Boron Cations

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

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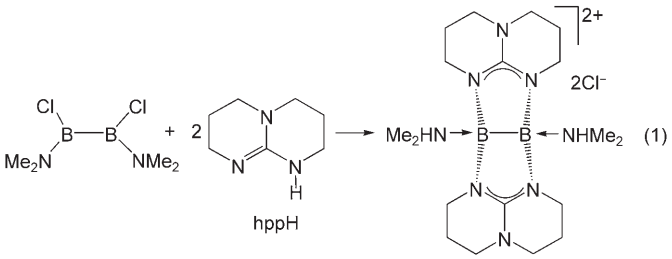
A number of boronium ions with the general formula $[R_2BL_2]^+$ (where L is a donor, such as an amine), some borenium $[R_2BL]^+$, and even borinium $[R_2B]^+$ ions have been synthesized and structurally characterized.[1] In all these compounds, boron has a formal oxidation state of +III. In addition to the academic interest in the bonding properties in these species, some of them have found application as catalysts in polymerization[2] or Diels–Alder reactions.[3] Boronium cations are also efficient initiators for the dehydrogenation of ammonia–borane.[4] 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,[5] feature an almost linear N–B–N unit.

Herein we report the synthesis of the dication $[\{(Me_2(H)N)B(hpp)\}_2]^{2+}$ (**1**; hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-a]pyrimidate), 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 $B_2(NMe_2)_4$,[6] with two equivalents of the free base hppH [see Eq. (1)]. Presumably, the



diborane(4) species $[\{Me_2NB(hpp)\}_2]$ forms initially, which then reacts with the released HCl to form the salt $[\{Me_2(H)NB(hpp)\}_2](Cl)_2$. 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

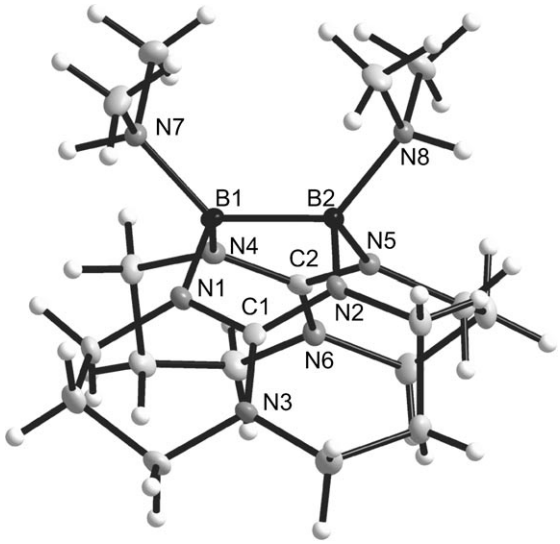


Figure 1. Molecular structure of the dication **1** derived from X-ray diffraction. Selected bond lengths [pm] and angles [°]: B1–B2 174.6(2), B1–N1 155.2 (4), B2–N2 154.3 (4), B1–N4 155.1(4), B2–N5 153.9(4), N1–C1 134.5(4), N2–C1 134.9(4), C1–N3 133.8(4), N4-C2 134.4(4), N5–C2 133.9(4), C2–N6 134.5(4),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

(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.[7] Recently we reported the synthesis of $[\{HB(hpp)\}_2]$[8] 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.[8] The B–$NHMe_2$ bond lengths are similar to those reported for amine adducts of BH_3. In H_3BNH_3,[9] H_3BNMe_3[10] and H_3B(quinuclidine),[11] B–N bonds of 156.4, 161.6, and 160.8 pm, respectively, were measured in the solid state. The

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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 dications are 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 $NHMe_2$ groups in **1** (d(Cl···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(Cl···H) = 255–268 pm, or 246–260 pm when normalized C–H bonds (108 pm) are used). The observation of a signal in the ESI spectra for [**1**+$(Cl)_2$-$(CH_2Cl_2)_5$] shows how significant these interactions are. The large shift the ^{1}H NMR spectrum for the N–H hydrogen atom of the NMe_2H groups (δ_H = 8.90 ppm) also indicates that the N-H···Cl contacts remain intact in solution. For comparison, a chemical shift of δ_H = 5.5 ppm was obtained for the corresponding signal in the adduct H_3BNMe_2H.[12]

Compound **1**-$(Cl)_2$ melts at 226 °C, but partial decomposition is observed below this temperature. Thermogravimetric analysis shows that **1**-$(Cl)_2$ without the cocrystallized CH_2Cl_2 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 $NHMe_2$ groups from **1**-$(Cl)_2$. To obtain further evidence, NMR spectra were recorded after the substance had been heated to 250 °C. These spectra confirmed the loss of the $NHMe_2$ groups (see Supporting Information). We were, however, not able to identify with certainty the decomposition product.

A C_2-symmetric energy minimum was found for **1** with DFT calculations (BP86/TZVPP)[13]. 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 also shed light on the B–$NHMe_2$ bond strength. For the removal of both NMe_2H groups from **1** to give the $[\{B(hpp)\}_2]^{2+}$ ion (see Figure 3), an energy change without and

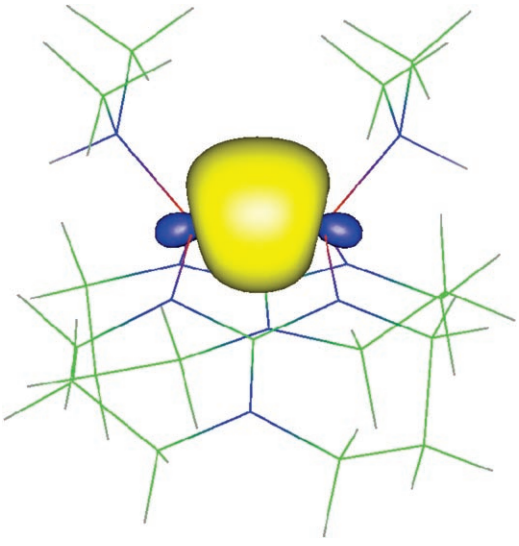


Figure 2. Illustration of the localized B–B bonding orbital of **1**. N blue, C green, H gray.

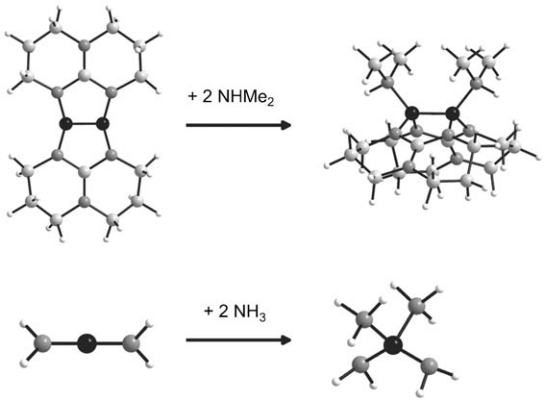


Figure 3. Calculated structures of $[\{B(hpp)\}_2]^{2+}$ and $[B(NH_2)_2]^+$ and the products of their reactions with two equivalents of an amine base.

with zero-point vibrational energy (ZPE) corrections of +248 and +227 kJ mol^{-1}, respectively, was calculated. The value of ΔG^0 (at 298 K and 1 bar) is +127 kJ mol^{-1}. For comparison, NH_3 elimination from the simple model boronium ion $[B(NH_2)_2(NH_3)_2]^+$ (**2**) has values of +259, +231, and +153 kJ mol^{-1} for ΔE, ΔE_{ZPE}, and ΔG^0, respectively (see Figure 3). The dissociation energies for the first and second NH_3 molecules in **2** were calculated to be 34 and 225 kJ mol^{-1}, respectively (adding up to 259 kJ mol^{-1}) and are thus very different. In previous restricted Hartree Fock (RHF) calculations,[14] the dissociation energy of $[B(NH_2)_2(NH_3)]^+$ was estimated to be 231 kJ mol^{-1}, a value which agrees well with our estimate. Our calculations predict that the $[\{B(hpp)\}_2]^{2+}$ ion has an almost planar central $N_2B_2N_2$ unit with a B–B bond length of 161.9 pm. As illustrated in Figure 3, the borinium ion $[B(NH_2)_2]^+$ has a D_{2d} 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[14] indicate that the planar, D_{2h}-symmetric form has an energy 75 kJ mol^{-1} higher than that with D_{2d} symmetry.

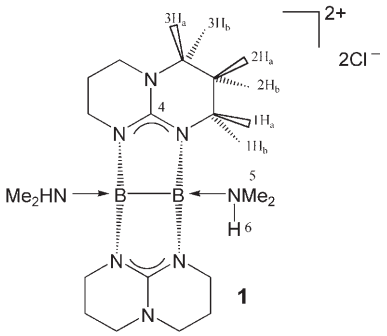
We calculated the fluoride ion affinity (FIA) of the $[\{B(hpp)\}_2]^{2+}$ ion and compared it with that of the borinium cation $[B(NH_2)_2]^+$. The energy change for reaction of two equivalents of F^- with $[\{B(hpp)\}_2]^{2+}$ was calculated to be 1695 kJ mol^{-1}. For comparison, reaction of one equivalent of F^- with $[B(NH_2)_2]^+$ to yield the neutral planar $B(NH_2)_2F$ involves an energy change of 973 kJ mol^{-1}, a value which is 57 % of that calculated for $[\{B(hpp)\}_2]^{2+}$ (reaction with two F^- ions instead of one). All these calculations indicate that the chemical reactivity of **1** is comparable to other boron cations.[15]

In summary, we have reported the first synthesis and characterization of a dinuclear B^{II} dication with the general formula $[\{R(L)(L')B\}_2]^{2+}$. 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.[5] $B_2(NMe_2)_4$ and hppH (98%) were purchased from Boron Molecular Pty Ltd. and Aldrich, respectively, and used as delivered.

1-$(Cl)_2{\cdot}5\,CH_2Cl_2$: $B_2Cl_2(NMe_2)_2$ (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. ^{1}H 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$^+$): m/z: 881.8 $[C_{23}H_{46}B_2N_8Cl_{12}]^+$, 809.7 $[C_{23}H_{45}B_2N_8Cl_{10}]^+$, 423.5 $[C_{18}H_{38}B_2N_8Cl]^+$, and 387.5 $[C_{18}H_{38}B_2N_8]^+$. 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 $[\{Me_2(H)NB(hpp)\}_2]Cl_2{\cdot}5\,CH_2Cl_2$: $C_{23}H_{48}B_2Cl_{12}N_8$, $M_r = 883.71$, $0.20 \times 0.20 \times 0.10$ mm^3, 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^3, $Z = 2$, $\rho_{calcd} = 1.488$ Mg m^{-3}, $Mo_{K\alpha}$ radiation (graphite monochromated, $\lambda = 0.71073$ Å), $T = 100(2)$ K, θ_{range} 1.9 to 26.7°. Reflections 37530 measured, 8381 independent, $R_{int} = 0.070$, semi-empirical absorption correction.[19] 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,[20] refinement by full-matrix least-squares on $F2$: SHELXL-97.[21] 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.

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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,[16] and the preparation of dinuclear zinc species featuring a direct Zn–Zn bond were reported only recently.[17] 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 $[\{(Me_2HN)Zn(hpp)\}_2]$ is 230.2 pm, and is close to that measured in $[Zn_2Cp^*_2]$ (231 pm, $Cp^* = C_5(CH_3)_5$).[17] According to our calculations, the Mg–Mg bond length in $[\{(Me_2HN)Mg(hpp)\}_2]$ 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.[18] It has to be determined whether the bridging hpp ligands are in part responsible for the significantly shorter Mg–Mg distance in [{(Me$_2$HN)Mg(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.

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