

“Anti-Crown” Chemistry: Synthesis of [9]Mercuracarborand-3 and the Crystal Structure of Its Acetonitrile Complexes

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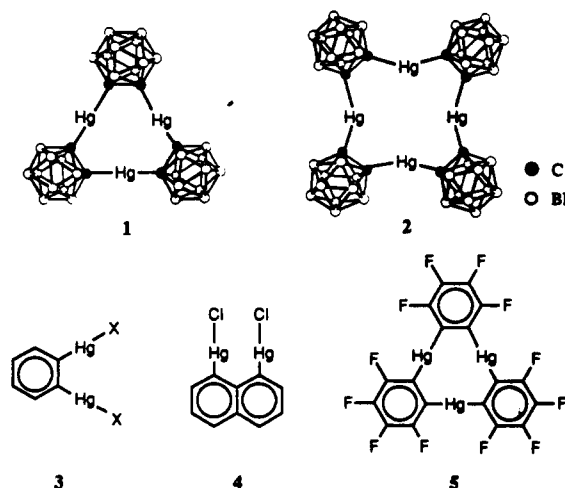
Abstract: The reaction of mercuric acetate with *clos*-1,2-Li₂-1,2-C₂B₁₀H₁₀ yielded [9]mercuracarborand-3, (C₂B₁₀H₁₀Hg)₃ (1), in 60% yield. Compound 1 was characterized by multinuclear NMR spectroscopy and its chloride ion complex, 1·Cl⁻, by negative ion FAB mass spectroscopy. The structure of 1 was determined by X-ray crystallography. 1 crystallized from acetonitrile in the monoclinic space group P2₁/c with *a* = 13.358 (2), *b* = 26.846 (4), and *c* = 20.375 Å, β = 109.694 (5)°, *V* = 7909 Å³, and *Z* = 4. Data were collected on a Picker FACS-1 diffractometer, using Mo Kα radiation, to a maximum 2θ = 45°, giving 10 348 unique reflections, and the structure was solved by heavy atom methods. The final discrepancy index was *R* = 0.044, *R_w* = 0.049 for 5193 independent reflections with *I* > 3σ(*I*). The chloride ion complex of 1, 1·ClLi, was formed upon treatment of 1 with LiCl. The complexation behavior of 1 in acetone was studied by ¹⁹⁹Hg NMR spectroscopy.

Introduction

The anion complexation by multidentate Lewis acid hosts has recently attracted increasing attention¹ since anion and nucleophile complexation by such hosts is of importance to the areas of molecular recognition, enzyme modeling, ion transport, and catalysis.²⁻⁴ The utilization of main group elements such as mercury,^{1a-c,5-7} boron,^{1h-k} silicon,^{3a} and tin^{1e-g,3b} as Lewis acid binding sites for anions and nucleophiles is of special interest. Several Lewis acid hosts which contain mercury atoms such as 3-5 have been reported to bind halide ions and nucleophilic solvent molecules.^{1a-c,6,7} We have recently reported the macrocyclic tetradentate Lewis acid host [12]mercuracarborand-4, cyclo-(C₂B₁₀H₁₀Hg)₄ (2), which tightly binds halide ions and nucleophilic donor solvents⁵ due to the presence of their electron-withdrawing *o*-carborane cages as well as their multidentate nature. In this article, we describe the synthesis of a novel tridentate Lewis acid host, cyclo-(C₂B₁₀H₁₀Hg)₃ (1), a charge-reversed analogue of [9]crown-3, and the molecular structures of two different acetonitrile adducts of 1, 1A and 1B, which cocrystallize.

Experimental Section

General Considerations. Standard Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive com-



pounds. Diethyl ether was distilled from sodium benzophenone ketyl. Mercuric acetate (Allied Chemical) and *n*-butyllithium (2.5 M solution in hexane) (Aldrich) were used without further purification. IR spectra of KBr pellets were recorded with a Beckman FT-1100 instrument. ¹H, ¹³C, and ¹¹B NMR spectra were recorded with Bruker AF 200, AM 360, and AM 500 spectrometers, respectively. Chemical shifts for ¹H and ¹³C NMR spectra were referenced to the residual protons and carbons in deuterated solvents. Chemical shift values for ¹¹B spectra were referenced relative to external BF₃·OEt₂ (δ 0.0 ppm with negative δ value upfield). The ¹⁹⁹Hg NMR spectra were recorded at 25 °C with a Bruker 500 spectrometer at 89.6 MHz by using broad band decoupling. External 1.0 M PhHgCl/DMSO-*d*₆ solution was used as the reference at -1187 ppm⁸ relative to neat Me₂Hg.

Preparation of 1. A solution of *n*-BuLi (58.3 mmol, 23.3 mL, 2.5 M in hexane) was added to an ethereal solution (200 mL) of *o*-carborane (27.7 mmol, 4.00 g) at 0 °C, and the slurry was stirred at room temperature under argon. After 2 h, the mixture was treated with solid Hg(OAc)₂ (27.6 mmol, 8.80 g) and stirred overnight at room temperature. The mixture was then treated with 100 mL of H₂O, and the organic phase was washed three times with H₂O (100 mL) and dried over MgSO₄. The solvent was removed and the residue was recrystallized from ether to give 1 in 65% yield: m.p. > 300 °C; ¹H NMR (200 MHz, (CD₃)₂CO, 25 °C) δ 1.0-3.6; ¹³C{H} NMR (90 MHz, (CD₃)₂CO, 25 °C) δ 95; ¹¹B{H} NMR (160 MHz, (CH₃)₂CO, 25 °C, BF₃·Et₂O external) δ 1.6, -5.4, -8.5 (2:2:6); ¹⁹⁹Hg{H} NMR (89.6 MHz, (CD₃)₂CO, 25 °C) δ -1364; IR (KBr) ν (cm⁻¹) 2561 (BH). Elemental analyses were unavailable due to the presence of solvents in the sample.

Preparation of 1·ClLi. The salt, 1·ClLi, was prepared in the same fashion as 1, except that the reaction mixture was quenched with an aqueous 3 M HCl solution, 70% yield: mp > 300 °C; ¹H NMR (200 MHz, (CD₃)₂CO, 25 °C) δ 1.0-3.5; ¹³C{H} NMR (90 MHz, (CD₃)₂CO, 25 °C) δ 94.5; ¹¹B{H} NMR (160 MHz, (CH₃)₂CO, 25 °C, BF₃·Et₂O external) δ 1.0, -5.3, -7.9 (2:2:6); ¹⁹⁹Hg{H} NMR (89.6 MHz, (CD₃)₂-

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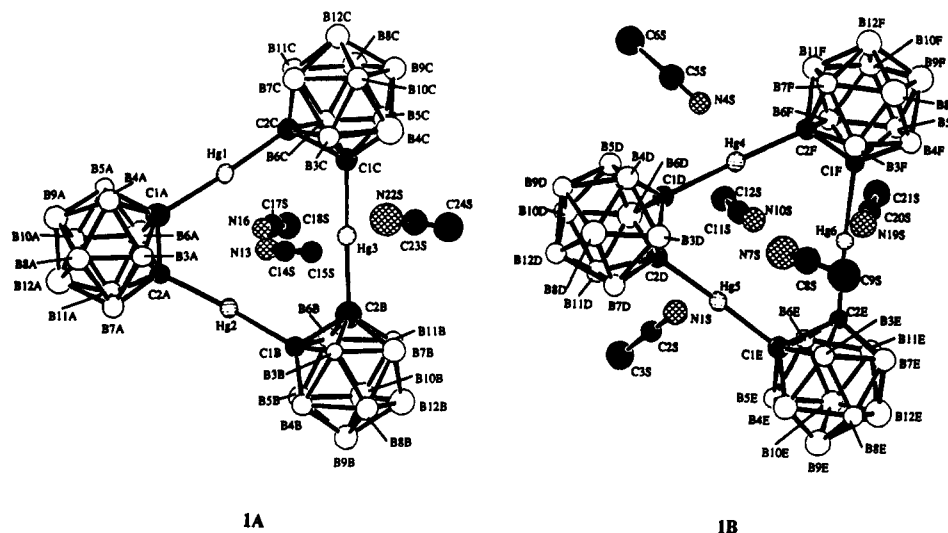


Figure 1. ORTEP representations of the acetonitrile complexes of 1 with hydrogen atoms removed for clarity.

Table I. Crystallographic Data for $1_2 \cdot (\text{CH}_3\text{CN})_8$

formula	$\text{C}_{28}\text{H}_{84}\text{B}_{60}\text{N}_8\text{Hg}_6$
space group	$P2_1/c$
<i>a</i> , Å	13.358 (2)
<i>b</i> , Å	26.846 (4)
<i>c</i> , Å	20.375 (3)
β , deg	109.694 (5)
<i>V</i> , Å ³	7909
<i>Z</i>	4 ^a
density (calcd), g/cm ³	1.99
μ , cm ⁻¹	116.4
temp, °C	-117
radiation (graphite monochromator)	Mo K α
wavelength, Å	0.7107
scan width	
below K α_1	1.3
above K α_2	1.6
scan rate, deg/min	6.0
no. of unique reflns	10348
no. of observed (<i>I</i> > 3 σ (<i>I</i>)) reflns	5194
2 θ_{max} , deg	45
data collected	+ <i>h</i> , + <i>k</i> , \pm <i>l</i>
no. of params refined	173 + 173 + 122 (3 blocks)
<i>R</i> , <i>R</i> _w , GOF ^b	0.044, 0.049, 1.43

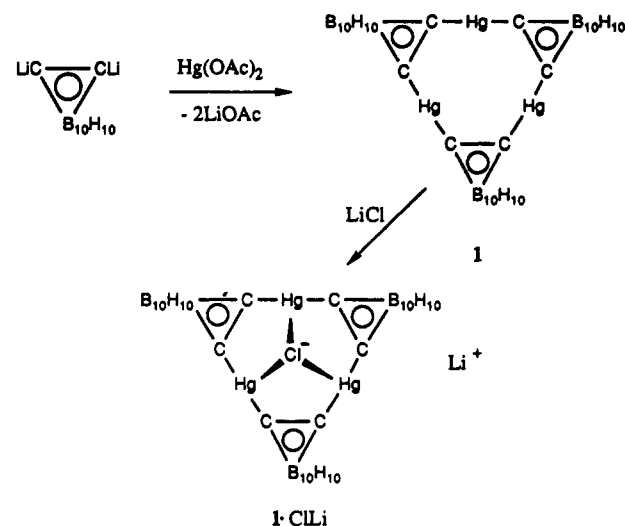
^a The asymmetrical unit contains two molecules of 1, one as the complex 1-3(CH₃CN) and one as the complex 1-5(CH₃CN). ^b GOF = $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_c)]^{1/2}$, where $w = 1/(\sigma^2(F_o))$. $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o^2)]^{1/2}$.

CO, 25 °C) δ -1021; IR (KBr) ν (cm⁻¹) 2562 (BH); negative ion FAB *m/z* 1064 (1-Cl⁻, 100).

X-ray Diffraction. A colorless crystal, grown from acetonitrile, was sealed in a capillary and placed on a Picker FACS-1 diffractometer equipped with a graphite-monochromatized Mo source and a gas-stream low-temperature device. Systematic absences were found for *h*0*k* reflections for which *k* \neq 2*n* and for *h*0*l* reflections for which *l* \neq 2*n*. Unit cell parameters were determined from a least-squares fit of 41 accurately centered reflections ($8.5 < 2\theta < 19.3^\circ$). The crystallographic data are summarized in Table I. Data were collected at -117 °C in the θ - 2θ scan mode. Three intense reflections (4 0 0, 0 10 -3, 1 3 5) were monitored every 97 reflections to check stability. Intensities of these reflections decayed less than 5% during the course of the experiment (106.5 h). Of the 10384 unique reflections measured, 5193 were considered observed (*I* > 3 σ (*I*)) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for secondary extinction and absorption but not for decay.

Atoms were located by use of heavy atom methods. All calculations were performed on a VAX 3100 computer in the J. D. McCullough X-ray Crystallography Laboratory. All mercury atoms were refined with anisotropic parameters. All methyl H's were included in calculated positions as members of rigid groups: C-H = 1.0 Å, H-C-H = 109.5°. Other H's were included in located positions. Four of the 60 carboranyl H's were not located. H atoms were assigned isotropic displacement values based approximately on the value for the attached atom. Scattering factors for H were obtained from ref 9. Anomalous dispersion

Scheme I



terms were included for the scattering of Hg. The largest peak on a final difference electron density map, located near Hg, was 0.7 e/Å³. Final positional and thermal parameters for non-hydrogen atoms are given in the supplementary material.

Results and Discussion

The reaction of 1,2-Li₂-1,2-C₂B₁₀H₁₀ with Hg(OAc)₂ in diethyl ether at room temperature afforded [9]mercuracarborand-3, cyclo-(C₂B₁₀H₁₀Hg)₃ (1), which was isolated in 65% yield. The addition of Cl⁻ to the solution of 1 produced 1·ClLi as shown in Scheme I. The cyclic structure of 1 was initially deduced from its multinuclear NMR spectra, and the trimeric nature of 1 was confirmed from the negative ion FAB mass spectrum of its chloride ion complex, 1·ClLi. The host, 1, is air stable and readily soluble in diethyl ether, THF, and acetonitrile.

The structures of the two cocrystallized acetonitrile adducts of 1, 1A and 1B, were elucidated by an X-ray single-crystal structure analysis and are shown in Figure 1. There are equal numbers of these two different cyclo-(C₂B₁₀H₁₀Hg)₃ trimer adducts present in the crystal. Three acetonitrile nitrogen atoms closely approach the three Hg centers of the trimer adduct, 1A, at distances ranging from 2.74 (3) to 3.07 (2) Å. Five other acetonitrile nitrogen atoms closely approach the three mercury atoms of the other adduct, 1B, at distances ranging from 2.74 (2) to 3.13 (2) Å. Both types of acetonitrile adducts contain three bivalent 1,2-C₂B₁₀H₁₀ cages connected by three mercury atoms

Table II. Selected Bond Distances (Å) and Angles (deg) for 1A and 1B

1A		1B	
Hg(1)–C(1A)	2.12 (2)	Hg(4)–C(1D)	2.15 (2)
Hg(1)–C(2C)	2.06 (2)	Hg(4)–C(2F)	2.06 (2)
Hg(2)–C(2A)	2.09 (2)	Hg(5)–C(2D)	2.10 (2)
Hg(2)–C(1B)	2.08 (2)	Hg(5)–C(1E)	2.08 (2)
Hg(3)–C(2B)	2.15 (3)	Hg(6)–C(2E)	2.08 (2)
Hg(3)–C(1C)	2.11 (3)	Hg(6)–C(1F)	2.13 (2)
C(1A)–C(2A)	1.65 (3)	C(1D)–C(2D)	1.62 (3)
C(1B)–C(2B)	2.15 (3)	C(1E)–C(2E)	1.76 (3)
C(1C)–C(2C)	1.79 (3)	C(1F)–C(2F)	1.63 (3)
Hg(1)–N(13S)	2.87 (2)	Hg(4)–N(7S)	3.09 (2)
Hg(1)–N(16S)	2.95 (2)	Hg(4)–N(10S)	2.82 (2)
Hg(2)–N(13S)	2.96 (2)	Hg(4)–N(4S)	2.95 (2)
Hg(2)–N(16S)	2.87 (2)	Hg(5)–N(7S)	3.05 (2)
Hg(3)–N(13S)	3.07 (2)	Hg(5)–N(10S)	2.87 (2)
Hg(3)–N(16S)	2.924 (17)	Hg(5)–N(1S)	2.84 (2)
Hg(3)–N(22S)	2.74 (3)	Hg(6)–N(7S)	3.13 (2)
		Hg(6)–N(10S)	2.74 (2)
		Hg(6)–N(19S)	2.86 (2)
C(1A)–Hg(1)–C(2C)	177.0 (9)	C(1D)–Hg(4)–C(2F)	177.8 (8)
C(2A)–Hg(2)–C(1B)	176.1 (8)	C(2D)–Hg(5)–C(1E)	174.7 (8)
C(2B)–Hg(3)–C(1C)	178.2 (9)	C(2E)–Hg(6)–C(1F)	174.1 (8)

in a cyclic trimer. The average Hg–C distance is 2.10 (2) Å and the average C–C distances are 1.69 (3) and 1.67 (3) Å. The average C–Hg–C angles are 177.1 (8) and 175.5 (8)°, and the average C–C–Hg angles are 118.7 (14) and 119.3 (13)° for 1A and 1B, respectively. The Hg₃C₆ rings of both trimers are nearly planar with most Hg–C–C–Hg torsion angles equal to or smaller than 2 (2)° and the only exception, the Hg(1)–C(1A)–C(2A)–Hg(2) angle, equal to 10 (2)°. Average Hg–Hg distances are 3.729 (1) and 3.734 (1) Å, which implies that 1 has a larger cavity than that observed in trimeric *o*-phenylenemercury. The trimer of *o*-phenylenemercury has a planar structure with an average Hg–C distance of 2.10 Å, an average C–Hg–C angle of 177.7°, and an average Hg–C–C angle of 120.5° for the orthorhombic crystal.^{10,11} Consequently, 1 is structurally similar to trimeric *o*-phenylenemercury. On the other hand, the THF adduct of the tetramer (C₂B₁₀H₁₀Hg)₄ (2) has a nonplanar structure with nonlinear mercury coordination.^{5c} The halide ion complexes of (C₂B₁₀H₁₀Hg)₄ (2) have planar host structures with the mercury atoms moved inward toward the center of the cycle.^{5a,b}

The binding of the acetonitrile molecules of 1 is quite unusual, with nitrogen atoms of two CH₃CN molecules binding to three acidic Hg sites of 1A or 1B (Figure 2). N(7S) and N(10S) bond to Hg(4), Hg(5), and Hg(6) via two four-center two-electron bonds. N(13S) and N(16S) both bond to Hg(1) and Hg(2) via two three-center two-electron bonds and simultaneously to Hg(3) through the donation of pπ-electrons of the acetonitrile nitrogen atoms. The distances between nitrogen atoms and mercury atoms, ranging from 2.74 (3) to 3.13 (2) Å, are smaller than the van der Waals distance (3.23 Å).¹² The unusual binding ability of 1 toward acetonitrile is expected to extend to a variety of other nitrogen-containing bases including some of biological interest, such as adenine, guanine, cytosine, and thymine.

It has been reported that the cyclic trimer of *o*-perfluorophenylenemercury, (*o*-C₆F₄Hg)₃, is capable of binding halide ions.⁷ Similarly, compound 1 efficiently binds nucleophilic ions and molecules. The ¹⁹⁹Hg NMR chemical shift of 1 appears at –1364 ppm in acetone-*d*₆ and that of 1·ClLi at –1021 ppm in the same solvent. The incremental addition of chloride ion to an acetone

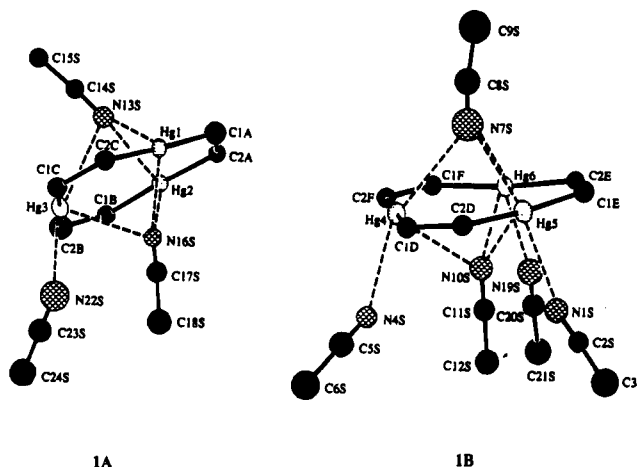


Figure 2. Side views of the coordination of acetonitrile molecules to the C₆Hg₃ ring of 1 with boron and hydrogen atoms removed for clarity.

solution of 1 results in the proportional downfield shift of the mercury resonance. Similarly, the addition of iodide ion to the solution of 1 also results in the proportional downfield shift of the single ¹⁹⁹Hg resonance. These results suggest that more than one mercury species is present in the halide ion-containing solutions and that the observed chemical shifts are time averaged and result from rapid ion exchange.¹³ It is noteworthy that, in the case of 2, two resonances are observed, corresponding to 2·I[–] and 2·I₂^{2–}. Apparently, 2 is a more effective Lewis acid than 1, and the iodide ion exchange with 2 is slower on the NMR time scale. We propose that 1·ClLi has the structure shown in Scheme I with chloride simultaneously bonded to three Lewis acidic centers. The [(*o*-C₆F₄Hg)₃·Br]Ph₄P complex has a poly-decker sandwich structure with each bromide ion sandwiched between two planar trimer hosts in the crystal.⁷

The utilization of anions as templates in a vanadium pentoxide self-assembly process has been recently discussed.¹⁴ We have previously postulated^{5a} that the efficient assembly of halide ion complexes of the tetrameric [12]mercuracarborand-4 (2), [(C₂B₁₀H₁₀Hg)₄·X_n]_nLi_n (X = Cl, Br, n = 1; X = I, n = 1, 2), must be due to a template effect with halide ion serving as the template, since a trimeric structure is stereochemically more attractive than the tetrameric product actually observed in such cases. The synthesis of 1 from a mercuric salt containing a bulky, charge-dispersed anion, mercuric acetate, reinforces this suggestion. Moreover, the reaction of *clos*-1,2-Li₂-1,2-C₂B₁₀H₁₀ with Hg(SCN)₂ produced a cyclic pentamer (C₂B₁₀H₁₀Hg)₅, [15]mercuracarborand-5, which also binds SCN[–] and halide ions and is under active investigation.

Acknowledgment. We are grateful to the National Science Foundation (CHE-91-11437) for support of this work.

Supplementary Material Available: Tables of positional and thermal parameters, bond lengths and angles, and crystallographic data (16 pages); table of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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