crystals containing compound **6**, with small amounts of **5** and **7**. Compound **6**: ^{11}B NMR (160.5 MHz, Freon 113, $BF_3 \cdot Et_2O$ external): $\delta = -17.7$ (s); ^{19}F NMR (499.3 MHz, Freon 113, 5% $CDCl_3$): $\delta = -51.7$ (d, 30F, ^2J(B,F) = 55 Hz; CF_3); ^{1}H NMR (499.8 MHz, Freon 113, 5% $CDCl_3$): $\delta = 5.1$ (s); HR-MS (CI): *m*/*z*: calcd 826.0608, found 826.0586; compound **7**: ^{11}B NMR (160.5 MHz, Freon 113, $BF_3 \cdot Et_2O$ external) $\delta = -15.8$ (s), -17.7 (s); ^{19}F NMR (499.3 MHz, Freon 113, 5% $CDCl_3$): $\delta = -49.1$ (d, 30F, ^2J(B,F) = 60 Hz, CF_3), -51.7 (d, 30F, ^2J(B,F) = 55 Hz, CF_3), -157.5 (s, 1F, CF); ^{1}H NMR (499.8 MHz, Freon 113, 5% $CDCl_3$): $\delta = 5.1$ (s); HR-MS (CI): *m*/*z*: calcd 844.0514, found 844.0538.

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Modular Self-Assembly of a Microporous Solid Based upon Mercuracarborand-4 and a New Bonding Motif**

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M. Frederick Hawthorne*

Mercuracarborands[1] comprise a class of novel macrocyclic multidentate Lewis acids[2] and possess useful properties in molecular recognition,[1, 3] optical sensors,[4] and catalysis.[5] Macrocyclic mercuracarborands are composed of alternating *ortho*-carborane icosahedra and mercury atoms linked by C-Hg-C moieties. The electron-withdrawing character of the *o*-carborane cage strengthens the Lewis acidity of the mercury centers, thereby enhancing the ability of the mercuracycle to function as a host for electron-rich guests.[2] An added benefit derived from the carborane cage is the fact that the boron vertices can be selectively functionalized to manipulate solubility[6, 7] and/or structural features required for supramolecular self-assembly.[8] The majority of carborane self-assembly chemistry is directed by the acidic C–H vertices of the carborane[9] and examples in which nonacidic B–H vertices direct self-assembly are limited.[10] As part of our ongoing investigation of mercuracarborand chemistry, we now report the synthesis and solid-state structure of $Li_2[(HgC_2B_{10}H_8I_2)_4 \cdot I_2]$ ($Li_2[\mathbf{1} \cdot I_2]$), an example of self-assembly directed by novel B–I ··· Li ··· I–B linkages which form microporous channels subsequently occupied by solvent molecules.

Electrophilic iodination at the electron-rich 9,12-vertices of *ortho*-carborane[6] followed by lithiation of the C–H vertices[11] provided the corresponding dilithium reagent, $Li_2C_2B_{10}H_8I_2$. The reaction of $Li_2C_2B_{10}H_8I_2$ with one molar equivalent of HgI_2 in dry diethyl ether at room temperature afforded the diiodide ion complex, $Li_2[\mathbf{1} \cdot I_2]$, of the *bis*-iodo-tetrameric cycle, **1**, in 78% yield. The resulting $Li_2[\mathbf{1} \cdot I_2]$ species is an air- and moisture-stable crystalline solid that is soluble in a variety of organic solvents such as acetone, acetonitrile, diethyl ether, and dichloromethane. The ^{1}H, ^{13}C, and ^{11}B NMR spectra of $Li_2[\mathbf{1} \cdot I_2]$ revealed a highly symmetrical structure in solution. The ^{199}Hg NMR spectrum of $Li_2[\mathbf{1} \cdot I_2]$ in acetone exhibits a sharp singlet at $\delta = -622$ which is essentially independent of concentration at room temperature. The negative-ion fast atom bombardment mass spectrum exhibits a peak centered at *m*/*z* 2640, with the isotopic pattern expected for $Li[\mathbf{1} \cdot I_2]^-$, and an anion envelope at *m*/*z* 2505, which corresponds to $[\mathbf{1} \cdot I]^-$. The species at *m*/*z* 2505 is presumed to arise through the elimination of LiI from $Li[\mathbf{1} \cdot I_2]^-$, since a second resonance signal was not observed in the ^{199}Hg NMR spectrum of the latter.

A single crystal of $[Li_2\{(CH_3)_2CO\}_6][\mathbf{1} \cdot I_2] \supset 4\,H_2O$, grown from an acetone/dichloromethane solution, was selected for an X-ray diffraction study.[12] It crystallized in the monoclinic space group *C*2/*m*. The $Li_2[\mathbf{1} \cdot I_2]$ structure consists of four divalent 9,12-I_2-1,2-$C_2B_{10}H_8$ cages linked at carbon by four Hg atoms in a cyclic tetramer with an iodide ion located above and below the tetramer cavity (Figure 1). The four Hg atoms are coplanar and lie in a parallelogram with sides of Hg1 ··· Hg2 3.901(1) Å and internal angles of Hg2-Hg1-Hg2′ 87.40(4)° and Hg1-Hg2-Hg1′ 92.60(4)°. Iodide ions are located 1.912(1) Å above and below the plane of the four Hg atoms. Each iodide ion is bonded to all four Hg atoms; the Hg ··· I distances range from 3.213(2) to 3.607(2) Å, that is less than the sum of the van der Waals radii of 3.88 Å (Hg = 1.73[13] and I = 2.15 Å[14]). The Hg ··· I distances are comparable to those in previously reported mercuracyclic Hg ··· I complexes (3.249–3.487 Å).[3, 7, 15, 16] The Hg ··· I coordination in $[\mathbf{1} \cdot I_2]^{2-}$ arises from the interaction of filled iodide ion p orbitals with empty mercury p orbitals that have the proper orientation to form three-center, two-electron bonds.[1]

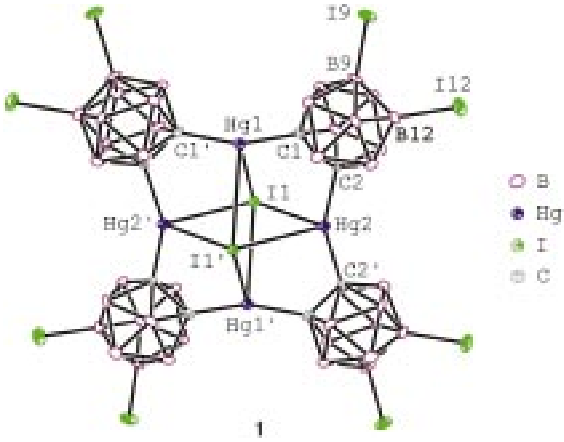

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Figure 1. Structure of the building block $[\mathbf{1} \cdot I_2]^{2-}$ (ORTEP diagram; solvent molecules and hydrogen atoms omitted for clarity). Selected interatomic distances [Å] and bond angles [°]: Hg1-I1 3.213(2), Hg2-I1 3.313(1), Hg1-I1′ 3.607(2), Hg1-C1 2.07(1), Hg2-C2 2.134(9), Hg1 ··· Hg2 3.901(1), B9-I9 2.20(1), B12-I12 2.19(1); C1-Hg1-C1′ 157.4(6), C2-Hg2-C2′ 151.9(5), Hg1-C1-C2-Hg2 1(1).

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A crystal packing diagram of $[Li_2\{(CH_3)_2CO\}_6][\mathbf{1}\cdot I_2]\supset 4H_2O$ shows infinite one-dimensional chains composed of $Li_2[\mathbf{1}\cdot I_2]$ units linked by intermolecular B–I···Li···I–B bonds (Figure 2). The $Li_2[\mathbf{1}\cdot I_2]$ units of the polymeric chains are arranged in layers. The polymeric chains assemble to produce linear channels perpendicular to the polymer chains. The Li1···I12 distance (3.753(7) Å) is shorter than the van der Waals separation of 3.97 Å (Li = 1.82[17] and I = 2.15 Å) and the I12-Li1-I12′ angle is 162(1)°. The other I substituent, I9, participates in intermolecular I···I contacts (B9–I9···I9′–B9′ 3.870 Å) between the polymeric chains, and the distance is within known I···I contacts.[18] The remaining ligands of the Li coordination sphere are three acetone molecules with distances of Li1–O1S 3.11(5) and two of Li1–O2S 3.20(4) Å.

The cross-section of the channels adopts the approximate shape of a rectangle whose sides are effectively 8.6 and 11.5 Å (Figure 3).[19] These distances are comparable with the dimensions of channels present in other metal-organic porous solids.[20] In the present case, the channels contain water molecules (eight per unit cell) which are separated by a distance of O1W···O1W′ 4.72(5) Å, along the channel. The water molecules are not coordinated to the Li or Hg atoms; nearest distances: O1W···Li1 5.58(5), O1W···Hg2 5.52(2), Hg1···O1W 8.57(2) Å. Between the layers, the interlayer Hg···I distance is 4.396(2) Å between Hg1 and I1′. The shortest I···I distance between two mirror-related anions is 7.416(4) Å.

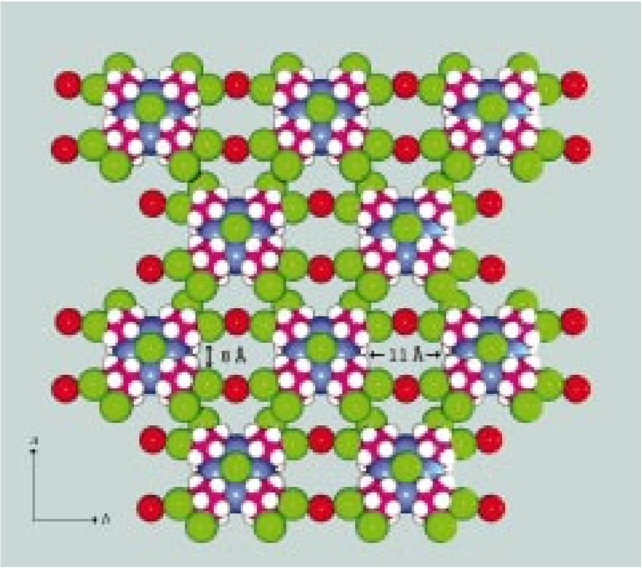

Figure 3. Space-filling model of the packing lattice of $Li_2[\mathbf{1}\cdot I_2]$. The acetone and water molecules are omitted for clarity. Color code: B: purple; C: gray; H: white; Hg: blue; I: green; Li: red.

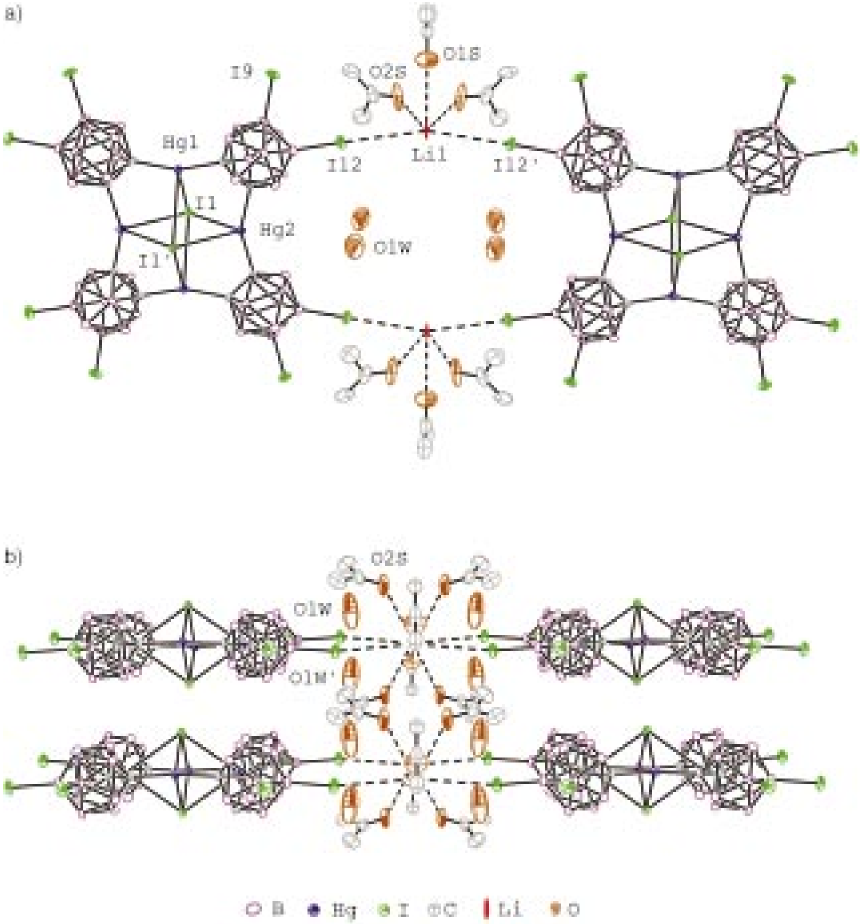

Figure 2. Crystal packing representation of $[Li_2((CH_3)_2CO)_6][\mathbf{1}\cdot I_2]\supset 4(H_2O)$ (ORTEP diagram; hydrogen atoms omitted for clarity). a) Projection perpendicular to the Hg_4 plane. b) Projection parallel to the Hg_4 plane. Selected interatomic distances [Å] and bond angles [°]: I12···Li1 3.753, Li1···O1S 3.114, Li1···O2S 3.20(4), O1W···O1W′ 4.72(5); I12···Li1···I12′ 162(1).

Previously reported crystal structures of $Li_2[(HgC_2B_{10}H_8R_2)_4\cdot I_2]$ (R = H, CH_3, CH_2CH_3) species do not demonstrate the formation of self-assembled porous material in the solid state.[1, 3] Presumably, the heretofore unobserved B–I···Li and B–I···I–B interactions of $Li_2[\mathbf{1}\cdot I_2]$ direct crystal lattice organization. This intermolecular interaction provides a new bonding motif for supramolecular self-assembly which involves nucleophilic halogen centers attached to electron-rich boron vertices of carborane cages. Recently, microporous materials have been utilized in enantioselective separation and catalysis.[21] Currently, the molecular inclusion properties of $Li_2[\mathbf{1}\cdot I_2]$ are under investigation.

Experimental Section

$Li_2[\mathbf{1}\cdot I_2]$: To a dry ethereal solution (20 mL) of *closo*-9,12-I_2-1,2-$C_2B_8H_{10}I_2$[6] (0.210 g, 0.530 mmol) at 0 °C was added *n*-butyllithium (1.1 mmol, 0.44 mL, 2.4 M solution in hexanes), and the resulting mixture was stirred at room temperature under nitrogen. After 4 h, the mixture was cooled back to 0 °C and treated with HgI_2 (0.241 g, 0.530 mmol). The reaction was stirred at room temperature for 8 h, then quenched with water, and the organic phase was separated. The water layer was extracted with diethyl ether (3 × 10 mL). The combined organic phase was dried over anhydrous magnesium sulfate and filtered. The solvent was removed under vacuum and triturated with pentane to give $Li_2[\mathbf{1}\cdot I_2]$ as a white solid in 78 % yield. $[Li_2\cdot\{(CH_3)_2CO\}_6][\mathbf{1}\cdot I_2]\supset 4H_2O$ forms on crystallization from acetone. ^1H NMR (400 MHz, $[D_6]$acetone, 25 °C): $\delta = 3.5-2.0$ (B–H); $^{13}C\{^1H\}$ NMR (100 MHz, $[D_6]$acetone, 25 °C): $\delta = 89.5$ (carborane-C); $^{11}B\{^1H\}$ NMR (160 MHz, acetone, 25 °C, $BF_3\cdot Et_2O$

external): $\delta = -5.8, -10.5, -16.0$ (2:6:2); ^{199}Hg{^{1}H} NMR (89.6 MHz, acetone, 25 °C, external 0.5 M PhHgCl in [D$_6$]DMSO: chemical shift $\delta = -1187$[22] upfield from neat Me_2Hg): $\delta = -622$; negative-ion FAB-MS: m/z (%): 2505 (100) $[\mathbf{1} \cdot I]^-$, 2640 (45) $Li[\mathbf{1} \cdot I_2]^-$.

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[12] Crystallographic data collection for $[Li_2\{(CH_3)_2CO\}_6][\mathbf{1}_2 \cdot I] \supset 4\,H_2O$: $C_{13}H_{34}B_{20}Hg_2I_5LiO_5$, $M_r = 1529.22$, crystal dimensions $= 0.15 \times 0.15 \times 0.25$ mm^3, monoclinic, space group $C2/m$, $a = 31.26(1)$, $b = 22.14(1)$, $c = 7.068(3)$ Å, $\beta = 94.463(9)°$, $V = 4876(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.083$ mg cm^{-3}, $T = 100(2)$ K, absorption coefficient $\mu = 9.476$ mm^{-1}. Data were collected on a Bruker SMART CCD diffractometer, using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined from a least-squares fit of 916 accurately centered reflections ($4.33° < 2\theta < 55.80°$). A total of 6001 unique reflections were measured, of which 3832 reflections were considered observed with $I > 2\sigma(I)$. All reflections were used for structure analysis. The intensity data were corrected for Lorentz and polarization effects, absorption, and secondary extinction. Atoms were located by use of heavy atom methods. With the exception of Li, all non-hydrogen atoms were refined with anisotropic parameters. With the exception of H of water (not located), all H were included in structure factor calculations but parameters were not refined. The H atoms were assigned isotropic displacement values based approximately on the value for the attached atom. The final discrepancy index was $R = 0.055$, $R_w = 0.133$ ($w = 1/\sigma^2(|F_0|)$ for 3832 independent reflections with $I > 2\sigma(I)$. The largest peak maximum and minimum on a final difference electron density map were 2.724 and -3.020 e Å^{-3}, both near Hg. Data were processed by using the Bruker SMART 1000 software package. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158870. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Optically Tuning the Rate of Stoichiometry Changes: Surface-Controlled Oxygen Incorporation into Oxides under UV Irradiation

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Stoichiometry changes are fundamental to all solid-state chemical reactions and thus one of the most central processes in solid-state chemistry. Moreover, the relevant stoichiometry determines whether an ionic material is ionically or electronically conducting, whether it is an n- or p-type electronic conductor, and may even determine whether or not it is superconducting. The kinetics of in- and excorporation reactions are also directly involved in the functioning of electroceramic devices, such as permeation membranes, electrodes in fuel cells, and chemical sensors.[1–4] The stoichiometry change process consists of surface reaction steps in series with a bulk diffusion step, of which the former become increasingly important at lower temperatures.

In this Communication, we present results on the use of UV light to tune the rate of oxygen incorporation into the bulk of a model mixed conductor, iron-doped $SrTiO_3$, by altering the rate of the surface reaction under conditions where the surface reaction determines the overall kinetics of the stoichiometry change. While the effects of illumination on the surface composition (see, for example, refs. [5, 6]) and on the catalytic activity of wide-bandgap semiconductors have drawn much attention, for example with regard to the photolysis of water, the selective oxidation of hydrocarbons, and the removal of organic pollutants from air or water,[7–10] the effect of irradiation on the kinetics of bulk stoichiometry changes (in the surface-controlled regime) has, to the best of our knowledge, not yet been reported.

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