

Polymorphism of Trimeric Perfluoro-*ortho*-phenylene Mercury, $[\text{Hg}(o\text{-C}_6\text{F}_4)]_3$

Mason R. Haneline and François P. Gabbaï

Chemistry Department, Texas A&M University 3255 TAMU, College Station, Texas 77843-3255, USA

Reprint requests to Prof. Dr. F. P. Gabbaï. Fax: (1) 979-845-4719.
E-mail: gabbai@mail.chem.tamu.edu

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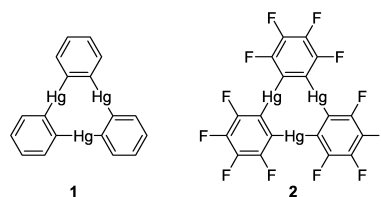
Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Three new modifications of trimeric perfluoro-*ortho*-phenylene mercury (**2**) have been investigated by single crystal X-ray diffraction. In each of these modifications, the molecules of **2** form extended stacks. Within each stack, the successive molecules are parallel and separated by approximately 3.3 – 3.4 Å. The packing observed in the different structures is rationalized on the basis of secondary mercury- π interactions, mercuriophilic interactions and electrostatic interactions. Altogether, little preference is given for one particular type of interaction. The packing appears to be dominated by non-directional van der Waals interactions between molecules of **2** which are largely aromatic and whose overall polarizability is magnified by relativistic effects at the mercury(II) centers.

Key words: Polymorphism, Mercury, Stacking, Metallophilic Interactions, van der Waals Interactions

Introduction

Trimeric *ortho*-phenylene mercury derivatives have been known for over half a century [1–4]. These derivatives, which are air and water stable, have been widely used as reagents for the synthesis of organometallic derivatives featuring an *ortho*-phenylene backbone. For example, trimeric *ortho*-phenylene-mercury ($[o\text{-C}_6\text{H}_4\text{Hg}]_3$, **1**) [1] undergoes transmetalation reactions with a variety of main-group elements or low-valent main-group salts. The preparation of *ortho*-dilithiobenzene [1], tetrameric *ortho*-phenylenemagnesium [5], dimeric *ortho*-phenylenzinc [6] and 9,10-dibromo-9,10-dihydro-9,10-diindanthracene [7] are representative examples that demonstrate the importance of **1** as a reagent. These mercury derivatives can also be used in metathesis reactions; for example, trimeric perfluoro-*ortho*-phenylene mercury ($[o\text{-C}_6\text{F}_4\text{Hg}]_3$, **2**) reacts with BBr_3 to afford 1,2-bis(dibromoboryl)benzene [8]. More recently, the potential of such derivatives to serve as polyfunctional Lewis acid receptors for electron rich species has been uncovered. In particular, trimeric perfluoro-*ortho*-phenylene mercury (**2**) [3] complexes a number of electron rich



species [9,10], including halide anions, carborane anions, sulfides, organic carbonyls, sulfoxide and nitriles. In the resulting adducts, the halide anion or the electron rich terminus of the polyatomic substrate is typically bound simultaneously to the three mercury centers of **2**. Compound **2** also interacts with arenes including naphthalene, pyrene and triphenylene to afford binary stacks where the arene is π -coordinated to the mercury centers of **2** [9,11].

Based on a molecular weight determination as well as a tentative crystal structure [2,12], compound **1** was first proposed to exist in the form of an hexamer of general formula $[o\text{-C}_6\text{H}_4\text{Hg}]_6$. However, careful crystallographic work by Massey [13,14] demonstrated that **1** is in fact a trimer which can exist in a monoclinic as well as in an orthorhombic modification. Interestingly, although **2** has been known for almost four decades, its

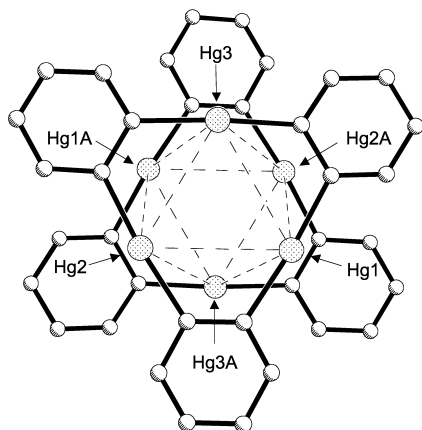


Fig. 1. Cofacial dimers observed in modification **A**. The fluorine atoms are omitted for clarity.

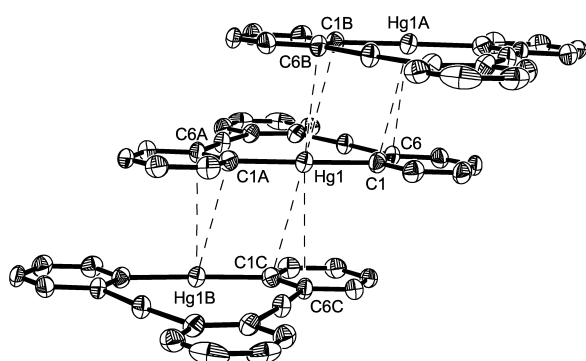


Fig. 2. Portion of a stack present in modification **B** (30% ellipsoids). The fluorine atoms are omitted for clarity. Selected intermolecular distances (Å): Hg(1)–C(1B) 3.385, Hg(1)–C(6B) 3.462, Hg(1)–C(1C) 3.385, Hg(1)–C(6C) 3.462.

crystal structure as a free acid had not been reported until recently. In 2002, we obtained a monoclinic modification (modification **A**, space group $P2_1/n$) of pure **2** by slow evaporation of a CS_2 solution. In this modification, molecules of **2** form compact cofacial dimers with a centroid distance of 3.38 Å (Fig. 1). This arrangement places the monomeric units in close contact, which results in intermolecular Hg...C distances of 3.443–3.650 Å and Hg...Hg distances of 3.811–4.093 Å. As part of our continuing interest in the chemistry of **2**, we have now characterized three additional modifications.

Results

Careful sublimation of **2** leads to the formation of crystals with both block and needle morphologies. The crystals which display a block morphology belong to

Table 1. Crystal data, data collections, and structure refinements for modifications **B**, **C** and **D** of $[\text{Hg}(o\text{-C}_6\text{F}_4)]_3$ (**2**).

Crystal data	Modification B	Modification C	Modification D
Formula	$\text{C}_{18}\text{F}_{12}\text{Hg}_3$	$\text{C}_{18}\text{F}_{12}\text{Hg}_3$	$\text{C}_{18}\text{F}_{12}\text{Hg}_3$
M_r	1045.95	1045.95	1045.95
Crystal size [mm ³]	$0.26 \times 0.15 \times 0.17$	$0.5 \times 0.07 \times 0.06$	$0.50 \times 0.25 \times 0.24$
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$C2/c$	$Pnma$	$P2_1/n$
a [Å]	16.841(3)	18.070(4)	11.123(2)
b [Å]	13.419(3)	21.200(4)	4.6306(9)
c [Å]	8.6790(17)	4.8030(10)	35.509(7)
β [°]	94.45(3)		97.29(3)
V [Å ³]	1955.5(7)	1840.0(6)	1814.1(6)
Z	4	4	4
$\rho_{\text{calcd.}}$ [gcm ^{−3}]	3.553	3.776	3.830
$\mu(\text{Mo-K}\alpha)$ [mm ^{−1}]	23.611	25.093	25.451
$F(000)$	1824	1824	1824
Data collection			
T/K	293(2)	293(2)	110(2)
Scan mode	ω	ω	ω
hkl Range	$-20 \rightarrow 20$, $-15 \rightarrow 15$, $-10 \rightarrow 10$	$-20 \rightarrow 20$, $-22 \rightarrow 23$, $-5 \rightarrow 5$	$-12 \rightarrow 12$, $-5 \rightarrow 5$, $-40 \rightarrow 41$
Measured refl.	9213	10141	11948
Unique refl.	1715	1381	3016
R_{int}	0.0508	0.0284	0.0350
Refl. used for refinement	1715	1381	3016
Absorption correction	SADABS	SADABS	SADABS
$T_{\text{min}}/T_{\text{max}}$	0.120405	0.175019	0.143309
Refinement			
Refined parameters	150	151	298
$R1, wR2$	0.0354, 0.0829	0.0582, 0.1196	0.0504, 0.1020
$[I > 2\sigma(I)]$	2.870, −1.510	2.703, −1.042	5.651, −2.678

the monoclinic space group $C2/c$ (modification **B**) (Table 1). In this modification, the molecules of **2** have C_2 symmetry (Fig. 2). Examination of the packing diagram reveals the existence of extended stacks that run parallel to one another. Within each stack, the planes defined by the trinuclear mercury cores of the successive molecules are parallel to one another and separated by 3.29 Å. These molecules, which adopt a staggered arrangement, are distinctly offset with respect to one another. As a result, the stacks are tilted and propagate in a direction that makes a tilt angle α of 40.7° with the vector perpendicular to the plane containing the three mercury atoms. This configuration leads to short distances between the mercury center Hg(1) and two of the carbon atoms of neighboring molecules

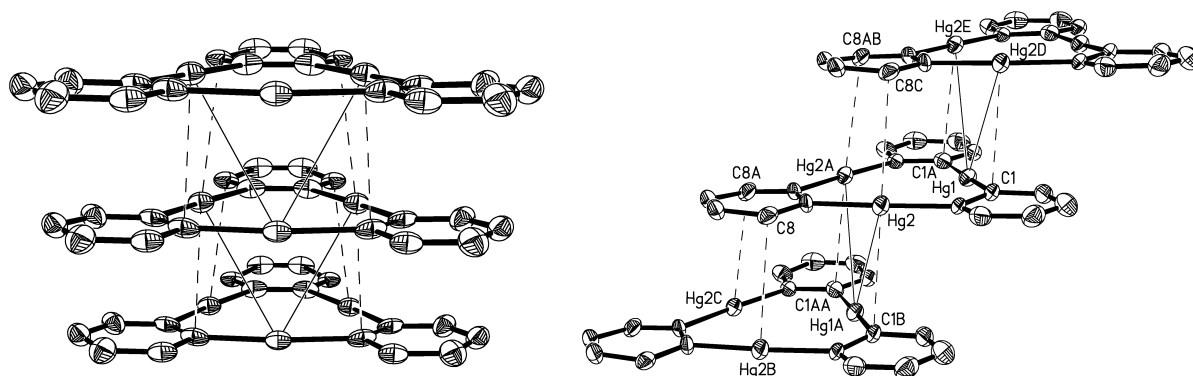


Fig. 3. Portion of the stacks present in modification **C** (30% ellipsoids). Views along two approximately perpendicular directions are provided. The Hg-Hg and Hg-C contacts are represented by thin and dashed lines, respectively. The fluorine atoms are omitted for clarity. Selected intermolecular distances (Å): Hg(2)-C(1B) 3.323, Hg(2)-C(8C) 3.385, Hg(1)-Hg(2E) 3.833.

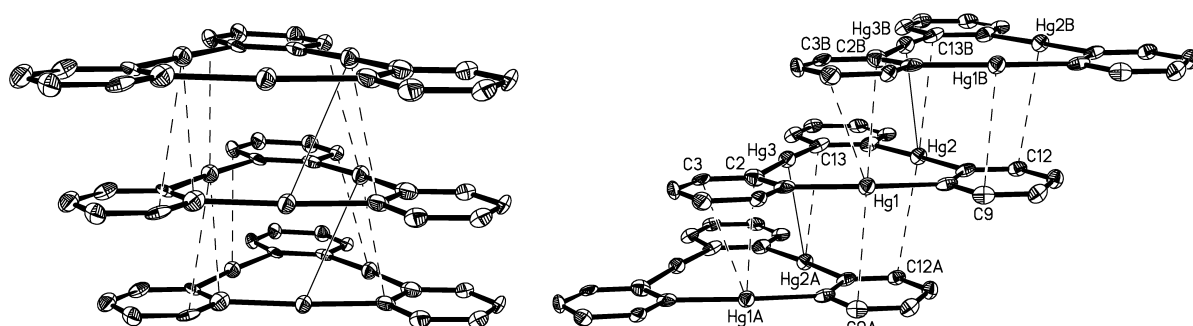


Fig. 4. Portion of the stacks present in modification **D** (30% ellipsoids). Views along two approximately perpendicular directions are provided. The Hg-Hg and Hg-C contacts are represented by thin and dashed lines, respectively. The fluorine atoms are omitted for clarity. Selected intermolecular distances (Å): Hg(1)-C(2B) 3.276, Hg(1)-C(3B) 3.449, Hg(1)-C(9A) 3.332, Hg(2)-C(12A) 3.385, Hg(2)-C(13B) 3.343, Hg(3)-Hg(2A) 3.564.

(Hg(1)-C(1B) 3.385 Å, Hg(1)-C(6B) 3.462 Å) (Fig. 2). The crystals which display a needle morphology belong to the orthorhombic space group $Pnma$ (modification **C**) (Table 1). The molecules of **2** have mirror symmetry and form extended stacks that retain the mirror symmetry (Fig. 3). These stacks also propagate parallel to one another. As in modification **B**, the molecules are offset so that the resulting stacks are tilted as indicated by the value of α which is equal to 45.9° . The planes defined by the trinuclear mercury cores of the neighboring molecules of **2** are once again parallel to one another with an inter-plane separation of 3.35 Å. Unlike in modification **B**, the successive molecules are eclipsed rather than staggered. As a result, one of the phenylene rings of a molecule of **2** sits directly over the center of a neighboring molecule of **1**. This arrangement leads to close intermolecular Hg-C distances (Hg(2)-C(1B) 3.323 Å, Hg(2)-C(8C) 3.385 Å) and results in Hg-Hg distances of 3.83 Å

between Hg(1) and two symmetry equivalent Hg(2) atoms of a neighboring molecule of **2**. A fourth crystalline form (modification **D**) has been obtained by recrystallization of **1** from CH_2Cl_2 solutions containing a small amount of 1,3,5-triisopropylbenzene (Table 1). The resulting crystals form thick needles and belong to the monoclinic space group $P2_1/n$ with one molecule of **2** in the asymmetric unit (Fig. 4). Examination of the packing diagram reveals the existence of stacks that are very similar to those found in form **C** (tilt angle $\alpha = 44.6^\circ$). Unlike in modification **C**, however, the stacks do not have mirror symmetry as a result of a sideways slippage of the molecules as depicted in Fig. 4. This arrangement leads to the formation of short intermolecular Hg-C distances (Hg(1)-C(2B) 3.276 Å, Hg(1)-C(3B) 3.449 Å, Hg(1)-C(9A) 3.332 Å, Hg(2)-C(12A) 3.385 Å, Hg(2)-C(13B) 3.343 Å). In addition Hg(3) and Hg(2A) are separated by only 3.564 Å. In all four modifications, the molecules of **2** display es-

essentially the same structure. Each mercury atom has an approximately linear geometry with an average C-Hg-C angle of 175° and there are no unusual Hg-C distances (av 2.07 Å).

Discussion

In modifications **A–D**, there are short contacts between the mercury centers of **2** and the carbon atoms of a neighboring molecule of **2**. These contacts range from 3.276 to 3.462 Å and are within the sum of the van der Waals radii of mercury (1.7–2.0 Å) [15, 16], and carbon in an aromatic system (1.7 Å) [17]. They indicate the presence of secondary Hg- π interactions occurring between the phenylene ring and the acidic mercury centers. Similar distances have been previously observed in adducts involving **2** and various arenes including benzene and naphthalene [9, 11]. Within each stack, the mean plane of the molecules are separated by 3.3–3.4 Å. This separation is essentially identical to that found in any π -stacked assemblies and appears to be in agreement with the involvement of van der Waals interactions. In addition, a short intermolecular Hg-Hg contact of 3.564 Å is found in form **D**. This Hg-Hg distance is similar to that observed in the structure of [2- μ_3 -acetone] which forms dimers held by mercuriophilic interactions of 3.512 Å [18b]. Also, it only slightly exceeds the Hg-Hg distance calculated by Pyykkö for the dimer of dimethyl mercury (3.41 Å) [15]. The Hg-Hg distances found in form **A** and **C** range from 3.811–4.093 Å and are therefore at the upper limit for the involvement of strong metal-philic interactions. Out of the four modifications thus far characterized, modification **B–D** displays stacks in which the juxtaposed molecules are offset. Since the electrostatic potential map of **2** shows that the center of the molecule is positively charged with an accumulation of negative charge at the periphery [19], it appears reasonable to invoke the participation of electrostatic interactions which would be maximized in these offset geometries.

Conclusion

Compound **2** displays a rich crystal polymorphism. While more modifications may still be discovered, the existence of these four forms suggests that there is little preference for directional interactions. Instead, the molecules of **2** appear to be able to glide somewhat freely with respect to one another. This feature indicates the preponderance of non-directional interactions such as van der Waals interactions between these molecules which are largely aromatic and whose overall polarizability is magnified by relativistic effects at the mercury(II) centers.

Experimental Section

Compound **2** was prepared by following the published procedure [3]. All solvents used were purchased from Aldrich and used as received. The modifications **B** and **C** were obtained by sublimation of **2** at 280 °C under vacuum (10^{-1} torr). Modification **D** was obtained upon slow evaporation of a solution containing **2** (20 mg), triisopropylbenzene (0.5 ml), in CH_2Cl_2 (5 ml). X-ray data were collected on a Bruker SMART-CCD diffractometer using graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å). Specimens of suitable size and quality were selected and glued onto a glass fiber with freshly prepared epoxy resin. The structures were solved by direct methods, which successfully located the mercury atoms. Subsequent refinements on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining carbon and fluorine atoms. Further crystallographic details can be found in Table 1. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC-247303 - 247305. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

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