complexes derived from the corresponding unreduced salen ligand class similar fragmentation patterns have been observed [11b,c].

As far as possible, complexes **1** and **2** have been characterized further by spectroscopic methods (IR, <sup>1</sup>H, <sup>13</sup>C and <sup>11</sup>B NMR) and X-ray crystallography. Because of the N→B bond formation, in the IR spectra the stretching vibrations of the N–H hydrogen atoms are shifted to lower wavenumbers when compared to the starting materials [18],  $\tilde{\nu} = 3207$  versus  $3286\text{ cm}^{-1}$  for **1** and  $3251$  versus  $3298\text{ cm}^{-1}$  and  $3324\text{ cm}^{-1}$  for **2**.

The existence of N→B coordinative bonds in solution could be evidenced also by <sup>1</sup>H NMR spectroscopy, and in the case of compound **1** a boron complex having an asymmetric heterocyclic ring structure was formed: the signal patterns at  $\delta = 3.54$  and  $3.74$  ppm for the N–CH<sub>2</sub>–Ar hydrogen atoms indicate the presence of two different AB systems (each boron is chiral), and those at  $\delta = 2.74$ ,  $2.91$  and  $3.01$  indicate an ABCD spin system for the NCH<sub>2</sub>CH<sub>2</sub>N bridge. For comparison, in the <sup>1</sup>H NMR spectrum of the starting ligand, only two signals are observed ( $\delta = 3.99$  ppm for NCH<sub>2</sub>Ar and  $\delta = 2.83$  ppm for NCH<sub>2</sub>CH<sub>2</sub>N). For **1**, the <sup>11</sup>B NMR spectrum contains signals at  $\delta = 1.5$  and  $20.4$  ppm, of which the first is in the region for four-coordinate and the second in the region for three-coordinate boron atoms [11–13].

Since the ligand used for the preparation of compound **2** has been derived from *trans*-1,2-cyclohexanediamine, a complex with chiral boron atoms having C<sub>2</sub>-symmetry was obtained. This is evidenced by <sup>1</sup>H NMR spectroscopy, since only one AB system is detected for the two N–CH<sub>2</sub>–Ar methylene groups ( $\delta = 4.22$  ppm). When compared to the ligand, the signal is shifted to higher frequencies ( $\Delta\delta = 0.23$  ppm). The <sup>11</sup>B NMR spectrum shows three signals at  $\delta = 1.4$ ,  $3.1$  and  $19.6$  ppm: the signal at  $\delta = 3.1$  ppm corresponds to the boron atom in the cationic [B(salceanH<sub>2</sub>)]<sup>+</sup> complex, while the remaining two can be attributed to the boron atoms in the [B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sup>-</sup> anion [19].

**Table 1**  
Crystallographic data for compounds **1** and **2**.

Crystal data <sup>a</sup>	<b>1</b>	<b>2</b>
Formula	C <sub>16</sub> H <sub>19</sub> BN <sub>2</sub> O <sub>6</sub> , DMSO	4(C <sub>20</sub> H <sub>28</sub> B <sub>6</sub> N <sub>2</sub> O <sub>12</sub> ), 9MeCN
MW (g mol <sup>-1</sup> )	445.89	2582.70
Space group	I4 <sub>1</sub> cd	C2/c
T (K)	293(2)	100(2)
a (Å)	25.2524(13)	13.3817(7)
b (Å)	25.2524(13)	20.6147(12)
c (Å)	13.3087(10)	45.077(3)
α (°)	90	90
β (°)	90	92.237(1)
γ (°)	90	90
V (Å <sup>3</sup> )	8486.7(9)	12425.5(12)
Z	16	4
μ (mm <sup>-1</sup> )	0.196	0.105
ρ <sub>calc</sub> (g cm <sup>-3</sup> )	1.396	1.381
R <sup>b,c</sup>	0.067	0.057
R <sub>w</sub> <sup>d,e</sup>	0.167	0.129

<sup>a</sup> λ<sub>MoKα</sub> = 0.71073 Å.

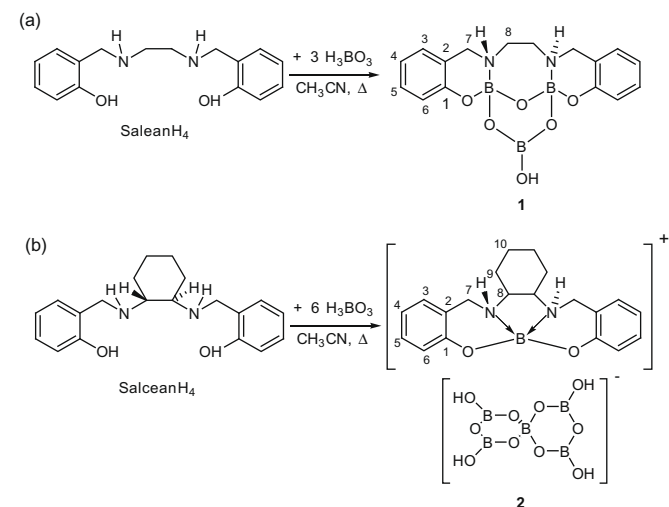
<sup>b</sup> F<sub>o</sub> > 4σ(F<sub>o</sub>).

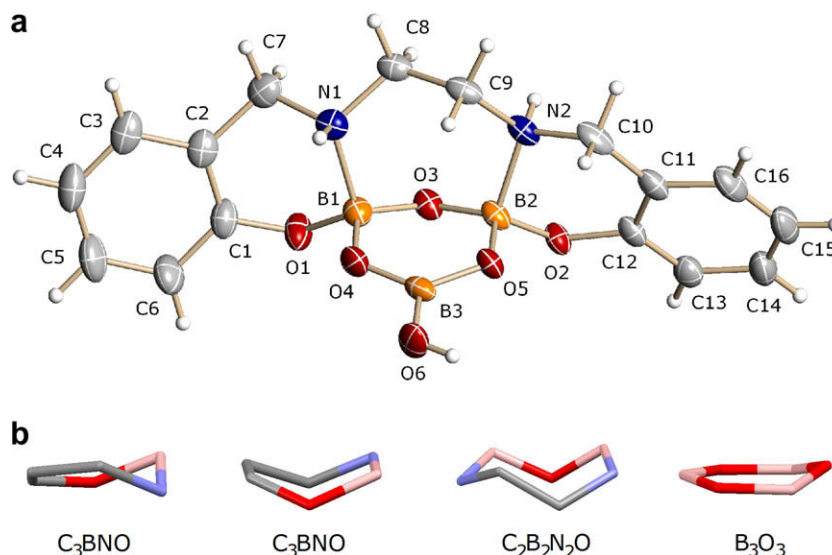
<sup>c</sup> R = Σ||F<sub>o</sub> – |F<sub>c</sub>|| / Σ|F<sub>o</sub>|.

<sup>d</sup> All data.

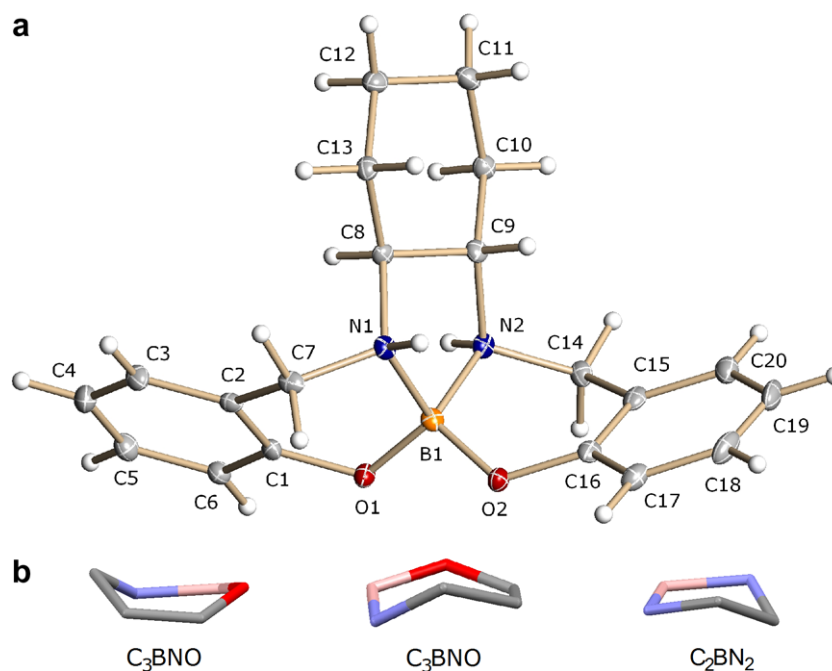
<sup>e</sup> R<sub>w</sub> = [Σw(F<sub>o</sub><sup>2</sup> – F<sub>c</sub><sup>2</sup>)<sup>2</sup> / Σw(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>.

**Scheme 1.** Reaction of the reduced salen complexes saleanH<sub>4</sub> and salceanH<sub>4</sub> with boric acid gave two different products: the neutral trinuclear boron complex **1** and the boronium salt **2**.





**Fig. 1.** Perspective views of (a) the molecular structure of salceanH<sub>2</sub>{[B–O–B][O<sub>2</sub>B(OH)]} (**1**) and (b) the conformations of the six- and seven-membered heterocyclic rings. Ellipsoids are shown at the 30% probability level.



**Fig. 2.** Perspective view of (a) the molecular structure of the [B(salceanH<sub>2</sub>)]<sup>+</sup> cation in [B(salceanH<sub>2</sub>)]<sub>2</sub>[B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>] (**2**) and (b) the conformations of the five- and six-membered heterocyclic rings. For clarity only one of the two independent molecules in the asymmetric unit is shown. Ellipsoids are given at the 30% probability level.

### 3.2. X-ray crystallographic studies

The molecular structures of compounds **1** and **2** have been further examined by X-ray crystallographic studies (Table 1) and are shown in Figs. 1 and 2, respectively. Selected bond lengths, bond angles and torsion angles are summarized in Tables 2 and 3.

The molecular structure of **1** is trinuclear, containing two four-coordinate and one three-coordinate boron atom (Fig. 1a). In agreement with the NMR spectroscopic data, the central seven-membered {C<sub>2</sub>B<sub>2</sub>N<sub>2</sub>O} heterocycle adopts an asymmetric chair-boat conformation (Fig. 1b). Probably due to the steric hindrance between the N1–H hydrogen atom and the B<sub>3</sub>O<sub>3</sub> fragment, the N1→B1 coordinative bond is significantly longer than the N2→B2 bond, 1.714(6) versus 1.662(5) Å. For the structurally related

salen{[B–O–B][O<sub>2</sub>B(OH)]} complex **3** the corresponding N→B bond lengths are 1.612(7) and 1.597(6) Å [11c], indicating annular strain in the present case [20]. This is confirmed by a comparison of the tetrahedral character [1a] of the boron atoms in compounds **1** and **3**: 79% and 76% for **1** versus 86% and 87% for **3** [11c]. The bond angles around the boron atoms that deviate most from the ideal tetrahedral angle involve the oxygen atoms of the {B<sub>3</sub>O<sub>3</sub>} ring (O3–B1–O4 = 116.6(4)° and O3–B2–O5 = 116.4(3)°). As observed previously for the analogous Salen complex, the B–O<sub>Ph</sub> bond lengths are significantly longer than those within the B1–O3–B2 bridge, 1.457(5) and 1.463(6) Å versus 1.400(5) and 1.402(5) Å. The B1–O4 and B2–O5 bonds are slightly longer (1.428(6) and 1.437(5) Å), while the B–O bonds around the trigonal-planar B3 atom are significantly shorter, 1.346(6)–1.367(5) Å due to p<sub>π</sub> · p<sub>π</sub>

**Table 2**  
Selected bond lengths [Å], bond angles [°] and torsion angles [°] for compound **1**.

Bond lengths			
B1–N1	1.714(6)	B1–N2	1.662(5)
B1–O1	1.463(6)	B2–O2	1.457(5)
B1–O3	1.400(5)	B2–O3	1.402(5)
B1–O4	1.428(6)	B2–O5	1.437(5)
B3–O4	1.357(6)	B3–O5	1.367(5)
B3–O6	1.346(6)	O1–C1	1.346(5)
O2–C12	1.365(5)		
Bond angles			
O1–B1–N1	106.3(3)	O2–B2–N2	104.2(3)
O3–B1–N1	108.6(3)	O3–B2–N2	107.8(4)
O4–B1–N1	103.5(3)	O5–B2–N2	105.3(3)
O1–B1–O3	109.3(3)	O2–B2–O3	110.1(3)
O1–B1–O4	111.3(4)	O2–B2–O5	112.1(4)
O3–B1–O4	116.6(4)	O3–B2–O5	116.4(3)
O4–B3–O5	120.9(4)	O4–B3–O6	117.6(4)
O5–B3–O6	121.5(4)	B2–O2–C12	119.9(3)
B1–O1–C1	119.4(3)	O2–C12–C12	122.3(4)
O1–C1–C2	119.5(4)	C12–C11–C10	121.7(4)
C1–C2–C7	116.2(4)	C11–C10–N2	111.3(3)
C2–C7–N1	110.2(4)	B2–N2–C10	110.0(3)
B1–N1–C7	112.8(3)	B2–N2–C9	114.0(3)
B1–N1–C8	115.6(3)	N2–C9–C8	113.6(3)
N1–C8–C9	116.3(3)		
B1–O3–B2	119.4(3)		
Torsion angles			
B1–O1–C1–C2	48.6(6)	B2–O2–C12–C11	–17.8(5)
O1–C1–C2–C7	1.4(6)	O2–C12–C11–C10	–0.5(6)
C1–C2–C7–N1	–48.3(5)	C12–C11–C10–N2	17.8(5)
C2–C7–N1–B1	–47.2(4)	C11–C10–N2–B2	–47.9(4)
C7–N1–B1–O1	6.1(4)	C10–N2–B2–O2	61.8(4)
N1–B1–O1–C1	–42.4(5)	N2–B2–O2–C12	46.0(4)
B1–N1–C8–C9	–56.1(4)	B1–O3–B2–O5	–25.9(5)
N1–C8–C9–N2	88.9(4)	O3–B2–O5–B3	–8.1(5)
C8–C9–N2–B2	66.7(4)	B2–O5–B3–O4	7.8(6)
C9–N2–B2–O3	–56.9(4)	O5–B3–O4–B1	6.1(6)
N2–B2–O3–B1	–92.1(4)	B3–O4–B1–O3	–11.3(6)
B2–O3–B1–N1	–88.8(4)	O4–B1–O3–B2	–27.6(5)
O3–B1–N1–C8	–15.5(5)		

**Table 3**  
Selected bond lengths [Å], bond angles [°] and torsion angles [°] for compound **2**.<sup>a</sup>

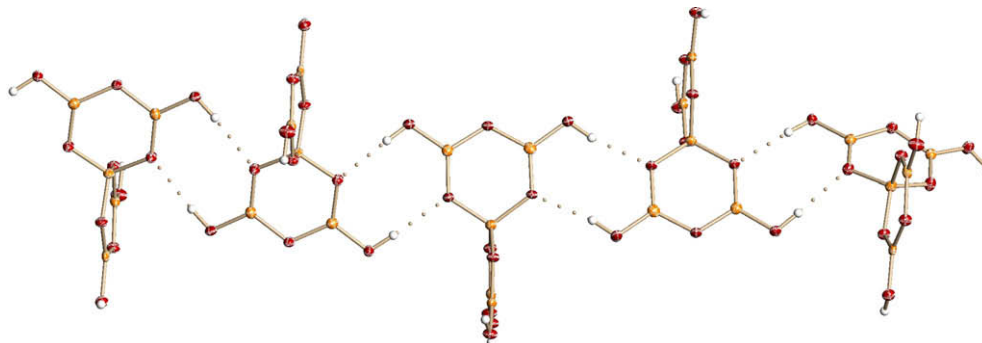
Bond lengths			
B1–N1	1.613(4)/1.623(4)	B1–N2	1.622(3)/1.603(4)
B1–O1	1.423(3)/1.430(4)	B1–O2	1.428(4)/1.422(3)
O1–C1	1.375(3)/1.377(3)	O2–C16	1.375(3)/1.383(3)
Bond angles			
O1–B1–N1	112.2(2)/112.3(2)	B1–N1–C8	105.8(2)/106.5(2)
O2–B1–N1	111.4(2)/110.8(2)	N1–C8–C9	102.9(2)/103.3(2)
O1–B1–N2	112.0(2)/111.6(2)	C8–C9–N2	103.4(2)/102.2(2)
O2–B1–N2	111.7(2)/112.2(2)	C9–N2–B1	106.5(2)/105.9(2)
O1–B1–O2	109.1(2)/109.7(2)	N1–B1–N2	100.2(2)/99.9(2)
N1–B1–N2	100.2(2)/99.9(2)		
B1–O1–C1	121.8(2)/119.6(2)	B1–O2–C16	120.9(2)/122.9(2)
O1–C1–C2	119.7(2)/119.3(2)	O2–C16–C15	119.8(2)/120.4(3)
C1–C2–C7	117.7(2)/118.4(2)	C16–C15–C14	117.9(2)/118.5(2)
C2–C7–N1	108.8(2)/109.2(2)	C15–C14–N2	109.7(2)/109.7(2)
B1–N1–C7	111.6(2)/113.0(2)	B1–N2–C14	113.4(2)/112.0(2)
Torsion angles			
B1–O1–C1–C2	–33.9(3)/–39.9(3)	B1–O2–C16–C15	–37.4(3)/–26.4(4)
O1–C1–C2–C7	–0.4(3)/1.0(3)	O2–C16–C15–C14	0.1(4)/1.5(4)
C1–C2–C7–N1	43.8(3)/42.7(3)	C16–C15–C14–N2	–42.2(3)/–41.1(3)
C2–C7–N1–B1	54.1(3)/48.9(3)	C15–C14–N2–B1	49.1(3)/53.5(3)
C7–N1–B1–O1	–25.2(2)/–16.2(3)	C14–N2–B1–O2	–17.7(3)/–29.7(3)
N1–B1–O1–C1	19.4(3)/29.0(3)	N2–B1–O2–C16	26.2(3)/10.6(4)
B1–N1–C8–C9	–40.4(2)/–34.2(3)	C9–N2–B1–N1	–9.8(3)/–20.4(2)
N1–C8–C9–N2	46.8(2)/47.5(2)	N2–B1–N1–C8	18.6(2)/8.5(2)
C8–C9–N2–B1	34.5(3)/42.1(3)		

<sup>a</sup> The asymmetric unit contains two independent molecules.

slightly distorted from planarity in direction of an envelope conformation (Fig. 1b).

Within the crystal structure the boron complexes are linked through N2–H···O2' hydrogen-bonding interactions (N2–H, 0.86; H···O2, 2.14 Å; N2···O2, 2.993(4) Å, 172°) into infinite helicoidal chains of 4<sub>1</sub>-symmetry that run parallel to the *c*-axis. The DMSO solvate molecules form bifurcated hydrogen bonds with the N1–H hydrogens and the B–OH groups.

The boron atoms in the two independent mononuclear [B(salceanH<sub>2</sub>)<sup>+</sup> cations found in the crystal structure of compound **2** are covalently bound to two oxygen atoms and further involved in two coordinate-covalent N→B bonds (Fig. 2a). Due to the presence of two N→B bonds the B–O<sub>ph</sub> bonds are significantly shorter than in compound **1** (1.422(3)–1.430(4) Å for **2** versus 1.457(5) and 1.463(6) Å for **1**). The N→B bonds range from 1.603(4) to 1.623(4) Å, thus being among the shortest coordinative N(sp<sup>3</sup>)→B(sp<sup>3</sup>) bonds known so far [1a,20]. Similar bond lengths have been observed also for previously reported boronium cations [3w]. The boron atoms are embedded in distorted tetrahedral coordination environments, in which only the N–B–N bond angles vary significantly from the ideal tetrahedral angle value, 100.2(2) and 99.9(2)°; the remaining values range from 109.7(2) to 112.3(2)°.

**Fig. 3.** Within the crystal lattice of compound **2** the pentaborate units are linked to infinite 1D chains through (B)O–H···O(B) hydrogen-bonding interactions.

giving boron tetrahedral characters of 79% [1a]. The central heterocyclic rings in the  $[B(\text{salceanH}_2)]^+$  ions are five-membered and have envelope conformations (Fig. 2b). The molecules possess pseudo  $C_2$ -symmetry, which is in agreement with the NMR spectroscopic data (vide supra). The six-membered  $\{C_3BNO\}$  heterocycles adopt approximate boat conformations (Fig. 2b, Table 3).

As shown in Fig. 3, within the crystal lattice the pentaborate anions are linked to infinite 1D chains through  $(B)O-H \cdots O(B)$  hydrogen-bonding interactions ( $O-H$ , 0.84;  $H \cdots O$ , 1.92–1.95 Å;  $O \cdots O$ , 2.746(3)–2.786(3) Å,  $170-178^\circ$ ), this pattern being typical for pentaborate anions [22]. For the formation of the polymeric supra-molecular chain two of the four  $(B)-OH$  groups are required. The remaining two  $(B)-OH$  functions interact with the acetonitrile molecules included in the solid-state structure. The anionic chains and  $[B(\text{salceanH}_2)]^+$  cations are connected through  $N-H \cdots O(B)$  interactions ( $N-H$ , 0.86;  $H \cdots O$ , 1.92–1.95 Å;  $N \cdots O$ , 2.746(3)–2.786(3) Å,  $170-178^\circ$ ), thus forming an overall 3D hydrogen bonded network, which is further stabilized by  $C-H \cdots O$  interactions between the boronium cations [23].

#### 4. Conclusions

This contribution has shown that flexible  $N_2O_2$ -type ligands can give rise to mononuclear boron compounds, in addition to the previously reported di-, tri- and tetranuclear boron complexes. The mononuclear boronium complex described herein has been prepared from a relatively inert boron chemical,  $H_3BO_3$ , thus showing that it is possible to obtain borocations from airstable starting materials. Both boron compounds described herein might have applications, the trinuclear species as Lewis acid catalyst and the borocation as positively charged counterion for voluminous anions [24].

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#### Appendix A. Supplementary data

CCDC 730574 and 730575 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.07.004](https://doi.org/10.1016/j.jorganchem.2009.07.004).

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