Supramolecular Chemistry: Molecular Aggregates of Closo-$B_{10}H_{10}^{2-}$ with [12]Mercuracarborand-4

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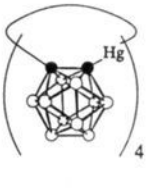
Supramolecular chemistry, the extension of host–guest chemistry, has attracted increasing attention because of its relationship to molecular recognition, reactivity and catalysis, transport processes, molecular assemblies, and the design of supramolecule-based devices.[1,2] In the construction of supramolecular structures, the component molecules associate *via* intermolecular interactions such as hydrogen bonds, Lewis acid–base interactions, and van der Waals forces in complementary fashions. So far, supramolecular chemistry has relied on more or less rigid synthetic molecular receptors for achieving molecular recognition.[1a,2] Recently, supramolecular assemblies such as mesophases,[3] liquid crystalline and 2D polymers,[4] and ordered solid-state structures[5] have been reported. Moreover, self-assembly of molecules assisted by metal ions has been used to prepare organized double-helical metal complexes[6] and artificial polypeptide helix bundles.[7] We have recently reported a family of multidentate Lewis acid hosts, exemplified by **1**, which bind anions and other nucleophilic species.[8] The possibility that these hosts form supramolecules with complex nucleophilic species such as polyhedral borane anions was explored, and the preliminary result is communicated here.



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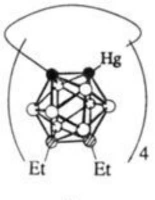

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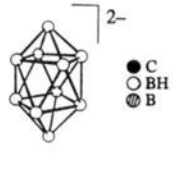

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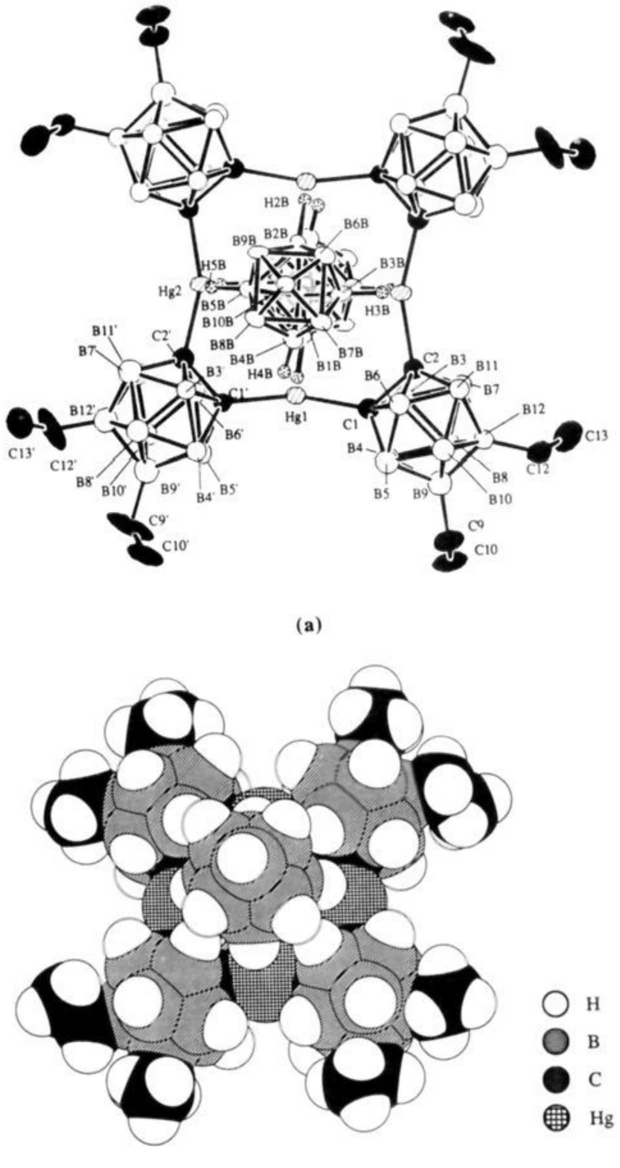

(a)

(b)

Figure 1. (a) ORTEP representation of anion $\mathbf{2}\cdot(\mathbf{3})_2$ with hydrogen atoms removed for clarity except those bonded to Hg atoms. Some selected interatomic distances (Å) and angles (deg) are as follows: Hg1–H4B = 2.18(12), Hg1,2–H2B = 3.1(1), Hg2–H5B = 2.75(12), Hg2,2–H3B = 2.84(12); Hg–B4B = 3.55(1), Hg1,2–B2B = 3.49(1), Hg2–B5B = 3.37(1), Hg2,2–B3B = 3.56(1), Hg1–C1 = 2.077(11), Hg1–C1′ = 2.076(12), Hg2–C2 = 2.112(13), Hg2–C2′ = 2.129(12), C1–C2 = 1.63(2), C1′–C2′ = 1.66(2); C1–Hg–C1′ = 164.6(4), C2–Hg2–C2′,2 = 157.7(5). Atoms denoted by ,2 are related to atoms in the *x,y,z* position by a center of symmetry at 0, 0, 1/2. (b) Space-filled model of $\mathbf{2}\cdot(\mathbf{3})_2$.

The intermolecular interaction of closo-$B_{10}H_{10}^{2-}$ (**3**) with [12]-mercuracarborand-4 (**1**) and its octaethyl derivative **2**[9] was studied in organic solvents (acetone, CH_2Cl_2, and CH_3CN) using ^{11}B and ^{199}Hg NMR spectroscopy.[11] The ^{11}B NMR spectrum of $\mathbf{3}$-$(MePh_3P)_2$ in CH_2Cl_2 exhibited two doublets at 0.83 and –27.3 ppm with a 1:4 ratio, corresponding to axial boron and equatorial boron atoms, respectively. Upon the addition of 1 equiv of **1** or **2**, the doublet at –27.3 ppm splits into a broad singlet at –23.3 ppm and a sharp doublet of equal intensity at –26.9 ppm, which can be explained by the formation of adducts of **3** with **1** or **2** in which four equatorial BH groups of **3** bind to four mercury atoms

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[9] The host **2** was prepared from the reaction of AgOAc and $\mathbf{2}\cdot I_2Li_2$, which is formed from the reaction of 9,12-Et_2-1,2-Li_2-1,2-$C_2B_{10}H_8$ (ref 10) and HgI_2. The syntheses and spectroscopic characterizations of $\mathbf{2}\cdot I_2Li_2$ and **2** are given in the supplementary material.

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[11] ^{11}B and ^{199}Hg NMR were obtained at 160.46 and 89.6 MHz, respectively, on a Bruker AM 500 spectrometer. Chemical shift values for ^{11}B spectra were referenced relative to external $BF_3\cdot OEt_2$ (0.00 ppm) and ^{199}Hg spectra to external 1.0 M PhHgCl in DMSO-d_6 at 1187 ppm upfield from neat Me_2Hg.

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in **1** or **2**. Further addition of 1 equiv of **1** or **2** results in no further change in the ^{11}B NMR. Apparently, **3** is not sufficiently nucleophilic to simultaneously bind two host molecules and form a sandwich aggregate.

The ^{199}Hg NMR spectrum of the 1:1 aggregate of $B_{10}H_{10}^{2-}$ and **1** exhibits a resonance at −1002 ppm in $CDCl_3/CH_2Cl_2$ (1:1), while the free host **1** itself appears at −1200 ppm in the same solvents. In comparison, $\mathbf{1}\cdot Cl^-$ in acetone exhibits a resonance at −1077 ppm. Two resonances which correspond to the 1:1 adduct and free **1** were observed when $\mathbf{3}$-$(MePh_3P)_2$ and **1** were combined in $CDCl_3/CH_2Cl_2$ solution in a 1:2 ratio, thus substantiating the suggestion that **3** cannot simultaneously bind two molecules of **1**. Similarly, $\mathbf{2}\cdot\mathbf{3}$-$(MePh_3P)_2$ in CH_3CN/acetone-d_6 displays a ^{199}Hg NMR resonance at −939 ppm. Addition of $\mathbf{3}$-$(MePh_3P)_2$ to this $\mathbf{2}\cdot\mathbf{3}$ solution results in no change of the chemical shift. This fact may indicate that the $\mathbf{2}\cdot(\mathbf{3})_2$ adduct is not present in solution, even though in the solid state $\mathbf{2}\cdot(\mathbf{3})_2$-$(MePh_3P)_4$ was crystallized from CH_3CN solution and characterized by X-ray crystallography.[12]

An ORTEP drawing and a space-filling model of $\mathbf{2}\cdot(\mathbf{3})_2$ are shown in Figure 1. The tetraanion aggregate with a crystallographically imposed inversion symmetry consists of a planar macrocyclic tetradentate Lewis acid host and two bicapped square antiprismatic borane cages. The complexed host **2** consists of four bivalent 9,12-Et_2-1,2-$C_2B_{10}H_8$ cage fragments linked by four Hg atoms in a cyclic tetramer with structural parameters similar to those observed[8] in $\mathbf{1}\cdot Cl^-$ and $\mathbf{1}\cdot I_2^{2-}$. The **3** components of the aggregate have a bicapped square antiprismatic structure, as expected. The eight apex–equatorial B–B distances of each complexed **3** average to 1.69(2) Å, the four equatorial-equatorial B–B distances adjacent to the host average to 1.84(2) Å, and the remaining four average to 1.85(2) Å. The remaining eight interactions across the equatorial belt of **3** average to 1.81(2) Å. All of these distances are quite similar to the values previously reported for $Cu_2B_{10}H_{10}$.[13] The bonding of **3** with **1** or **2** appears to consist of equatorial B–H–Hg three-center–two-electron interactions with Hg–H distances ranging from 2.18 to 3.1 Å. Similar interactions were observed in $Cu_2B_{10}H_{10}$ with Cu–H distances of 1.7–2.2 Å.[13] The van der Waals distance of Hg–H is 2.93 Å (1.73 + 1.20 Å). The borane cages are slightly tilted with one toward Hg1 giving a short Hg1-H4B (2.18 Å) and long Hg1,2-H2B (3.1 Å). The second cage is tilted toward Hg1,2 in a symmetry related fashion.

Water-insoluble salts of **3** are formed with cations such as Ag^+, Cu^+, and Hg^{2+}.[14] Significant covalent interactions were observed between these cations and **3** and characterized by IR spectroscopy[15] and X-ray crystallography.[13] Normal ionic salts (Na^+, K^+, $MePh_3P^+$) of **3** display a very strong absorption at about 2470 cm^{-1} (equatorial B–H stretch).[14] However, covalent $\mathbf{3}\cdot Cu_2$ exhibits this stretching mode as a broad band at 2100–2300 cm^{-1}.[15] In addition to the B–H stretching absorption at 2535 cm^{-1} (carborane B–H), $\mathbf{2}\cdot(\mathbf{3})_2(MePh_3P)_4$ displays a B–H stretching absorption at 2422 cm^{-1}, which corresponds to the equatorial B–H stretch of **3** in the aggregate (Nujol mull). Compared with B–H–M interactions observed in $\mathbf{3}\cdot M_2$ (M = Cu, Ag, Hg) and $(PPh_3)_2CuB_3H_8$,[16] the weaker B–H–Hg interaction in $\mathbf{2}\cdot(\mathbf{3})_2$ is expected, since the Hg(II) centers in **1** and **2** have no formal charge. The stability of the supramolecular aggregates reported here must be due to the collective, cooperative, and complementary three-center–two-electron bonding of the four mercury atoms to four equatorial BH units in each complexed **3**, noting that planar **1** and **2** both have C_{4h} symmetry and **3** is D_{4d}. It is noteworthy that **1** and **2** do not interact with closo-$B_{12}H_{12}^{2-}$ and nido-7,8-$C_2B_9H_{12}^{1-}$, as revealed by ^{11}B NMR studies. The icosahedral closo-$B_{12}H_{12}^{2-}$ is less nucleophilic than **3**[13] and is sterically incompatible, as well. Consequently, both geometrical and electronic factors may account for the lack of interaction of closo-$B_{12}H_{12}^{2-}$ and nido-7,8-$C_2B_9H_{12}^{1-}$ with **1** or **2**. However, both **1** and **2** were found to bind a^2-$B_{20}H_{18}^{4-}$, which consists of two $B_{10}H_9^{2-}$ fragments connected through an apical–apical B–B bond (a^2),[17] forming 1:1 and 1:2 sandwich aggregates. Unfortunately, poor solubility of a^2-$B_{20}H_{18}(MePh_3P)_4$ in organic solvents hampered the structural characterization.

In summary, molecular aggregates of **3** with the macrocyclic Lewis acid hosts **1** and **2** have been detected and characterized both in solution and in the solid state. The multidentate feature of the Lewis acid hosts provides stabilization of the molecular aggregates through weak and complementary three-center–two-electron B–H–Hg interactions. The borane aggregates are easily dissociated in solution by the addition of halide ions. Both **1** and **2** have the potential to form a wide variety of supramolecules, and this chemistry is under investigation.

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Supplementary Material Available: Tables of position and thermal parameters, bond lengths and angles, and crystallographic data and synthesis and characterizations of $\mathbf{2}\cdot I_2Li_2$ and **2** (12 pages); listing of observed and calculated structure factors (45 pages). Ordering information is given on any current masthead page.

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(12) Crystallographic data for $\mathbf{2}\cdot(B_{10}H_{10})_2(PMePh_3)_4\cdot 2CH_3CN$: $C_{104}H_{170}N_2B_{60}P_4Hg_4$, the triclinic space group $P\bar{1}$ with $a = 15.583(2)$, $b = 15.861(2)$, and $c = 16.045(2)$ Å, $\alpha = 67.831(4)°$, $\beta = 70.713(4)°$, $\gamma = 86.371(4)°$, $V = 3457$ Å^3, and $Z = 1$. Data were collected on a Picker FACS-1 diffractometer at −117 °C, using Mo Kα radiation, to a maximum $2\theta = 52°$, giving 13 654 unique reflections, and the structure was solved by direct methods. The final discrepancy index was $R = 0.056$, $R_w = 0.064$ for 7609 independent reflections with $I > 3\,\sigma(I)$.

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