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Molecular Aggregates of Nitrate Ion with the Tetravalent Lewis Acid Host 12-Mercuracarborand-4: Novel Trihapto Coordination of NO_3^-

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Introduction

Anion complexation chemistry has recently received increasing attention because of its chemical and biological importance.[1−10] However, host−guest chemistry involving anion guests is less widely reported than that describing cationic guests, the latter having a long and rich history including the cation complexes of crown ethers,[11] cryptates,[12] and others.[13−15] We previously reported the synthesis and halide anion complexation chemistry of electrophilic mercuracarborand host molecules.[16] These macrocyclic Lewis acid hosts easily coordinate electron donor molecules such as tetrahydrofuran, acetone, ether, H_2O, acetonitrile, the halide anions (chloride, bromide, and iodide), and the polyhedral *closo*-$B_{10}H_{10}^{2-}$ ions among others. To extend our research to include more complex anion systems, we investigated the behavior of the tetrameric 12-mercuracarborand-4 host compound[17,18] toward a variety of oxo-anions. In this paper, we report the successful syntheses and structural characterization of two novel host−guest complexes which both contain nitrate ions.

Experimental Section

General Considerations. Acetone, *o*-dichlorobenzene, KNO_3, and 18-crown-6 were obtained from Aldrich and used without further purification. The 12-mercuracarborand-4 was synthesized prior to use as described in the literature.[17] IR spectra were recorded with a Perkin-Elmer 1600 FT-IR spectrophotometer in the range 4000−500 cm^{-1} and were taken as Nujol mulls with KBr salt plates. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer, while ^{11}B and ^{199}Hg NMR spectra were recorded on a Bruker AM 500 spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced to residual ^{1}H and ^{13}C atoms present in the deuterated solvents. Chemical shift values for ^{11}B spectra were referenced relative to external $BF_3\cdot OEt_2$ (1.0 M solution in $CHCl_3$; $\delta = 0.0$ ppm, with negative values upfield). Chemical shift values for ^{199}Hg NMR spectra were referenced relative to external PhHgCl (0.5 M solution in d_6-DMSO; $\delta = -1187$ ppm, upfield from neat Me_2Hg). All spectra were recorded at room temperature (25 °C). Additionally, ^{13}C and ^{11}B spectra were ^{1}H decoupled.

Preparation of Complex 1. Complex **1** was prepared by adding an acetone solution (20 mL) containing 686 mg (0.5 mmol) of 12-mercuracarborand-4 to a suspension of 120 mg (1.19 mmol) of KNO_3 and 289 mg (1.09 mmol) of 18-crown-6 in 15 mL of acetone and stirring for 15 h. The KNO_3 and crown ether were stirred in acetone for 24 h at 25 °C prior to use. Potassium nitrate which did not dissolve during that time did so within 30−40 min after the mercuracarborand host was added to this suspension. The removal of solvent in vacuo and recrystallization of the product from acetone gave **1** in 87% yield.

$[(C_2B_{10}H_{10}Hg)_4(NO_3)_2\cdot H_2O][K(18\text{-crown-6})]_2\cdot H_2O\cdot(CH_3)_2C{=}O$, **1**: mp > 300 °C; ^{1}H NMR (200 MHz, $(CD_3)_2CO$) $\delta = 1.0-3.6$ ppm; ^{13}C NMR (90 MHz, $(CD_3)_2CO$, decoupled) $\delta = 89.0$ ppm; ^{11}B NMR (160 MHz, $(CH_3)_2CO$) $\delta = 0.03, -6.91, -7.98$ ppm (2:2:6); ^{199}Hg (89.6 MHz, $(CD_3)_2CO$) $\delta = -1269$; IR ν (cm^{-1}) = 2580 (B−H), 1265 (ν_1 NO^{3-}), 1040 (ν_2 NO^{3-}), 1375 (ν_5 NO^{3-}); negative-ion FAB, *m*/*z* 1433 $\{[(C_2B_{10}H_{10}Hg)_4(NO_3)]^-\}$.

Preparation of Complex 2. Complex **2** was obtained by adding an acetone solution (20 mL) containing 685 mg (0.499 mmol) of 12-mercuracarborand-4 to a suspension of 161 mg (1.59 mmol) of KNO_3 and 418 mg (1.58 mmol) of 18-crown-6 in 20 mL of acetone and stirring for 18 h. The crown ether and KNO_3 were stirred in acetone for 24 h at 25 °C prior to use. Potassium nitrate which did not dissolve during that time did so within 2 h after the mercuracarborand host was added to this suspension. The removal of solvent in vacuo and recrystallization from acetone afforded a 92% yield of **2**.

$[(C_2B_{10}H_{10}Hg)_4(NO_3)_2][K(18\text{-crown-6})]_2$, **2**: mp > 300 °C; ^{1}H NMR (200 MHz, $(CD_3)_2CO$) $\delta = 1.0-3.6$ ppm; ^{13}C NMR (90 MHz, $(CD_3)_2CO$, decoupled) $\delta = 88.0$ ppm; ^{11}B NMR (160 MHz, $(CH_3)_2CO$) $\delta = 0.03, -6.91, -7.98$ ppm (2:2:6); ^{199}Hg (89.6 MHz, $(CD_3)_2CO$) $\delta = -1269$ ppm; IR ν (cm^{-1}) = 2580 (B−H), 1250 (ν_1 NO^{3-}), 1041 (ν_2 NO^{3-}), 1450 (ν_5 NO^{3-}); negative-ion FAB, *m*/*z* 1433 $\{[(C_2B_{10}H_{10}Hg)_4(NO_3)]^-\}$.

X-ray Crystallography. Colorless crystals of each of the respective compounds were mounted in a glass capillary and placed on a Huber diffractometer constructed by Prof. C. E. Strouse (UCLA) using Mo Kα radiation to a maximum $2\theta = 50°$ (**1**) and 60° (**2**), respectively. Data were collected at 25 °C in the $\theta-2\theta$ scan mode. Scattering factors for H were obtained from Stewart et al.[19] and for other atoms were taken from *International Tables for X-ray Crystallography*.[20] Methyl and methylene H were kept in calculated positions C−H = 1.0 Å, H−C−H angles =109.5°. Isotropic displacement parameters

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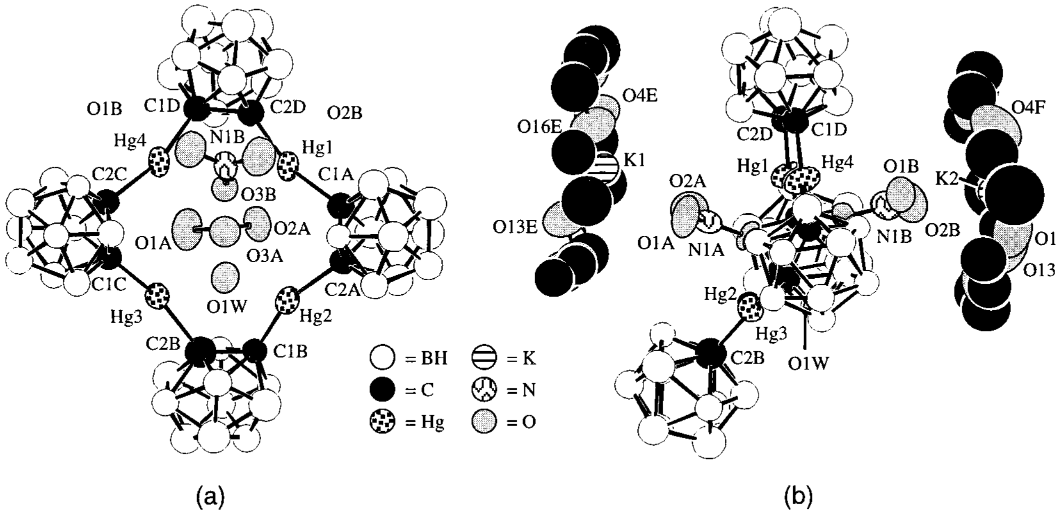

Figure 1. Top (a) and side (b) views of the structure of **1** (ORTEP, with hydrogen atoms, H_2O, and acetone molecules removed for clarity). For bond lengths and angles see text.

Table 1. Details of Crystallographic Data Collection for **1** and **2**

formula	$C_{35}H_{98}B_{40}Hg_4N_2K_2O_{21}$ (**1**)	$C_{32}H_{88}B_{40}Hg_4N_2K_2O_{18}$ (**2**)
fw	2196.187	2102.061
space group	$P2_1/n$	$P\bar{1}$
a, Å	21.9919(9)	12.4270(7)
b, Å	16.4156(7)	12.8421(7)
c, Å	23.3225(10)	13.6340(8)
α, deg		102.553(2)
β, deg	95.360(1)	100.626(3)
γ, deg		119.075(1)
V, Å^3	8383	1930
Z	4	1
temp, °C	25	25
λ, Å	0.7107	0.7107
ρ_{calcd}, g/cm^3	1.74	1.81
μ, cm^{-1}	74.6	80.9
R,[a] R_w[b]	0.063, 0.074	0.065, 0.076
GOF[c]	1.85	2.09

[a] $R = \sum||F_o| - |F_c||/|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2]^{1/2}$. [c] $GOF = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$.

for H were assigned based on the atom attached to H. Programs used in this work include locally modified versions of crystallographic programs listed in ref 21. All calculations were performed on a VAX 3100 computer in the J. D. McCullough X-ray Crystallography Laboratory. Table 1 lists a summary of crystallographic data for the structures of **1** and **2**.

Structural Analysis of 1. Crystals for X-ray structure analysis were grown at 25 °C from a supersaturated acetone solution. Unit cell parameters were determined from a least-squares fit of 99 accurately centered reflections (9.6° < 2θ < 20.3°). Three intense reflections (5 0 3, 0 4 0, 7 0−5) were monitored every 97 reflections to check stability. Intensities of these reflections decayed 5% during the course of the experiment (108.2 h). Of the 14 748 unique reflections measured, 5187 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for secondary extinction and absorption. Atoms were located by use of direct methods (SHELX86).[21] Only the Hg, K, and crown ether O atoms were refined anisotropically. Some H atoms (on H_2O and on the carborane moieties) were not located. Other H atoms on the carborane were included in located positions and were not refined. The largest peak on a final difference electron density map, near Hg3, was 0.77 e·Å^{-3}.

Structural Analysis of 2. Crystals for X-ray structure analysis were grown at 25 °C from a saturated *o*-dichlorobenzene/acetone solution. Unit cell parameters were determined from a least-squares fit of 66 accurately centered reflections (9.7° < 2θ < 20.5°). Three intense reflections (3 0 0, 1 −3 0, 1 0 4) were monitored every 97 reflections to check stability. Intensities of these reflections decayed 18% during the course of the experiment (112.4 h). Of the 11 258 unique reflections measured, 4564 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for decay, secondary extinction, and absorption. Atoms were located by use of heavy atom methods. Only the Hg and K atoms were refined anisotropically. H atoms on the carborane were included in located positions and were not refined. The largest peak on a final difference electron density map, near Hg, was 1.3 e·Å^{-3}.

Results and Discussion

The free host was obtained by removal of the iodide ions from the 12-mercuracarborand-4 diiodide[17] through metathesis with silver acetate. In order to eliminate this step, the direct exchange of iodide with NO_3^- in the diiodide complex was attempted using $AgNO_3$ (eq 1). However, crystals of sufficient quality for X-ray analysis could not be obtained by this process.

$$[C_2B_{10}H_{10}Hg]_4I_2Li_2 + 2AgNO_3 \rightarrow [(C_2B_{10}H_{10}Hg)_4(NO_3)_2]Li_2 + 2AgI \quad (1)$$

Suitable crystals of **1**, $[(C_2B_{10}H_{10}Hg)_4(NO_3)_2\cdot H_2O][K(18\text{-crown-}6)]_2\cdot H_2O\cdot (CH_3)_2C{=}O$, were obtained by reaction of the free host, 12-mercuracarborand-4, with 2 equiv each of KNO_3 and 18-crown-6 in acetone solvent.

The structure of **1** is shown in Figure 1. Selected bond distances and angles for **1** are given in Table 2. In contrast to the halide ion adducts of 12-mercuracarborand-4 reported previously,[16,22,23] the carbon vertices of the carborane cages in **1** do not adopt a planar conformation. The 12-mercuracarborand-4 host is puckered in the middle, resulting in a bent configuration. Until now, this butterfly type structure had only

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(21) CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; SHELX76 (Sheldrick) crystal structure package and SHELX86 (Sheldrick) crystal structure solution package; DIFABS (Walker and Stuart), empirical absorption correction; ABSCOR, absorption correction based on ψ scan; ORTEP (Johnson) and the UCLA Crystallographic Package.

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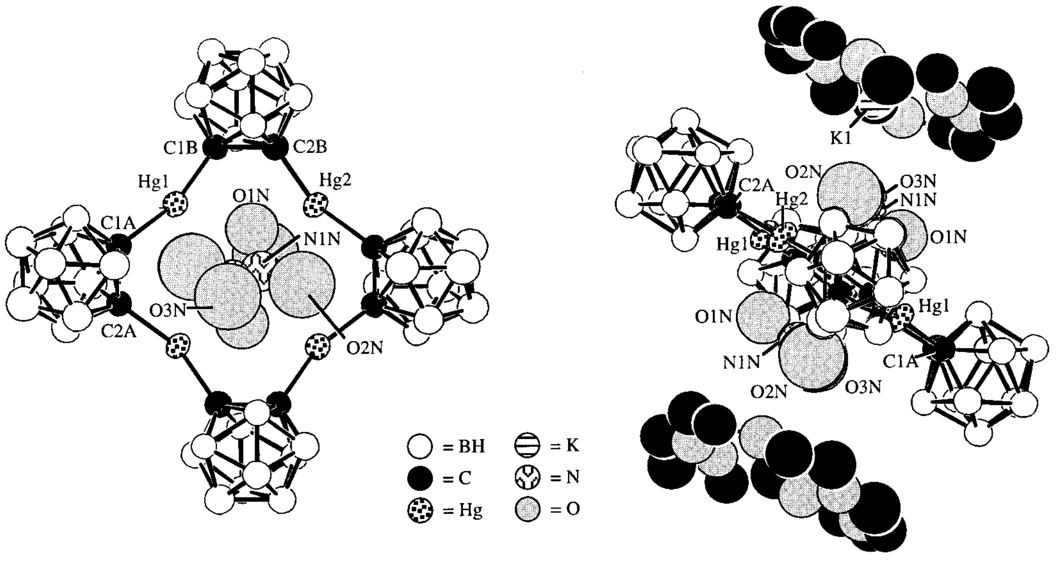

(a) (b)

Figure 2. Top (a) and side (b) views of the structure of **2** (ORTEP, with hydrogen atoms removed for clarity). For bond lengths and angles, see text.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **1**[a]

atoms	distance	atoms	distance
Hg1−C1A	2.10(2)	Hg2−C2A	2.12(2)
Hg1−C2D	2.06(2)	Hg2−C1B	1.92(2)
Hg3−C1C	2.02(2)	Hg4−C2C	2.07(2)
Hg3−C2B	2.25(3)	Hg4−C1D	2.06(2)
K1−O2A	2.94(2)	K1−O1A	3.01(2)
K2−O1B	3.06(2)	K2−O2B	2.72(2)
Hg1−Hg2	4.051(2)	Hg1−Hg3	5.535(2)
Hg1−Hg4	3.886(1)	Hg2−Hg3	3.909(1)
Hg2−Hg4	5.704(2)	Hg3−Hg4	4.064(2)
Hg1−O3A	2.82(2)	Hg1−O3B	2.75(2)
Hg2−O3A	2.89(2)	Hg2−O1W	2.74(2)
Hg3−O3A	2.88(2)	Hg3−O1W	2.82(2)
Hg4−O3A	3.08(2)	Hg4−O3A	2.60(2)

atoms	angles	atoms	angles
Hg1−Hg2−Hg3	88.09(3)	Hg2−Hg3−Hg4	91.33(3)
Hg3−Hg4−Hg1	88.23(3)	Hg4−Hg1−Hg2	91.85(3)
C1A−Hg1−C2D	163.3(9)	C2A−Hg2−C1B	159.2(9)
C2C−Hg4−C1D	163.2(9)	Hg1−C1A−C2A	126.4(15)
Hg2−C1B−C2B	123.1(16)	Hg3−C1C−C2C	131.5(15)
Hg4−C2C−C1C	120.6(15)	Hg4−C1D−C2D	122.6(15)
Hg1−C2D−C1D	122.0(15)		

[a] Esd in parentheses, in the units of least significant digit of the corresponding value.

been observed for host molecules in the absence of coordinating anions.[16,17] In the tetrahydrofuran-coordinated, unsubstituted 12-mercuracarborand-4•(THF)$_4$ structure,[17] the angle between the wings of the mercuracarborand host was 72°. The corresponding, but solvent free, octaethyl derivative[24] showed an even smaller angle of 61°. However, coordination of two NO_3^- ions to 12-mercuracarborand-4 in **1** causes the wings of the mercuracarborand butterfly to spread to an angle which is almost twice that observed for the unsubstituted hosts. The angle between the planes (Hg1, Hg2, C2A, C1A, B9A, B12A) and (Hg3, Hg4, C1C, C2C, B9C, B12C) is 137° (Figure 1b). These results prove that the 12-mercuracarborand-4 structure may adopt a variety of geometries to achieve stable structures depending upon the presence of a guest species and its identity.

The two nitrate anions in **1** are both monodentate through one oxygen to the mercury atoms of the host molecule. One of the nitrates, NO_3^-(A), is observed to bind through O3A to all four Hg atoms of the host, while the second nitrate, NO_3^-(B), binds to only two Hg atoms, Hg1 and Hg4, through O3B. The remaining coordination site between Hg2 and Hg3 is occupied by a water molecule. The oxygen atom in the water, O1W, is almost equidistant from Hg2 and Hg3, 2.74(2) and 2.82(2) Å, respectively. Similar Hg−O distances are observed between the coordinating nitrate oxygen atoms and the mercury atoms of the host. In nitrate A, O3A is almost equidistant from all four Hg atoms with an average measurement of 2.92 Å. In nitrate B, O3B is 2.75 Å from Hg1 and 2.60 Å from Hg4. The distances between O3B and the other two mercury atoms (Hg2 and Hg3) are much too long to be considered to have any interaction. The remaining oxygen atoms in nitrates A and B (O1A, O2A and O1B, O2B) coordinate with the crown-complexed potassium cations K1 and K2, respectively. The four Hg atoms of the host are in a nearly square arrangement with Hg−Hg distances ranging from 3.886(1) to 4.064(2) Å and Hg−Hg−Hg angles ranging from 88.1° to 91.9°. The four atoms are almost coplanar. The greatest deviation from their least-squares plane is 0.094(1) Å. The distance between the Hg atoms is longer than that found for the free host, but shorter that that observed for the mono chloride ion adduct, 3.654(1) and 4.129(1) Å, respectively.[11,17]

As an extension of the above procedure, an additional equivalent of KNO_3/18-crown-6 was added to the reaction mixture in order to coordinate a third NO_3^- anion to the host by replacing a water molecule. To our surprise, the resulting crystal structure revealed a centrosymmetric planar host which was sandwiched by two NO_3^- anions, complex **2**. The structure of **2** is shown in Figure 2, and selected bond distances and angles are given in Table 3. The two nitrate anions coordinate in a tridentate, face-on fashion. In each NO_3^- unit, the three oxygen atoms are observed to coordinate to the four mercury atoms of the mercuracarborand host. To our knowledge, this is the first documented example of a face-on trihapto coordination of NO_3^-

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Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **2**[a]

atoms	distance	atoms	distance
K1−O2N	2.98(1)	Hg2−O3N	2.67(2)
Hg1−O2N	2.81(4)	Hg2′−O1N	3.21(3)
Hg1′−O1N	3.00(2)	Hg2−C2A	2.067(15)
Hg1−C1A′	2.059(15)	Hg2−C2B	2.044(16)
Hg1−C1B	2.049(15)		

atoms	angles	atoms	angles
Hg1−Hg2−Hg1′	90.00(2)	Hg2−Hg1′−Hg2	90.00(2)
C1B−Hg1−C1A′	161.8(6)	C2A−Hg2−C2B	160.1(6)
Hg1′−C1A−C2A	128.1(10)	Hg2−C2A−C1A	125.0(10)
Hg1−C1B−C2B	125.0(10)	Hg2−C2B−C1B	123.7(10)

[a] Atoms denoted by primes are related in position to unprimed atoms by the center of symmetry at 0, 0, $^1/_2$. Esd in parentheses, in the units of least significant digit of the corresponding value.

to a macromolecular Lewis acid host. The four mercury atoms of the host molecule form a nearly perfect square, with Hg−Hg distances of 4.020(1) and 4.124(1) Å and exact 90.0(1)° Hg−Hg−Hg angles. Additionally, the carbon atoms of the carborane cages which are attached to mercury were found to deviate by no more than 0.08 Å from the plane through the four Hg atoms. Each mercury atom effectively coordinates 1.5 oxygen atoms. For example, the adjacent pair of mercury atoms Hg1 and Hg2 coordinate most closely with O2N and O3N, respectively, which are above the Hg_4 plane in Figure 2b (Hg1−O2N 2.67(2) Å, Hg2−O3N 2.81(4) Å). But on the opposite side of the Hg_4 plane, Hg1 and Hg2 share coordination of the bridging oxygen atom O1N (Hg1−O1N 3.00(2) Å, Hg2−O1N 3.21(3) Å). The potassium ion is coordinated to all six oxygen atoms of the 18-crown-6 molecule (distances ranging from 2.84(2) to 2.92(2) Å) and also to two oxygen atoms O2N and O3N of the nitrate anion (K1−O2N 2.98(3), K1−O3N 3.14(3) Å). Apparently, the coordination of the nitrate anion to potassium weakens the interaction between the nitrato oxygen atoms and the four Hg centers, resulting in a tilt of 5.4° between the Hg_4 plane and the plane defined by the three nitrato oxygen atoms.

^{199}Hg NMR. The ^{199}Hg NMR spectra of acetone solutions of **1** or **2** are identical. Only a single peak is observed at −1269 ppm. A change in the ratio of nitrate anion to mercuracarborand did not affect the observed chemical shift when the ratio of nitrate anion to mercuracarborand host was varied from 3:1 to 1:1. Temperature was also varied for each of three guest:host ratios of 3:1, 2:1, and 1:1 in the range 180−300 K, but no change in chemical shift was observed. These results are indicative of a highly fluxional structure in which a nitrate ion is weakly coordinated to the host molecule.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structural determination of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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