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Dimerization of the Trinuclear Mercury(II) Complex [(*o*-C$_6$F$_4$Hg)$_3$·μ_3-acetone] via Mercurophilic Interactions

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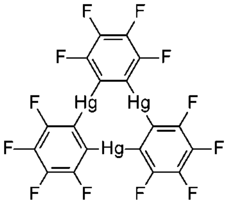
Received May 9, 2002

The occurrence of metallophilic contacts in the structural chemistry of gold(I) derivatives is a well-established phenomenon which likely originates from dispersion forces magnified by relativistic effects.[1,2] These interactions range from 2.8−3.5 Å, and their strength has been compared to that of hydrogen bonds.[3,4] Theoretical calculations suggest that such interactions should occur in the chemistry of mercury(II), which also features a 5d^{10} closed shell electronic configuration. In particular, as shown by Pyykkö, the occurrence of a metallophilic Hg(II)$\cdots$Hg(II) bond of 3.41 Å is predicted for the perpendicular (HgMe$_2$)$_2$ dimer.[5] So far, however, experimental observation of such contacts appears rather limited.[6] While short ligand enforced contacts are present in *peri*-mercurated-naphthalene complexes,[4] only on a few occasions have unsupported Hg−Hg interactions been observed.[5,7,8] In this communication, we report that trimeric perfluoro-*ortho*-phenylene mercury (**1**) forms a μ_3-acetone complex which associates into a cofacial dimer through formation of short Hg(II)$\cdots$Hg(II) interactions.



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The complexation of acetone by **1** has been the subject of previous studies, although no information on the stoichiometry and structure of the product was reported.[9] Recently, we found that **1** crystallizes from acetone to form a 1:3 complex that has been characterized by X-ray analysis and identified as [**1**·(acetone)(μ_3-acetone)$_2$].[10] We have now discovered that a 1:1 complex ([**1**·μ_3-acetone], (**2**)) can be isolated as a crystalline adduct upon evaporation of a 1,2-dichloroethane solution of **1** containing acetone (Figure 1). Owing to the toxic nature of organomercurials, great caution should be exercised in these experiments. Compound **2** forms large single crystals that do not decompose over the course of several weeks. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell.[11] Examination of the atomic connectivity confirms the simultaneous coordination of the carbonyl oxygen atom to the three mercury centers of **1**. The resulting Hg−O distances range from 2.810(12) to 2.983(12) Å and are well within the sum of the van der Waals radii for mercury ($r_{\text{vdw}} = 1.75$ Å)[5] and oxygen ($r_{\text{vdw}} = 1.54$ Å).[12] As a result of these interactions, the oxygen atom is essentially equidistant from the three Lewis acidic sites and sits at 1.970 Å from the plane defined by the three mercury atoms. The linear carbonyl functionality is perpendicular to the plane of the trinuclear complex with which it forms an angle of 90°. While the Hg−O bond distances are longer than those found for the chelate complex formed between 1,2-bis(chloromercurio)tetrafluorobenzene and acetone (av Hg−O = 2.73 Å),[13] the metrical and angular parameters observed in **2** resemble those encountered in [**1**·μ_3-acetaldehyde].[10] The IR spectrum of **2** features an intense carbonyl band at 1683 cm^{-1}, thus indicating a substantial weakening of the C═O bond ($\nu_{\text{CO}} = 1716$ cm^{-1} for neat acetone). In agreement with the triple coordination of the acetone molecule, this effect is more acute than in [1,2-bis(chloromercurio)tetrafluorobenzene·μ_2-acetone], where a stretching frequency of 1693 cm^{-1} has been measured for the doubly coordinated carbonyl functionality.[13]

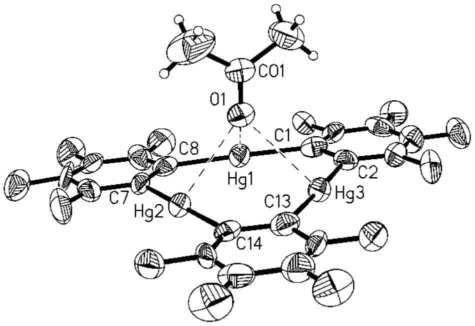

Figure 1. ORTEP diagram of **2** (50% ellipsoids). Selected bond lengths [Å] and angles [deg]: Hg(1)−C(1) 2.086(18), Hg(1)−C(8) 2.091(18), Hg(2)−C(7) 2.085(19), Hg(2)−C(14) 2.065(19), Hg(3)−C(2) 2.061(17), Hg(3)−C(13) 2.042(18), O(1)−C(01) 1.201(19); C(1)−Hg(1)−C(8) 177.3(6), C(7)−Hg(2)−C(14) 174.5(7), C(2)−Hg(3)−C(13) 175.2(8), C(01)−O(1)−Hg(2) 138.2(12), Hg(2)−O(1)−Hg(1) 75.9(3), Hg(2)−O(1)−Hg(3) 80.4(3), Hg(1)−O(1)−Hg(3) 76.0(3), O(1)−C(01)−C(08) 121.0(2), O(1)−C(01)−C(02) 120.6(18).

Inspection of the cell-packing diagram indicates that molecules of [**1**·μ_3-acetone] are associated into cofacial dimers. In this dimer, the parallel trinuclear mercury units are separated by 3.46 Å from one another and adopt an offset and staggered arrangement (Figure 2). As a result of this arrangement, the mercury center at Hg(1) approaches one of the tetrafluorophenylene rings of the juxtaposed molecule. The resulting Hg$\cdots$C distances (Hg(1)$\cdots$C(17) = 3.483, Hg(1)$\cdots$C(18) = 3.402 Å) are close to the sum of van der Waals radii of mercury and carbon in aromatic systems (r_{vdw}(C$_{\text{arom}}$) = 1.7 Å).[12] While these Hg$\cdots$C distances might reflect the formation of polyhapto−π interactions,[8] it should be kept in mind that by virtue of fluorination, the phenylene ring is electron poor and thus unlikely to significantly complex the mercury atom. Further inspection of the dimer reveals the presence of conspicuously short Hg$\cdots$Hg intermolecular contacts of 3.512 Å that involve Hg(2) and Hg(3). These intermolecular contacts are longer than the Hg−Hg distance observed in metallic mercury (3 Å).[14] They are, however, shorter than the Hg$\cdots$Hg distances observed intramolecularly (Hg(1)$\cdots$Hg(2), 3.572 Å; Hg(2)$\cdots$Hg(3), 3.636 Å; Hg(1)$\cdots$Hg(3), 3.570

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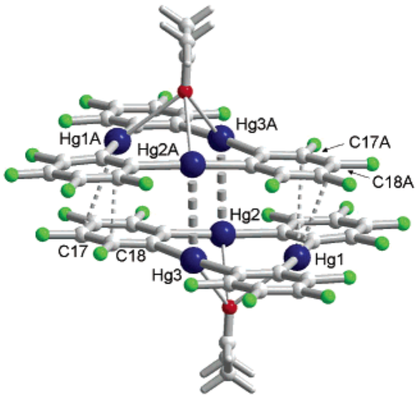

Figure 2. View of the dimer of **2** showing the mercurophilic interactions. Color code: C, gray; F, green; O, red; Hg, navy.

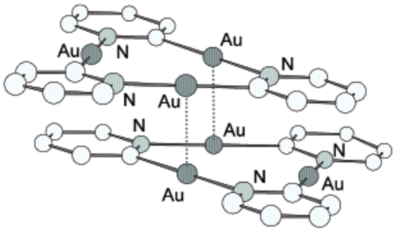

Figure 3. Schematic representation of the dimer of $[Au(NC_5H_4)]_3$[18] showing the structural similarity that exists with **2**.

Å) and only slightly exceed the mercurophilic interaction distance calculated for the perpendicular $(HgMe_2)_2$ dimer.[5]

The observation of short Hg⋯Hg contacts in the structure of **2** deserves further comment. In particular, the arrangement of the monomeric units in the cofacial dimer of **2** constitutes a déjà vu in the structural chemistry of related macrocyclic trinuclear gold complexes[15,16] such as $[(EtO)(p\text{-}MeC_6H_4N{=})CAu]_3$[17] and $[Au(NC_5H_4)]_3$.[18] These gold(I) complexes dimerize through formation of two aurophilic Au−Au interactions of 3.244(1) and 3.105(3) Å, respectively (Figure 3). Moreover, we note that trinuclear gold(I) complexes including $[(EtO)(p\text{-}MeC_6H_4N{=})CAu]_3$ interact with **1** to form stacks that exhibit intermolecular Hg⋯Au interactions of 3.2−3.3 Å.[19]

When irradiated with UV light in the crystalline state, compound **2** luminesces. Measurement of the emission spectrum at 298 K (λ_{ex} = 325 nm) reveals the existence of an emission band featuring a maximum at 480 nm and a shoulder at 520 nm. Upon cooling to 77 K, the emission spectrum of **2** becomes more intense and exhibits a broad and a sharp band at 450 and 480 nm, respectively (Figure 4). Apparently, and as observed in the chemistry of gold(I),[20] the luminescence properties of **2** appear to be correlated to the self-association observed in the solid. We have previously reported that dilute CH_2Cl_2 solutions of pure **1** do not luminesce, while solid **1**, which forms staggered dimers with long Hg⋯Hg contacts (3.811 < Hg⋯Hg < 4.093 Å), features an emission band with a maximum at 440 nm and a broad shoulder at 530 nm.[8] In the present case, CH_2Cl_2 solutions of **2** feature only a very faint emission.

All observations considered, we propose that the cofacial dimers observed in the structure of **2** are stabilized by the formation of two mercurophilic interactions.

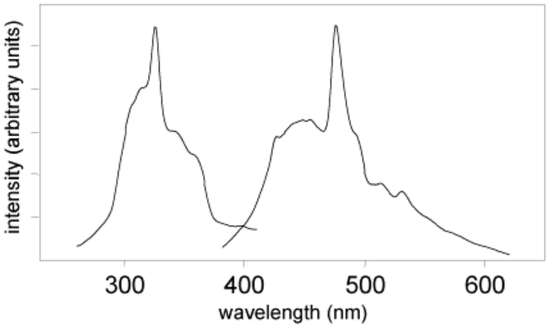

Figure 4. Excitation (λ_{em} = 480 nm) and emission (λ_{ex} = 325 nm) spectra of solid **2** recorded at 77 K.

Acknowledgment. Support from the National Science Foundation in the form of a CAREER award (CHE-0094264) and an equipment grant (CHE-9807975; purchase of the X-ray diffractometers) is gratefully acknowledged. We thank John Fackler for providing access to a luminescence spectrometer.

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

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(11) This structure was collected on a Bruker SMART-CCD area detector diffractometer, Mo Kα radiation ($\lambda = 0.71069$ Å) at $T = 110$ K, and was solved by direct methods, and refined by full-matrix least squares against F^2 using the SHELXTL/PC (ver. 5.10) package. **2**: $C_{21}H_6F_{12}Hg_3O$, M 1104.03, triclinic, space group *P-1*, $a = 10.601(2)$ Å, $b = 10.910(2)$ Å, $c = 11.259(2)$ Å, $\alpha = 77.88(3)°$, $\beta = 71.68(3)°$, $\gamma = 68.17(3)$, $V = 1141.1(4)$ Å^3, $Z = 2$, $\rho_{calc} = 3.213$ g cm^{-3}. Crystal size 0.31 × 0.17 × 0.24 mm^3, ω-scan mode, measurement range 1.92−24.00°, 9956 unique reflections, 3563 reflections with $I > 2\sigma(I)$, $\mu = 20.243$ mm^{-1}. R1 = 0.0676, wR2 = 0.1488 (all data).
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JA0268534