

at 25 °C. Phosphate buffer (50 mM, pH 8.0) was used as the running buffer. The chromatograms were monitored by UV absorption at 200 nm. Samples were injected into the capillary by high pressure nitrogen (20 psi) for 3 s. The capillary was regenerated by washing with 0.1 M NaOH for 5 min after purging with doubly distilled water for 3 min.

**Neuraminidase Hydrolysis:** Partially lactonized samples (10 µg) in ammonium acetate buffer (100 mM, pH 5) were digested with neuraminidase (1 mU) from *Anthrobacter ureafaciens* in 20-µL CE vials at room temperature. The progress of hydrolysis was monitored at each time interval by HPCE.

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## Octahedral Coordination of an Iodide Ion in an Electrophilic Sandwich\*\*

Hans Lee, Martin Diaz, Carolyn B. Knobler, and M. Frederick Hawthorne\*

Until now, no discrete six-coordinate iodide (–1 oxidation state) sandwich species has been reported. A limited number of octahedral complexes such as  $[\text{I}^{\text{VII}}\text{F}_6]^+$ ,<sup>[1]</sup>  $[\text{I}^{\text{VII}}(\text{OH})_6]^+$ ,<sup>[2]</sup> and  $[\text{I}^{\text{V}}\text{F}_6]^{-[3]}$  (distorted octahedral) with iodine in a formal +7 or +5 oxidation state are known. Multidentate Lewis acidic hosts form four- to six-coordinate iodine species, with iodine in a formal –1 oxidation state.<sup>[4, 5]</sup> The field of anion host–guest chemistry offers prospects for molecular recognition, anion transport, and catalysis.<sup>[4–6]</sup>

Penta-, tetra-, and tridentate organomercury receptors form complexes with halide anions and a variety of neutral electron-rich species. The cyclic pentameric  $[(\text{CF}_3)_2\text{CHg}]_5$  coordinates two halide anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ), one above and one below the center of the cavity.<sup>[7, 8]</sup> Similarly, tetrameric 12-mercuracarborand-4 ( $\text{C}_2\text{B}_{10}\text{H}_{10}\text{Hg}_4$ ) can also bind two iodide ions, while the smaller chloride and bromide ions usually reside within the cavity to produce 1:1 host–guest complexes.<sup>[9]</sup> Trimeric perfluoro-*o*-phenylenemercury coordinates halide ions in a 1:1 stoichiometric ratio of trimer:halide. The halide ions are situated above and below the cavity to form an infinite bent polydecker structure with the composition  $[(\text{o-C}_6\text{F}_4\text{Hg})_3\text{X}]^-$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) and a distorted octahedral geometry around the anion.<sup>[8, 10]</sup>

Here we report the synthesis and structural characterization of the first discrete octahedral sandwich complex  $[\mathbf{1}_2 \cdot \text{I}]^-$ , composed of two electroneutral trimeric *B*-hexamethyl-9-mercuracarborand-3  $[\mathbf{9}, 12-(\text{CH}_3)_2-\text{C}_2\text{B}_{10}\text{H}_8\text{Hg}]_3$  (**1**) receptors which simultaneously coordinate an iodide ion in a sandwich fashion.

The reaction of LiI with **1** results in the sandwich complex  $[\mathbf{1}_2 \cdot \text{I}]^-$  in 82 % yield.  $\text{Li}[\mathbf{1}_2 \cdot \text{I}]$  is an air- and moisture-stable crystalline solid. The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{11}\text{B}$  NMR spectra revealed that  $[\mathbf{1}_2 \cdot \text{I}]^-$  has a highly symmetrical structure, with chemical shifts nearly identical to those of the empty host **1**.<sup>[11]</sup> The  $^{199}\text{Hg}$  NMR spectrum of  $[\mathbf{1}_2 \cdot \text{I}]^-$  in acetone exhibits a singlet at  $\delta = -957$ , with no evidence of the empty host **1** ( $\delta = -1158$ ).<sup>[11]</sup> A downfield shift relative to the signal of **1** is diagnostic of coordination of a guest to the mercury atoms of **1**.<sup>[9]</sup> The  $^{199}\text{Hg}$  NMR chemical shifts of similar complexes of organomercury compounds exhibit strong dependencies on the nature of the solvent and the concentration of the complex.<sup>[12]</sup>  $\text{Li}[\mathbf{1}_2 \cdot \text{I}]$  has a  $^{199}\text{Hg}$  NMR chemical shift which is essentially independent of concentration at room temperature. This observation suggests that the solid-state structure of  $\text{Li}[\mathbf{1}_2 \cdot \text{I}]$  is maintained in solution.<sup>[9]</sup> The negative-ion fast atom bombardment (FAB) mass spectrum exhibits a peak centered at  $m/z$  2351, with the

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correct isotopic pattern for  $[\text{I}_2 \cdot \text{I}]^-$ , and an anion envelope at  $m/z$  1239, which corresponds to  $[\text{I} \cdot \text{I}]^-$ . The diiodide complex  $[\text{Li}(\text{I} \cdot \text{I}_2)]^-$  is not observed by negative-ion FAB-MS or  $^{199}\text{Hg}$  NMR spectroscopy. The  $[\text{I} \cdot \text{I}]^-$  species at  $m/z$  1239 is presumed to arise from cleavage of  $[\text{I}_2 \cdot \text{I}]^-$ , since only a single sharp signal is observed in the  $^{199}\text{Hg}$  NMR spectrum of the latter.

A single crystal of  $[\text{Li}(\text{H}_2\text{O})_4][\text{I}_2 \cdot \text{I}] \cdot 2\text{CH}_3\text{CN}$ , grown from acetonitrile/acetone, was selected for an X-ray diffraction study (Figure 1).<sup>[13]</sup> The centrosymmetric trimeric complex

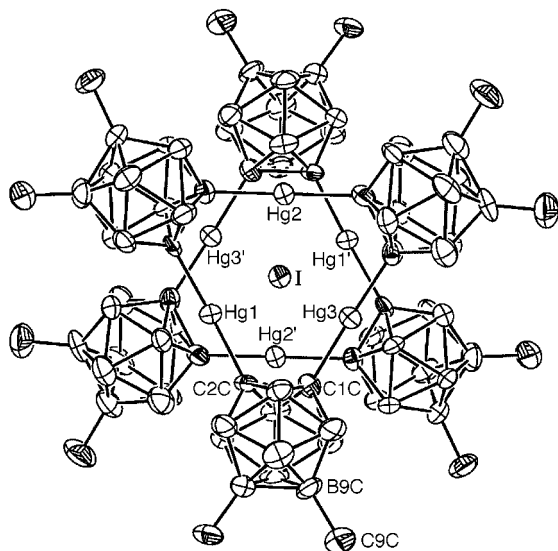


Figure 1. Structure of  $[\text{I}_2 \cdot \text{I}]^-$  (ORTEP plot; hydrogen atoms omitted for clarity). Selected distances [Å] and angles [°]:  $\text{Hg1} \cdots \text{I}$  3.2492(5),  $\text{Hg2} \cdots \text{I}$  3.2549(5),  $\text{Hg3} \cdots \text{I}$  3.2728(5);  $\text{Hg1-I-Hg1}'$  180,  $\text{Hg1-I-Hg2}$  69.95(1),  $\text{Hg1-I-Hg3}$  69.07(1),  $\text{Hg2-I-Hg3}$  69.81(1),  $\text{Hg1-I-Hg2}'$  110.05(1),  $\text{Hg1-I-Hg3}'$  110.93(1),  $\text{Hg2-I-Hg3}'$  110.19(1).

$[\text{I}_2 \cdot \text{I}]^-$  contains an iodide ion coordinated to six mercury atoms. The lithium ion is located on an inversion center and is coordinated to the oxygen atoms of four water molecules. The two trimeric hosts of  $[\text{I}_2 \cdot \text{I}]^-$  are inverted with respect to one another and separated by 4.902 Å. The iodide ion is located almost equidistant from each of the six mercury atoms ( $\text{Hg} \cdots \text{I}$  3.2492(5), 3.2549(5), 3.2728(5) Å) at less than the sum of the van der Waals radii (3.89 Å).<sup>[14, 15]</sup>  $[\text{I}_2 \cdot \text{I}]^-$  has shorter  $\text{Hg} \cdots \text{I}$  distances than the cyclic trimeric perfluoro-*o*-phenylenemercury iodide complex mentioned before (3.331–3.487 Å)<sup>[16]</sup> and the *B*-octamethyl-12-mercuracarborand-4 diiodide complex (3.438(4), 3.335(3) Å).<sup>[17]</sup> The three mercury atoms of **1** in  $[\text{I}_2 \cdot \text{I}]^-$  are arranged in a near-equilateral triangle ( $\text{Hg} \cdots \text{Hg}$  3.7285(8), 3.6975(7), 3.7352(7) Å;  $\text{Hg-Hg-Hg}$  59.39(1), 60.21(1), 60.39(1)°). The  $\text{Hg} \cdots \text{I}$  interactions and steric hindrance of the opposing icosahedra contribute to the observed deviation from linearity of the C-Hg-C angles (169.0(5) to 171.0(5)°) relative to those of the uncomplexed host **1** (172.7(6)–174.9(6)°).<sup>[11]</sup> The Hg-C-C-Hg torsion angles indicate the coplanarity of these four atoms, with values equal to or smaller than 1°.

The coordination of the iodide ion in  $[\text{I}_2 \cdot \text{I}]^-$  must arise from the interaction of its filled p orbitals with empty mercury p orbitals that have the proper orientation to form three

equivalent  $p_{\text{Hg}}-p_{\text{I}}-p_{\text{Hg}}$  three-center, two-electron bonds and a sandwich structure (Figure 2).

### Experimental Section

**Li $[\text{I}_2 \cdot \text{I}]$ :** A solution of **1**<sup>[11]</sup> (0.50 g, 0.45 mmol) in acetone (40 mL) was treated with LiI (0.15 g, 1.12 mmol) at room temperature for 12 h. The solvent was removed under vacuum, and the residual solid was washed with water and then extracted with diethyl ether (3 × 25 mL). The combined organic phase was dried over anhydrous magnesium sulfate and filtered. The solvent was removed under vacuum to give  $\text{Li}[\text{I}_2 \cdot \text{I}]$  in 82% yield.  $[\text{Li}(\text{H}_2\text{O})_4][\text{I}_2 \cdot \text{I}] \cdot 2\text{CH}_3\text{CN}$  is formed on repeated recrystallization from acetonitrile/acetone; m.p. > 300 °C.  $^1\text{H}$  NMR (400 MHz, acetone, 25 °C):  $\delta$  = 3.0–1.0 (B–H), 0.05 ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (90 MHz,  $[\text{D}_6]\text{acetone}$ , 25 °C):  $\delta$  = 89.4 (carborane-C), 0.81 (brs,  $\text{CH}_3$ );  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $[\text{D}_6]\text{acetone}$ , 25 °C, external  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ):  $\delta$  = 10.7, –3.3, –8.0 (2:2:6);  $^{199}\text{Hg}\{^1\text{H}\}$  NMR (89.6 MHz,  $[\text{D}_6]\text{acetone}$ , 25 °C, external 1.0 M  $\text{PhHgCl}$  in  $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = –1187<sup>[12]</sup> upfield from neat  $\text{Me}_2\text{Hg}$ :  $\delta$  = –957; negative-ion FAB-MS:  $m/z$  (%): 2351 (5)  $[\text{I}_2 \cdot \text{I}]^-$ , 1239 (100)  $[\text{I} \cdot \text{I}]^-$ .

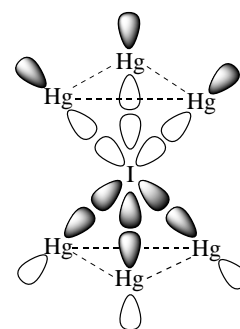


Figure 2. Orbital representation of  $[\text{I}_2 \cdot \text{I}]^-$  illustrating the three-center, two-electron bonds.

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- [13] Crystallographic data for  $[\text{Li}(\text{H}_2\text{O})_4][\text{I}_2 \cdot \text{I}] \cdot 2\text{CH}_3\text{CN}$ :  $\text{C}_{28}\text{H}_{98}\text{B}_{60}\text{Hg}_6\text{I}$ – $\text{LiN}_2\text{O}_4$ ,  $M_r$  = 2513.06, crystal dimensions 0.2 × 0.2 × 0.125 mm, triclinic, space group  $P\bar{1}$ ,  $a$  = 13.312(8),  $b$  = 13.983(9),  $c$  = 13.996(9) Å,  $\alpha$  = 61.16(2),  $\beta$  = 82.34(2),  $\gamma$  = 86.58(2)°,  $V$  = 2261(2) Å<sup>3</sup>,  $Z$  = 1,  $\rho_{\text{calc}}$  = 1.84 g cm<sup>–3</sup>,  $T$  = 25 °C, absorption coefficient  $\mu$  = 105.2 cm<sup>–1</sup>. Data were collected on a Huber diffractometer, with  $\text{MoK}_\alpha$  radiation ( $\lambda$  = 0.7107 Å). Unit cell parameters were determined from a least-squares fit of 47 accurately centered reflections ( $9.9 < 2\theta < 20.5^\circ$ ). A total of 13199 unique reflections were measured, of which 6469 reflections had  $I > 2\sigma(I)$ . All were retained for structure analysis. The intensity data were corrected for Lorentzian and polarization effects, absorption, and secondary extinction. Atoms were located by heavy-atom methods. With the exception of Li, all non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were included in structure factor calculations, but parameters were not refined. The hydrogen atoms were assigned isotropic displacement

values based approximately on the value for the attached atom. The final discrepancy index was  $R = 0.063$ ,  $R_w = 0.171$  ( $w = 1/\sigma^2(|F_o|)$ ) for 6469 independent reflections with  $I > 2\sigma(I)$ . The largest peak maximum and minimum on a final difference electron density map were 2.34 (near Hg) and  $-1.72 \text{ e } \text{\AA}^{-3}$ . Data were processed with the UCLA crystallographic package and SHELX93. 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-135263. 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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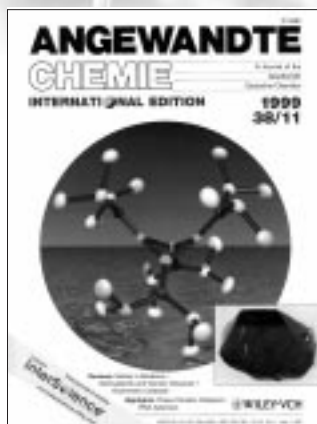
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