Salts of the Lewis-Acidic Dianion [Hg(*closo*-1-CB$_{11}$F$_{11}$)$_2$]$^{2-}$: Coordination of Acetonitrile and Water

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S *Supporting Information*

ABSTRACT: The coordination of acetonitrile and water to the Hg atom in [Hg(*closo*-1-CB$_{11}$F$_{11}$)$_2$]$^{2-}$ (**1**) reveals the Lewis acidity of the Hg^{II} center, which is unprecedented, since **1** is a dianion. Both coordination compounds were characterized by single-crystal X-ray diffraction, vibrational spectroscopy, and differential scanning calorimetry (DSC). In contrast, the Hg atom in [PhHg(*closo*-1-CB$_{11}$F$_{11}$)]$^-$ (**2**) does not coordinate to CH$_3$CN and H$_2$O, although it has only a single negative charge.

Mercury complexes of electron-poor organic ligands such as dicarba-*closo*-dodecaboranyl[1,2] or fluorinated aryl groups[3,4] contain Lewis acidic Hg^{II} centers that can coordinate neutral or anionic ligands. Such coordination compounds are of interest for a variety of applications associated with supramolecular chemistry,[1−4] for example, as materials for gas storage, as anion receptors, or in catalysis. A comparison of the two acetonitrile complexes **I**[5] and **II**[6] that contain trinuclear organomercury compounds demonstrates the structural analogy between Hg^{II} complexes with either dicarba-*closo*-dodecaboranyl or fluorinated aryl ligands and reveals their similar coordination ability (see Chart 1).

Although several complexes of type **I** and **II** or related Hg^{II} species with other neutral ligands than acetonitrile are known, only very few examples with water as weakly bonded ligand have been reported to date,[7−9] e.g., [{(9,12-(CH$_3$)$_2$-*closo*-1,2-C$_2$B$_{10}$-H$_8$Hg)$_3$(OH$_2$)$_2$}] (C$_6$H$_6$)[7] or [{(*o*-C$_6$F$_4$Hg)$_3$}$_2$-([*n*]crown-6)-(OH$_2$)$_2$] (*n* = 12, 18).[8]

Monocarba-*closo*-dodecaboranyl ligands are isoelectronic to dicarba-*closo*-dodecaboranyl ligands as presented in **I**. As a result of the negative charge of the {*closo*-1-CB$_{11}$} cluster, its complexes with metals should be more electron-rich, compared to analogous complexes with {*closo*-C$_2$B$_{10}$} clusters. However, the properties of the {*closo*-1-CB$_{11}$} cluster can be tuned by the substituents bonded to the cluster; for example, highly fluorinated derivatives reveal strongly different properties, compared to their nonfluorinated counterparts.[10−12] Here, we report on Hg^{II} complexes with the fluorinated monocarba-*closo*-dodecaboranyl ligand [*closo*-1-CB$_{11}$F$_{11}$]$^{2-}$ and on the coordination of acetonitrile and water to the dianion [Hg(*closo*-1-CB$_{11}$F$_{11}$)$_2$]$^{2-}$ (**1**). So far, only one complex with the [*closo*-1-CB$_{11}$F$_{11}$]$^{2-}$ ligand—[ClCu(*closo*-1-CB$_{11}$F$_{11}$)]$^{2-}$—is known,[10] and only two further complexes of other monocarba-*closo*-dodecaboranyl ligands have been described.[11,13]

The dianion [*closo*-1-CB$_{11}$F$_{11}$]$^{2-}$, which is accessible via deprotonation of [1-H-*closo*-1-CB$_{11}$F$_{11}$]$^-$ with ^{n}BuLi,[10] reacts with HgCl$_2$ and PhHgCl to result in **1** and **2**, respectively (see Scheme 1). Their tetraethylammonium salts are white solids that are air- and water-stable, and their decomposition starts above 200 °C, as determined by DSC measurements in a nitrogen atmosphere.

Crystallization of the tetraethylammonium salt of **1** from acetonitrile by slow diffusion of diethyl ether afforded colorless crystals of [Et$_4$N]$_2$[Hg(*closo*-1-CB$_{11}$F$_{11}$)$_2$(NCCH$_3$)]. The dianionic complex [**1**(NCCH$_3$)]$^{2-}$ is located on a mirror plane, and the acetonitrile molecule is coordinated to the Lewis-acidic mercury center (see Figure 1). The Hg—C distances of 211.3(14) and 202.5(17) pm are close to the values that have been reported for related Hg^{II} complexes of dicarba-*closo*-dodecaboranyl ligands.[2,5] The coordination of CH$_3$CN results in a bent C$_{cluster}$—Hg—C$_{cluster}$ unit, as expressed by a deviation from linearity by more than 10°. Furthermore, the two carboranyl ligands are not in an eclipsed conformation with a shortest F—F distance of 316(1) pm between the two ligands, which is longer than twice the van der Waals radius of fluorine (147 pm).[14] The coordination of the acetonitrile ligand is distorted from an end-on mode, as shown by the Hg···N—C angle of 145.7(7)°. According to a search in the Cambridge Crystallographic Database, the *d*(Hg—N) value of [**1**(NCCH$_3$)]$^{2-}$ (268.9(6) pm) is the shortest Hg—N distance for the coordination of a nitrile, compared to related complexes with dicarba-*closo*-dodecaboranyl or fluorinated aryl ligands, known so far. This indicates a relatively strong interaction between CH$_3$CN and mercury, which is supported by a relatively strong shift of ν(C≡N) to 2271 cm^{-1}, compared to free acetonitrile (2254 cm^{-1})[3] and by the thermal stability of the [**1**(NCCH$_3$)]$^{2-}$ complex, up to 90 °C (DSC).

Recrystallization of [Et$_4$N]$_2$[**1**(NCCH$_3$)] from acetone that contained a small amount of water resulted in crystals of an aqua complex of dianion **1**: [Et$_4$N]$_4$[**1**$_2$(OH$_2$)]. In this compound, the water molecule is trapped in a pocket formed by two dianions (see Figure 2). In the crystal structure determined at 107 K, the water molecule is disordered over two positions, with occupancies of 70% and 30%, respectively. The closest distances between the F atoms of the two dianions are in the range of 332.4(8) to 287.5(8) pm, which is close to twice the van der Waals radius of fluorine (147 pm).[14] The *d*(Hg—C) values are similar to the distances in [Et$_4$N]$_2$[**1**(NCCH$_3$)]. The deviation of the

Chart 1. Hg[II] Complexes with Bridging 1,2-dicarba-*closo*-dodecaboranyl and Fluorinated Aryl Ligands and Acetonitrile (I[5] and II[6])
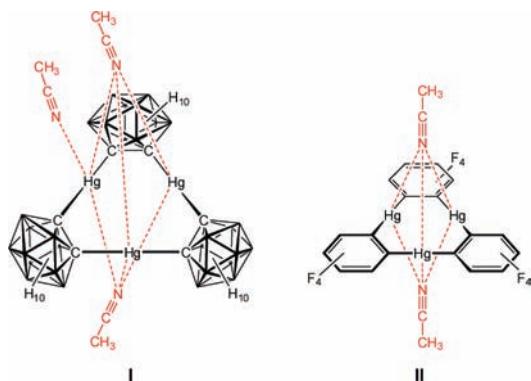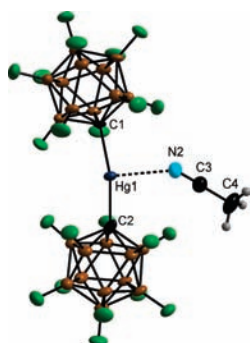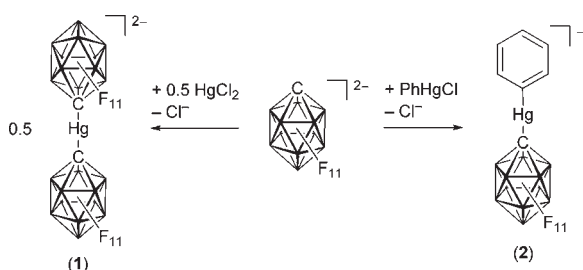

Scheme 1. Synthesis of 1 and 2

Figure 1. The anionic complex $[Hg(closo\text{-}1\text{-}CB_{11}F_{11})_2(NCCH_3)]^{2-}$ in the crystal of $[Et_4N]_2[\mathbf{1}(NCCH_3)]$ (displacement ellipsoids are at the 40% probability level). Selected bond lengths [pm]: Hg1−C1, 211.3(14); Hg1−C2, 202.5(17); Hg1⋯N2, 268.9(6); N2≡C3, 112.3(10); and C3−C4, 143.0(12). Selected bond angles [°]: C1−Hg1−C2, 167.9(6); Hg1⋯N2−C3, 145.7(7); C1−Hg1⋯N2, 96.3(4); C2−Hg1⋯N2, 95.8(4).

C_cluster−Hg−C_cluster angle in the dianion that is coordinated to the water molecule with the higher occupancy is larger (169.2(3)°), compared to the second dianion (171.3(3)°). The two carboranyl ligands in each dianion are close to an eclipsed conformation, as a result of the coordination of water. The Hg−O distance of 273.9(10) pm is at the shorter end of comparable d(Hg−O) values,[7−9] indicating a relatively strong interaction between water and mercury in **1**, as also observed for the respective acetonitrile complex.
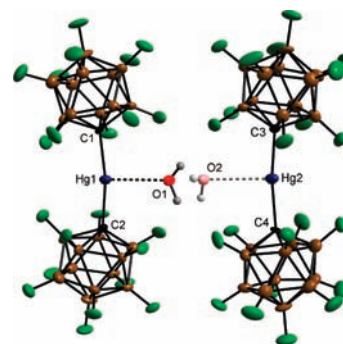

Figure 2. The anionic unit $[\{Hg(closo\text{-}1\text{-}CB_{11}F_{11})_2\}_2(OH_2)]^{4-}$ in the crystal of $[Et_4N]_4[\mathbf{1}_2(OH_2)]$ (displacement ellipsoids are at the 40% probability level). Occupancies: 70% for O1 and 30% for O2. Selected bond lengths [pm]: Hg1−C1, 211.3(8); Hg1−C2, 208.7(9); Hg1⋯O1, 273.9(10); Hg2−C3, 206.3(9); Hg2−C4, 212.4(8); and Hg2⋯O2, 285(2). Selected bond angles [°]: C1−Hg1−C2, 169.2(3); C1−Hg1⋯O1, 95.8(2); C2−Hg1⋯O1, 95.0(3); C3−Hg2−C4, 171.3(3); C3−Hg2⋯O2, 95.5(5); and C4−Hg2⋯O2, 92.7(5).

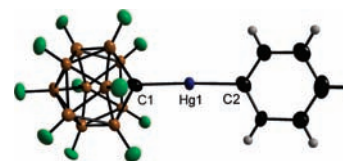**Figure 3.** The anionic complex $[PhHg(closo\text{-}1\text{-}CB_{11}F_{11})]^-$ in the crystal of $[Et_4N]\mathbf{2}$ (displacement ellipsoids are at the 40% probability level). Selected bond lengths [pm]: Hg1−C1, 211.1(12); and Hg1−C2, 206.2(11). Selected bond angle [°]: C1−Hg1−C2, 174.2(4).

The coordination of water in $[Et_4N]_4[\mathbf{1}_2(OH_2)]$ is confirmed by the IR spectrum that shows the three bands characteristic for water that is not involved in any further hydrogen bonding (3681 cm⁻¹, ν_{as}(O−H); 3583 cm⁻¹, ν_s(O−H); and 1587 cm⁻¹, δ(HOH)). The loss of the water from the crystalline material starts at 120 °C (DSC).

In contrast to **1**, the corresponding complex with the non-fluorinated monocarba-*closo*-dodecaboranyl ligand $[Hg(closo\text{-}1\text{-}CB_{11}H_{11})_2]^{2-}$ crystallizes without a further neutral ligand coordinated to the Hg[II] center.[15] Similarly, in the crystal structure of $[Et_4N]\mathbf{2}$, no coordination of a third ligand to the $[PhHg(closo\text{-}1\text{-}CB_{11}F_{11})]^-$ anion is observed, although the steric demand at mercury is reduced, compared to dianion **1** (see Figure 3). This observation shows that the Hg[II] center in **2** is a weaker Lewis acid than that in **1**, even though **2** is a dianion and **1** is a monoanion.

The different behaviors of **1** and **2** are also evident from the respective ¹⁹⁹Hg NMR spectra depicted in Figure 4. In the ¹⁹⁹Hg{¹H} NMR spectrum of **2** dissolved in CD₃CN, the signal (−975 ppm) is split into a sextet, as a result of the $^3J(^{199}Hg, ^{19}F)$ coupling of 185 Hz to the five upper-belt F atoms of the carboranyl ligand. In contrast, for the dianion **1**, a broad signal is observed in CD₃CN at −1064 ppm and the $^3J(^{199}Hg, ^{19}F)$ coupling that should result in an undecet is not resolved. However, the presence of the coupling was proven by a ¹⁹F decoupling experiment that resulted in a reduced line width of 411 Hz versus 1021 Hz without decoupling (see Figure 4). The respective coupling constant of 238 Hz was derived from the corresponding ¹⁹F{¹¹B} NMR spectrum (see Figure S1 in the Supporting Information). The line broadening in the ¹⁹⁹Hg
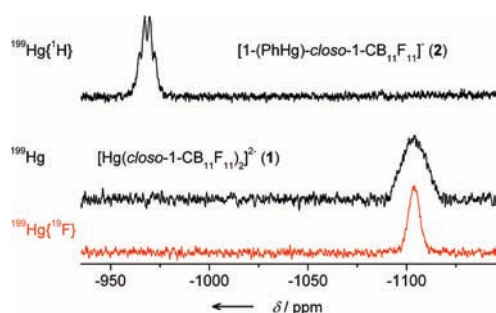
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Figure 4. ^{199}Hg NMR spectra of **1** and **2** in CD_3CN.

NMR spectrum of **1** is probably due to a strong interaction with the solvent, e.g., a fast ligand exchange at the mercury center, which is not present in the case of anion **2**.

In summary, we have demonstrated that the dianion $[Hg(closo\text{-}1\text{-}CB_{11}H_{11})_2]^{2-}$ (**1**) reveals coordination behavior and Lewis acidity that is similar to that of Hg^{II} complexes with electron-poor dicarba-*closo*-dodecaboranyl[1] and fluorinated aryl ligands.[3,4] This is unprecedented, because **1** is a dianion whereas the related Hg^{II} complexes are neutral. Especially $[\mathbf{1}_2(OH_2)]^{4-}$, which has one one water molecule trapped between the two mercury centers in a pocket formed by two dianions **1**, is unusual. In contrast, the monoanionic mixed complex **2** does not reveal a related coordination behavior, probably because of the more electron-rich phenyl ligand. Similarly, the dianion $[Hg(closo\text{-}1\text{-}CB_{11}H_{11})_2]^{2-}$ does not show an interaction with water or acetonitrile, as found for **1**,[15] which demonstrates the influence of the fluorine substituents on the electronic properties of the $\{closo\text{-}1\text{-}CB_{11}\}$ cluster. The synthesis and properties of salts of $[Hg(closo\text{-}1\text{-}CB_{11}H_{11})_2]^{2-}$ and of the corresponding dianions with $[closo\text{-}1\text{-}CB_{11}Hal_{11}]^{2-}$ (Hal = Cl, Br), which all do not form complexes with water and acetonitrile, will be reported elsewhere.

Dianion **1** is a model system for other Hg^{II} complexes of highly fluorinated carba-*closo*-dodecaboranyl ligands that contain one or more functional groups that are bonded to the cluster B atoms. Such building blocks that are dianions and combine a Lewis-acidic center with further functionalities will be of broad interest in supramolecular chemistry. Currently, we are investigating the synthesis of ligands of this type and the preparation and properties of their Hg^{II} complexes.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Experimental details, spectroscopic data, CIF files containing the structural data (CCDC Nos. 807089—807091), IR and Raman spectra of $[Et_4N]_4[\mathbf{1}_2(OH_2)]$, $[Et_4N]_2[\mathbf{1}(NCCH_3)]$, and $[Et_4N]\mathbf{2}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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