

## Synthesis and Structural Characterization of a Stable Dimeric Boron(II) Dication

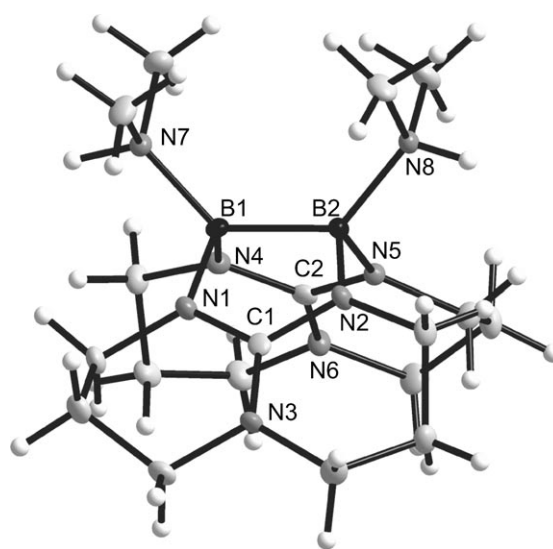
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A number of boronium ions with the general formula  $[R_2BL_2]^+$  (where L is a donor, such as an amine), some boronium  $[R_2BL]^+$ , and even borinium  $[R_2B]^+$  ions have been synthesized and structurally characterized.<sup>[1]</sup> In all these compounds, boron has a formal oxidation state of +III. In addition to the academic interest in the bonding properties in these species, some of them have found application as catalysts in polymerization<sup>[2]</sup> or Diels–Alder reactions.<sup>[3]</sup> Boronium cations are also efficient initiators for the dehydrogenation of ammonia–borane.<sup>[4]</sup> The boron atom of the boronium ions is more or less tetrahedrally coordinated by the two substituents R (for example, amido groups) and two donor ligands L (such as pyridine). In contrast, uncoordinated borinium species, such as the (dimethylamido)(2,2,6,6-tetramethylpiperidino)boron cation,<sup>[5]</sup> feature an almost linear N–B–N unit.

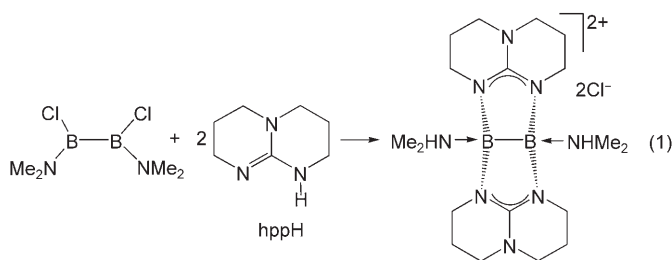
Herein we report the synthesis of the dication  $[[Me_2(H)NB(hpp)]_2]^{2+}$  (**1**; hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine), the first representative of a new class of boron dications with the general formula  $[[R(L)(L')B]_2]^{2+}$  (R being an amido group) having two boron atoms in the formal oxidation state +II. The surprisingly simple synthesis of **1** involves treating diborane(4)  $B_2Cl_2(NMe_2)_2$ , prepared from  $B_2(NMe_2)_4$ ,<sup>[6]</sup> with two equivalents of the free base hppH [see Eq. (1)]. Presumably, the

$[[Me_2(H)NB(hpp)]_2](Cl)_2$ . The hpp ligands stabilize the dinuclear species and protect it from oxidation or disproportionation.

The chloride salt of **1** can be crystallized as a dichloromethane solvate from a mixture of dichloromethane/hexane. The structure of **1** as determined by X-ray diffraction measurements is given in Figure 1. The B–B bond



**Figure 1.** Molecular structure of the dication **1** derived from X-ray diffraction. Selected bond lengths [pm] and angles [°]: B1–B2 174.6(2), B1–N1 155.2(4), B2–N2 154.3(4), B1–N4 155.1(4), B2–N5 153.9(4), N1–C1 134.5(4), N2–C1 134.9(4), C1–N3 133.8(4), N4–C2 134.4(4), N5–C2 133.9(4), C2–N6 134.5(4), B1–N7 160.1(4), B2–N8 160.6(4): N1–B1–N4 111.8(2), N2–B2–N5 112.2(2), N1–C1–N2 115.0(2), N4–C2–N5 115.2(2), N7–B1–B2 130.7(2), N8–B2–B1 130.1(2).



diborane(4) species  $[[Me_2NB(hpp)]_2]$  forms initially, which then reacts with the released HCl to form the salt

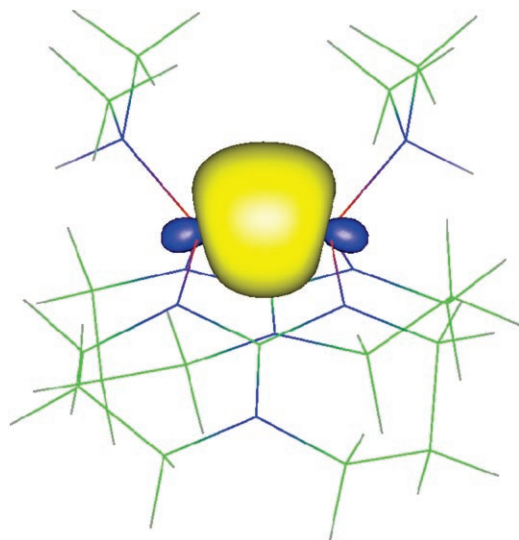
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(174.6 pm) lies well within the range of typical B–B single bonds. For example, gas-phase electron diffraction measurements of  $B_2(NMe_2)_4$  and  $B_2(OMe)_4$  gave B–B bond lengths of 176.2(1.1) and 172.0(6) pm, respectively.<sup>[7]</sup> Recently we reported the synthesis of  $[[HB(hpp)]_2]$ <sup>[8]</sup> containing a slightly longer B–B single bond (177.2(3) pm). The B–N bonds to the hpp ligands in **1** are 153.9–155.2 pm long, and the bonds to the two  $NMe_2H$  ligands have lengths of 160.1 and 160.6 pm. For comparison, the B–N bonds to the hpp ligands in  $[[HB(hpp)]_2]$  fall within the range 156.3(3)–158.2(3) pm.<sup>[8]</sup> The B– $NHMe_2$  bond lengths are similar to those reported for amine adducts of  $BH_3$ . In  $H_3BNH_3$ ,<sup>[9]</sup>  $H_3BNMe_3$ <sup>[10]</sup> and  $H_3B(\text{quinclidine})$ ,<sup>[11]</sup> B–N bonds of 156.4, 161.6, and 160.8 pm, respectively, were measured in the solid state. The

two boron atoms and the four hpp nitrogen atoms that are directly bound to boron in **1** form the vertices of a trigonal prism with N-B-N angles of approximately 112°. In the solid state, the dication is packed in such a way that large channels form, which are filled with the chloride ions and dichloromethane (five molecules per dication). The chloride ions are involved in hydrogen bonding with the hydrogen atoms of the two NHMe<sub>2</sub> groups in **1** ( $d(\text{Cl}\cdots\text{H}) = 210, 225$  pm, or 209, 213 pm when normalized N-H bonds (101 pm) are used). Furthermore, somewhat weaker hydrogen bonds are present between the chloride ions and the hydrogen atoms of the dichloromethane molecules ( $d(\text{Cl}\cdots\text{H}) = 255\text{--}268$  pm, or 246–260 pm when normalized C-H bonds (108 pm) are used). The observation of a signal in the ESI spectra for  $[\mathbf{1}+(\text{Cl})_2(\text{CH}_2\text{Cl}_2)_5]$  shows how significant these interactions are. The large shift in the <sup>1</sup>H NMR spectrum for the N-H hydrogen atom of the NMe<sub>2</sub>H groups ( $\delta_{\text{H}} = 8.90$  ppm) also indicates that the N-H $\cdots$ Cl contacts remain intact in solution. For comparison, a chemical shift of  $\delta_{\text{H}} = 5.5$  ppm was obtained for the corresponding signal in the adduct H<sub>3</sub>BNMe<sub>2</sub>H.<sup>[12]</sup>

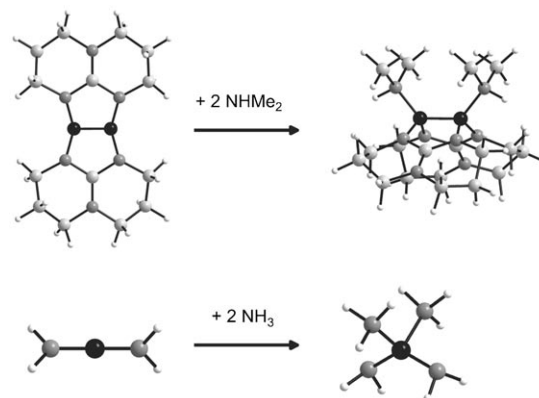
Compound **1**-(Cl)<sub>2</sub> melts at 226 °C, but partial decomposition is observed below this temperature. Thermogravimetric analysis shows that **1**-(Cl)<sub>2</sub> without the cocrystallized CH<sub>2</sub>Cl<sub>2</sub> loses about 20% of its weight in two steps. These steps reach their turning points at 138 and 197 °C (see Supporting Information). The mass loss for the two steps combined is in agreement with the expected loss for removal of the two NHMe<sub>2</sub> groups from **1**-(Cl)<sub>2</sub>. To obtain further evidence, NMR spectra were recorded after the substance had been heated to 250 °C. These spectra confirmed the loss of the NHMe<sub>2</sub> groups (see Supporting Information). We were, however, not able to identify with certainty the decomposition product.

A C<sub>2</sub>-symmetric energy minimum was found for **1** with DFT calculations (BP86/TZVPP)<sup>[13]</sup>. Two of the canonical frontier orbitals show significant B-B bonding contributions. Localization of the orbitals confirmed the existence of a purely B-B bonding orbital (see Figure 2). The calculations



**Figure 2.** Illustration of the localized B-B bonding orbital of **1**. N blue, C green, H gray.

also shed light on the B-NHMe<sub>2</sub> bond strength. For the removal of both NMe<sub>2</sub>H groups from **1** to give the  $[\{\text{B}(\text{hpp})\}_2]^{2+}$  ion (see Figure 3), an energy change without and



**Figure 3.** Calculated structures of  $[\{\text{B}(\text{hpp})\}_2]^{2+}$  and  $[\text{B}(\text{NH}_2)_2]^+$  and the products of their reactions with two equivalents of an amine base.

with zero-point vibrational energy (ZPE) corrections of +248 and +227 kJ mol<sup>-1</sup>, respectively, was calculated. The value of  $\Delta G^0$  (at 298 K and 1 bar) is +127 kJ mol<sup>-1</sup>. For comparison, NH<sub>3</sub> elimination from the simple model boronium ion  $[\text{B}(\text{NH}_2)_2(\text{NH}_3)_2]^+$  (**2**) has values of +259, +231, and +153 kJ mol<sup>-1</sup> for  $\Delta E$ ,  $\Delta E_{\text{ZPE}}$ , and  $\Delta G^0$ , respectively (see Figure 3). The dissociation energies for the first and second NH<sub>3</sub> molecules in **2** were calculated to be 34 and 225 kJ mol<sup>-1</sup>, respectively (adding up to 259 kJ mol<sup>-1</sup>) and are thus very different. In previous restricted Hartree Fock (RHF) calculations,<sup>[14]</sup> the dissociation energy of  $[\text{B}(\text{NH}_2)_2(\text{NH}_3)]^+$  was estimated to be 231 kJ mol<sup>-1</sup>, a value which agrees well with our estimate. Our calculations predict that the  $[\{\text{B}(\text{hpp})\}_2]^{2+}$  ion has an almost planar central N<sub>2</sub>B<sub>2</sub>N<sub>2</sub> unit with a B-B bond length of 161.9 pm. As illustrated in Figure 3, the boronium ion  $[\text{B}(\text{NH}_2)_2]^+$  has a D<sub>2d</sub> ground-state geometry featuring B-N and N-H bond lengths of 133.7 and 102.2 pm, and H-N-H angles of 113.8°. Previous quantum-chemical calculations<sup>[14]</sup> indicate that the planar, D<sub>2h</sub>-symmetric form has an energy 75 kJ mol<sup>-1</sup> higher than that with D<sub>2d</sub> symmetry.

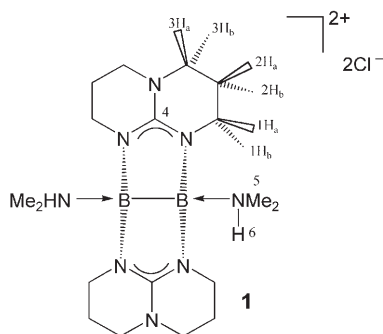
We calculated the fluoride ion affinity (FIA) of the  $[\{\text{B}(\text{hpp})\}_2]^{2+}$  ion and compared it with that of the boronium cation  $[\text{B}(\text{NH}_2)_2]^+$ . The energy change for reaction of two equivalents of F<sup>-</sup> with  $[\{\text{B}(\text{hpp})\}_2]^{2+}$  was calculated to be 1695 kJ mol<sup>-1</sup>. For comparison, reaction of one equivalent of F<sup>-</sup> with  $[\text{B}(\text{NH}_2)_2]^+$  to yield the neutral planar B(NH<sub>2</sub>)<sub>2</sub>F involves an energy change of 973 kJ mol<sup>-1</sup>, a value which is 57% of that calculated for  $[\{\text{B}(\text{hpp})\}_2]^{2+}$  (reaction with two F<sup>-</sup> ions instead of one). All these calculations indicate that the chemical reactivity of **1** is comparable to other boron cations.<sup>[15]</sup>

In summary, we have reported the first synthesis and characterization of a dinuclear B<sup>II</sup> dication with the general formula  $[\{\text{R}(\text{L})(\text{L}')\text{B}\}_2]^{2+}$ . This compound has been characterized by various spectroscopic techniques and by X-ray diffraction measurements, and quantum-chemical calculations have been carried out.

## Experimental Section

All reactions were carried out under a dry argon atmosphere using standard Schlenk techniques. All solvents were dried using standard methods and then distilled.  $B_2Cl_2(NMe_2)_2$  was prepared according to literature procedure.<sup>[5]</sup>  $B_2(NMe_2)_4$  and hppH (98%) were purchased from Boron Molecular Pty Ltd. and Aldrich, respectively, and used as delivered.

$1-(Cl)_2 \cdot 5CH_2Cl_2 \cdot B_2Cl_2(NMe_2)_2$  (0.185 g, 1.02 mmol) was slowly added to a stirred solution of hppH (0.285 g, 2.05 mmol) in toluene (15 mL). The reaction mixture was then stirred at room temperature



for 14 h. The product was separated by filtration and washed several times with toluene (5 mL) to give, after recrystallization from  $CH_2Cl_2$ , a colorless solid in 57% yield (0.51 g, 0.58 mmol). X-ray quality crystals were grown from a mixture of dichloromethane/hexane at room temperature.  $^1H$  NMR (400 MHz,  $CD_2Cl_2$ ):  $\delta$  = 8.90 (septet, H6, 2H,  $^3J(H6-H5)$  = 5.5), 3.67 (dt, H1a, 4H,  $^2J(H1a-H1b)$  = 12.8 Hz,  $^3J(H1a-H2)$  = 5.0 Hz), 3.30 (dt, H1b, 4H,  $^2J(H1b-H1a)$  = 12.8 Hz,  $^3J(H1b-H2)$  = 6.3 Hz), 3.19 (dt, H3a, 4H,  $^2J(H3a-H3b)$  = 11.9 Hz,  $^3J(H3a-H2)$  = 5.0 Hz), 3.12 (dt, H3b, 4H,  $^2J(H3b-H3a)$  = 11.9 Hz,  $^3J(H3b-H2)$  = 6.5 Hz), 2.42 (d, H-5, 12H,  $^3J(H6-H5)$  = 5.5 Hz), 1.89 ppm (q, H2, 8H,  $^3J(H2-H)$  = 5.0, 6.5 Hz).  $^{13}C$  NMR (100.56 MHz,  $CD_2Cl_2$ ):  $\delta$  = 158.36 (C4), 47.79 (C1), 40.39 (C3), 39.86 (C5), 22.18 ppm (C2).  $^{11}B$  NMR (128.3 MHz,  $CD_2Cl_2$ ):  $\delta$  = 1.43. MS (ESI<sup>+</sup>):  $m/z$ : 881.8 [ $C_{23}H_{46}B_2N_8Cl_{12}$ ]<sup>2+</sup>, 809.7 [ $C_{23}H_{45}B_2N_8Cl_{10}$ ]<sup>+</sup>, 423.5 [ $C_{18}H_{38}B_2N_8Cl$ ]<sup>+</sup>, and 387.5 [ $C_{18}H_{38}B_2N_8$ ]<sup>+</sup>. IR ( $CH_2Cl_2$ ):  $\tilde{\nu}$  = 3945 (w), 3691 (w), 3055 (vs, C-H), 2987 (vs, C-H), 2686 (w), 2522 (w), 2411 (w), 2306 (s), 1590/1562 (s), 1422 (vs), 1326 (w), 1271/1269  $cm^{-1}$  (vs, B-N).

Crystal data for  $[(Me_2(H)NB(hpp))_2]Cl_2 \cdot 5CH_2Cl_2$ :  $C_{23}H_{48}B_2Cl_{12}N_8$ ,  $M_r$  = 883.71,  $0.20 \times 0.20 \times 0.10$  mm<sup>3</sup>, triclinic, space group  $P\bar{1}$ ,  $a$  = 10.0946(8),  $b$  = 10.7605(8),  $c$  = 18.2651(14) Å,  $\alpha$  = 93.798(2),  $\beta$  = 92.7700(10),  $\gamma$  = 93.593(2)°,  $V$  = 1973.0(3) Å<sup>3</sup>,  $Z$  = 2,  $\rho_{calcd}$  = 1.488 Mg m<sup>-3</sup>, MoK $\alpha$  radiation (graphite monochromated,  $\lambda$  = 0.71073 Å),  $T$  = 100(2) K,  $\theta_{range}$  1.9 to 26.7°. Reflections 37530 measured, 8381 independent,  $R_{int}$  = 0.070, semi-empirical absorption correction.<sup>[19]</sup>  $R$  indices [ $I > 2\sigma(I)$ ]:  $R1$  = 0.0454,  $wR2$  = 0.1077. All non-hydrogen atoms were given anisotropic displacement parameters. All hydrogen atoms were included in calculated positions except those on N7 and N8, which were taken from a difference Fourier map. During refinement, the hydrogen atoms were treated with a riding model. One of the five dichloromethane molecules was found to be disordered around its molecular  $C_2$  axis. Structure solution using direct methods: SHELXS-97,<sup>[20]</sup> refinement by full-matrix least-squares on  $F^2$ : SHELXL-97.<sup>[21]</sup> CCDC-650824 contains 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).

**Keywords:** boron · cations · quantum chemistry · subvalent compounds

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- [15] The dication **1** is formally valence isoelectronic to the neutral  $[(Me_2(H)NMg(hpp))_2]$  and  $[(Me_2(H)NZn(hpp))_2]$  molecules, which feature two  $Mg^I$  or  $Zn^I$  atoms directly connected to each other. No example of a stable molecular compound featuring a  $Mg-Mg$  single bond is known,<sup>[16]</sup> and the preparation of dinuclear zinc species featuring a direct  $Zn-Zn$  bond were reported only recently.<sup>[17]</sup> Major difficulties are disproportionation reactions leading to elemental magnesium or zinc and a mononuclear metal(II) compound. Calculations were carried out to shed light on the likely structures of such species (see Supporting Information). The  $Zn-Zn$  bond in  $[(Me_2(H)N)Zn(hpp)]_2$  is 230.2 pm, and is close to that measured in  $[Zn_2Cp^{*2}]$  (231 pm,  $Cp^* = C_5(CH_3)_5$ ).<sup>[17]</sup> According to our calculations, the  $Mg-Mg$  bond length in  $[(Me_2(H)N)Mg(hpp)]_2$  is 264.2 pm. For

comparison, the Mg–Mg bond in HMgMgH in its  $^1\Sigma_g^+$  electronic ground state was calculated with B3LYP/6-311++G(3df,3pd) to be 286.7 pm.<sup>[18]</sup> It has to be determined whether the bridging hpp ligands are in part responsible for the significantly shorter Mg–Mg distance in  $[\{(\text{Me}_2\text{HN})\text{Mg}(\text{hpp})\}_2]$ . The hpp ligand might be ideally suited to engage not only two boron, but also two zinc or even magnesium atoms in direct bonding to each other.

[16] See the discussion in A. Schnepf, H.-J. Himmel, *Angew. Chem.* **2005**, *117*, 3066–3068; *Angew. Chem. Int. Ed.* **2005**, *44*, 3006–3008.

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