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The Synthesis of $[Me_4N]_2[a^2\text{-}B_{20}H_{16}(NH_3)_2]$ and *trans*-$B_{20}H_{16}(NH_3)_2$ from $[Me_3NH][cis\text{-}B_{20}H_{17}NH_3]$ and Their Structural Characterization

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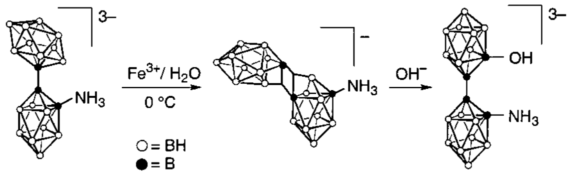
The chemistry of novel polyhedral borane derivatives has recently attracted new interest because of their potential application in the liposome-mediated boron neutron capture therapy (BNCT) of cancer.[1−4] The $[trans\text{-}B_{20}H_{18}]^{2-}$ polyhedral borane anion[5−9] has been found to be a versatile source for a variety of these boron-rich derivatives.[10−14]

The synthesis of the stereochemically unprecedented $[cis\text{-}B_{20}H_{18}]^{2-}$ and the ammonio-substituted anion $[cis\text{-}B_{20}H_{17}NH_3]^-$ ($[\mathbf{2}]^-$)[10] has been reported (Scheme 1). The two three-center two-electron bonds of $[\mathbf{2}]^-$ are electron deficient and susceptible to nucleophilic attack, and the reaction of $[\mathbf{2}]^-$ with hydroxide ion produced disubstituted $[a^2\text{-}B_{20}H_{16}NH_3(OH)]^{3-}$ ($[\mathbf{3}]^{3-}$)[10] (Scheme 1). A recent investigation of the reaction of $[\mathbf{2}]^-$ with liquid ammonia has led to the discovery of the diammonio-substituted anion, $[a^2\text{-}B_{20}H_{16}(NH_3)_2]^{2-}$ ($[\mathbf{4}]^{2-}$). Subsequent aqueous ferric ion oxidation of $[\mathbf{4}]^{2-}$ resulted in the neutral derivative, *trans*-$B_{20}H_{16}(NH_3)_2$ (**5**). We report here the syntheses and structures of $[\mathbf{4}]^{2-}$ and **5**.

Scheme 1



$[\mathbf{1}]^{3-}$ $[\mathbf{2}]^{-}$ $[\mathbf{3}]^{3-}$

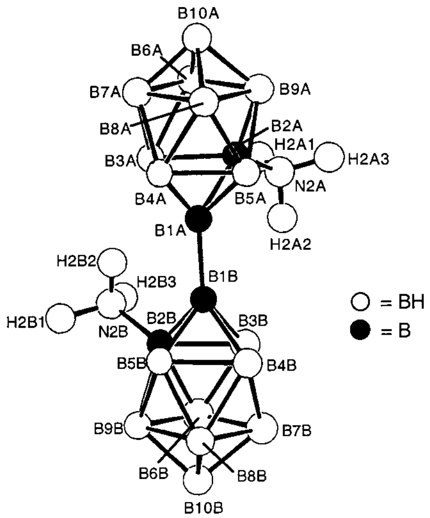
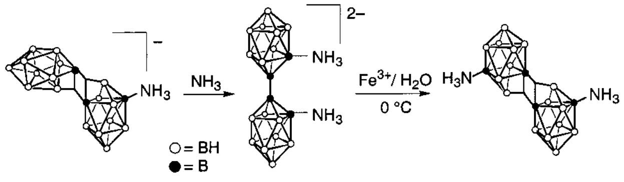


Figure 1. ORTEP representation of the $[\mathbf{4}]^{2-}$ anion showing the atom-numbering scheme. For purposes of clarity, the terminal B−H hydrogen atoms have been omitted. Selected bond distances (Å) and bond angles (deg) are as follows (estimated standard deviations in parentheses): N(2A)−B(2A) 1.560(8), B(1A)−B(2A) 1.691(10), B(1A)−B(1B) 1.696(10), N(2B)−B(2B) 1.571(9), B(1B)−B(2B) 1.698(10); B(2A)−B(1A)−B(3A) 63.6(4), B(2A)−B(1A)−B(4A) 96.6(5), B(3A)−B(1A)−B(5A) 98.7(5), B(3A)−B(1A)−B(1B) 132.4(5), N(2A)−B(2A)−B(1A) 117.0(5), N(2A)−B(2A)−B(3A) 129.8(5), N(2A)−B(2A)−B(6A) 117.8(5).

The dissolution of $[Me_3NH][\mathbf{2}]$ in liquid ammonia, followed by evaporation of the solvent, produced the disubstituted derivative of $[a^2\text{-}B_{20}H_{18}]$,[4−15] the $[a^2\text{-}B_{20}H_{16}(NH_3)_2]^{2-}$ anion ($[\mathbf{4}]^{2-}$),[16] isolated as its tetramethylammonium salt in 83% yield (Scheme 2). The product was characterized by ^{11}B NMR and electrospray ionization mass spectrometry (ESI-MS). The structure of $[Me_4N]_2[\mathbf{4}]$ was determined by X-ray crystallography, and an ORTEP representation[17] is presented in Figure 1. The anion $[\mathbf{4}]^{2-}$ is composed of two equivalent $[B_{10}H_8NH_3]^-$ cages linked together by a two-center bond joining apical boron atoms of each cage. This is the first disubstituted derivative of $[a^2\text{-}B_{20}H_{18}]^{4-}$ to be structurally

Scheme 2



$[\mathbf{2}]^{-}$ $[\mathbf{4}]^{2-}$ **5**

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(7) The discovery of the previously unknown cis fusion of two $[B_{10}H_9]^-$ cages to form the new so-called $[cis\text{-}B_{20}H_{18}]^{2-}$ isomer (ref 10) demands that the $[B_{20}H_{18}]^{2-}$ isomer originally reported (refs 5 and 6) now be described as $[trans\text{-}B_{20}H_{18}]^{2-}$. The unique photochemical isomer (refs 8 and 9) is denoted as $[h\nu\text{-}B_{20}H_{18}]^{2-}$.

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(16) Spectroscopic data for $[\mathbf{4}]^{2-}$. $^{11}B\{^1H\}$ NMR (ppm, H_2O): 7.9 (2B, B−B); −5.5 (2B, apical B−H); −14.4 (2B, B−N); −24.7, −25.8, −29.2, and −31.1 (total of 14B, B−H). ESI-MS (*m/z*): 267 $\{(H)[B_{20}H_{16}(NH_3)_2]\}^-$.

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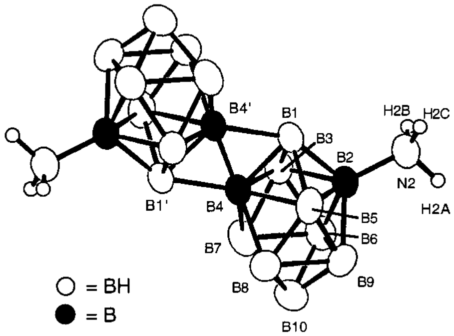

Figure 2. ORTEP representation of **5** showing the atom-numbering scheme. For purposes of clarity, the terminal B−H hydrogen atoms have been omitted. Primed and unprimed atoms are related through a center of symmetry. Selected bond distances (Å) and bond angles (deg) are as follows (estimated standard deviations in parentheses): B(1)−B(4) 1.669(4), B(1)′−B(4) 1.872(4), B(2)−B(3) 1.788(4), B(2)−B(5) 1.783(5), B(8)−B(9) 1.791(5), B(8)−B(10) 1.684(5), B(9)−B(10) 1.696(5), B(2)−N(2) 1.548(4); B(4)−B(1)−B(4)′ 56.7(2), B(1)−B(4)−B(1)′ 123.3(2), B(2)−B(1)−B(4) 95.0(2), B(2)−B(1)−B(4)′ 151.7(2), N(2)−B(2)−B(3) 127.4(2), N(2)−B(2)−B(5) 128.4(2).

characterized. As in the case of the solid-state structure of [a^2-$B_{20}H_{18}$]$^{4-}$,[18] the equatorial boron atoms of the two B_{10} cages are virtually eclipsed with respect to the corresponding equatorial boron atoms of the opposite cage. The dihedral angle B(3A)−B(1A)−B(1B)−B(2B) is only 2.0(11)°. However, the two B−N bonds are not eclipsed, which could be due to steric and electronic repulsion.

Neutral aqueous solutions of [**4**]$^{2-}$ are relatively stable at room temperature, although the rearrangement of [**4**]$^{2-}$ to another, as yet unidentified, isomer is observed in acidic solution. The half-peak oxidation potential of [**4**]$^{2-}$ vs Ag/AgCl in acetonitrile is +236 mV, which suggested that this anion could be chemically oxidized by ferric ion. Thus, at 0 °C the aqueous Fe^{3+} oxidation of [**4**]$^{2-}$ produced $B_{20}H_{16}(NH_3)_2$ (**5**),[19] which slowly precipitated from solution as a yellow powder in 23% yield. The species **5** was characterized by ^{11}B NMR and ESI-MS, as well as by single-crystal X-ray diffraction (Figure 2). Other neutral, disubstituted derivatives of [*trans*-$B_{20}H_{18}$]$^{2-}$ ($B_{20}H_{16}L_2$, where L is a neutral two-electron donor such as $(CH_3)_2S$) have been reported to result from the oxidation of [$B_{10}H_9L$]$^{2-}$,[20] but these species were not structurally characterized and the substitution pattern is uncertain.

An ORTEP representation[21] of **5** is shown in Figure 2. The molecule is centrosymmetric, and the two decaborate cages are linked through three-center two-electron bonds similar to those which were originally observed in [*trans*-$B_{20}H_{18}$]$^{2-}$.[5,22]

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Supporting Information Available: Experimental synthetic procedures, and X-ray crystallographic files in CIF format for the structure determinations of $[Me_4N]_2$[**4**] and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) $[Me_4N]_2$[**4**] crystallized in the monoclinic space group $P2_1/c$ with a = 13.544(9) Å, b = 14.936(10) Å, c = 13.592(9) Å, β = 102.75(2)°, V = 2682 Å^3, and Z = 4. Data were collected using Cu Kα radiation, to a maximum 2θ = 115°, giving 3119 unique reflections, and the structure was solved by direct methods. The final discrepancy indices were R = 0.086, R_w = 0.092 for 1804 independent reflections with $I > 2\sigma(I)$.

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(19) Spectroscopic data for **5**. $^{11}B\{^1H\}$ NMR (160 MHz, ppm, H_2O): 32.5 (2B, apical B−H); 16.4 (2B, equatorial B); 3.8 (2B, B−N); −12.3, −14.1, −19.0, and −25.0 (total of 14B, B−H). ESI-MS (*m*/*z*): 265.3 $\{B_{20}H_{16}(NH_3)(NH_2)\}^-$.

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(21) The neutral derivative **5** crystallized in the triclinic space group $P\bar{1}$ with a = 6.976(3) Å, b = 8.648(4) Å, c = 10.600(4) Å, α = 75.87(1)°, β = 85.30(1)°, γ = 77.73(1)°, V = 606 Å^3, and Z = 1. Data were collected using Mo Kα radiation, to a maximum 2θ = 55°, giving 2919 unique reflections, and the structure was solved by direct methods. The final discrepancy indices were R = 0.064, R_w = 0.206 for 1189 independent reflections with $I > 2\sigma(I)$.

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