

Trimeric Perfluoro-*ortho*-phenylenemercury: A Versatile Lewis Acidic Host

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Abstract: Trimeric perfluoro-*ortho*-phenylenemercury (**1**) constitutes one of the simplest trifunctional Lewis acidic hosts. In addition to cooperative effects arising from the proximity of the mercury(II) centers, the electron-withdrawing properties of the backbone and the accessibility of the electrophilic sites lead to the facile complexation of neutral and electron rich substrates. The planarity of the structure as well as its overall polarizability compounded with relativistic effects at mercury also permits the occurrence of non-covalent interactions and accounts for the tendency of this compound to form cofacial dimers. Collectively, the Lewis acidic properties of **1** as well as its ability to engage in non-covalent interactions can be held responsible for its ability to form extended binary supramolecular stacks with arenes. The photoluminescence observed in some of these supramolecular complexes corresponds to the phosphorescence of the aromatic substrate and indicate the occurrence of a mercury heavy atom effect.

Keywords: Lewis acids • mercury • metallophilicity • pi interactions • supramolecular chemistry

Introduction

For several decades, the field of supramolecular chemistry has been dominated by studies dealing with multidentate Lewis bases. More recently, the lack of receptors capable of complexing both neutral and anionic electron-rich substrates led to the emergence of polydentate Lewis acids.^[1] Typically, such derivatives are comprised of several electrophilic main-

group element moieties linked by organic or inorganic backbones. Polyfunctional organomercurials constitute one of the most developed classes of polydentate Lewis acids. In addition to being air and water stable, the unsaturated mercury(II) centers of these derivatives exhibit appreciable Lewis acidity in a direction perpendicular to the primary bonds. Taking advantage of these properties, several polydentate organomercurial species have been constructed and have now emerged as useful Lewis acidic hosts^[2-5] and catalysts.^[6-8] Most of the compounds used as anion receptors are macrocyclic species. These include tri- and tetranuclear mercuracarborands developed by Hawthorne^[2] as well as a series of fluorinated species investigated by the group of Shur.^[3, 4] In this collection of species, trimeric perfluoro-*ortho*-phenylenemercury ($[(o-C_6F_4Hg)_3]$, **1**) stands out as a unique tridentate Lewis acid. The nature of the metal, the planarity of the structure, the electron-withdrawing properties of the backbone, as well as the proximity and accessibility of the mercury(II) centers make for a distinctive set of chemical properties, which will be showcased in this Concept article.

Synthesis

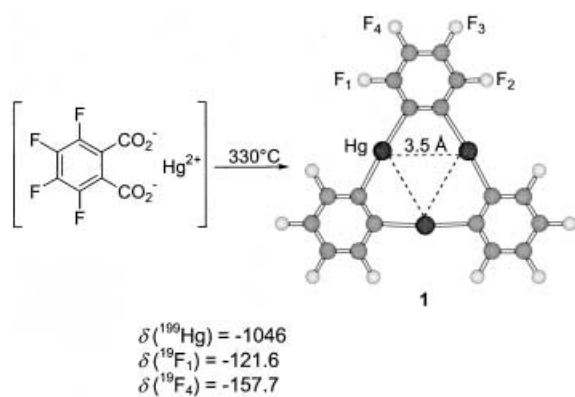
The synthesis of this compound was reported several decades ago and involves the decarboxylation of the tetrafluorophthalatemercury salt (Scheme 1).^[9] The molecule possesses three mercury(II) centers located at approximately 3.5 Å from one another thus forming an equilateral triangle. The ¹⁹⁹Hg and ¹⁹F NMR-active nuclei can be used as spectroscopic handles to monitor its chemistry (Scheme 1).^[10]

Cooperative Effects and Lewis Acidic Properties

In addition to cooperative effects arising from the proximity of the mercury(II) centers, the electron-withdrawing properties of the backbone and the accessibility of the mercury centers convey unusual Lewis acidic properties to the molecule.^[11] The importance of this electronic effect is nicely illustrated by the relative halophilicity of **1** and that of its non-fluorinated analogue trimeric *ortho*-phenylenemercury ($[(o-C_6H_4Hg)_3]$).^[12] As shown by Shur, while both molecules interact with halide ions in solution, the lability of the complex formed by $[(o-C_6H_4Hg)_3]$ impedes their isolation and

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NMR coupling constant in Hz in 1				
	F ₂	F ₃	F ₄	Hg
F ₁	18.5	3.5	27	393
F ₂		23	3.5	19
F ₃			15	103
F ₄				19

Scheme 1. Synthesis of **1**; ^{19}F and ^{199}H NMR spectroscopic features in CH_2D_2 (CFCl_3 and Me_2Hg external reference).

structural characterization.^[13] With **1**, however, a number of anionic complexes including bromide, iodide, and thiocyanate salts have been isolated.^[13–15] These anionic complexes adopt multidecker structures with the anions sandwiched between successive molecules of **1** (Figure 1). As a result of this

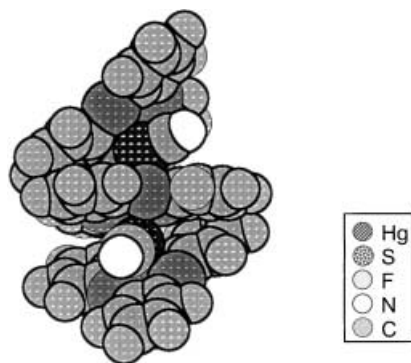


Figure 1. Space-filling model of a portion of the polymeric structure of $[\mathbf{1} \cdot \text{SCN}]^-$.^[15]

structure, the anion interacts with all neighboring mercury centers and is, therefore, hexacoordinate. It is worth noting that ESI mass spectrometric studies carried out in collaboration with Russell suggest the gas-phase formation of stable 2:1 complexes in which the halide, that is, fluoride, chloride, bromide, or iodide, is sandwiched by two molecules of **1** (Figure 2).^[16] While these 2:1 complexes have not been detected in solution, Chistyakov and co-workers have predicted their existence on the basis of quantum chemical calculations.^[4a] We also note that Hawthorne has isolated discrete sandwich species in which a halide anion is octahedrally coordinated to the mercury centers of two mercuracarborand-3 receptors.^[17] Related double-decker anionic sandwich complexes involving two molecules of **1** and a *closo*-borane such as $[\text{B}_{10}\text{H}_{10}]^{2-}$ or $[\text{B}_{12}\text{H}_{12}]^{2-}$ have been recently isolated and structurally characterized.^[3] In this case the dianionic guests form multiple B-H-Hg bridges with the mercury centers of **1**.

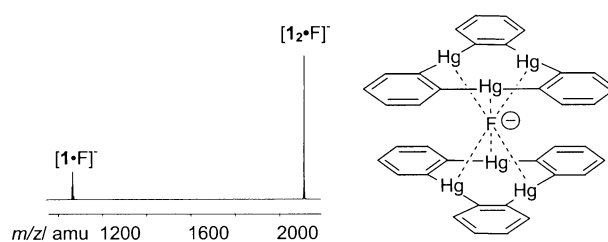


Figure 2. Left: ESI MS-MS spectra of the bridged fluoride complex $[\mathbf{1}_2 \cdot \text{F}]^-$ observed at m/z 2118.8. Right: putative structure of the $[\mathbf{1}_2 \cdot \text{F}]^-$; phenylene F atoms omitted.^[16]

The Lewis acidic properties of this derivative are also substantiated by its propensity to form adducts with neutral electron-rich substrates. While this chemical trait was brought to light several decades ago by Massey,^[18] the structural characterization of some of these adducts has only been recently achieved. As shown by the structures of the HMPA, DMSO, DMF, ethyl acetate, and acetonitrile adducts,^[10, 19, 20] complex **1** is able to coordinate two molecules of the donor above and below the plane formed by the three mercury atoms. In the case of the DMSO and ethyl acetate adducts, a third molecule of the organic substrate binds to one of the mercury centers in a terminal fashion. In all adducts, the three mercury centers of **1** cooperatively interact with the electron-rich terminus of the triply bridging organic substrates. The formation of adducts is not limited to the cases of sulfoxides, formamides, and nitriles; rather it also includes less basic substrates such as ketones and aldehydes.^[21] For example, we found that the crystallization of **1** from pure acetaldehyde leads to the formation of the 1:1 complex $[\mathbf{1} \cdot \mu_3\text{-(CH}_3\text{COH)}]$ in which the three mercury centers of **1** cooperatively interact with the oxygen atom of the organic carbonyl (Figure 3).^[22]

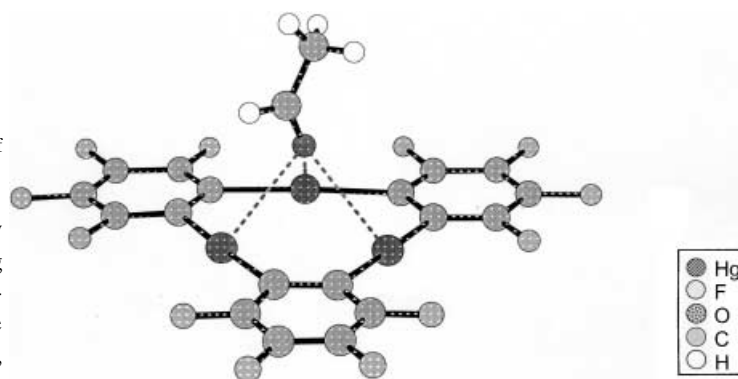


Figure 3. Molecular structure of $[\mathbf{1} \cdot \mu_3\text{-acetaldehyde}]$ showing the triple coordination of the carbonyl oxygen atom.^[22]

The resulting Hg–O distances range from 2.912(13) to 2.965(8) Å and are within the sum of the van der Waals radii for oxygen ($r_{\text{vdw}} = 1.54$ Å)^[23] and mercury ($r_{\text{vdw}} = 1.73$ –2.00 Å),^[24, 25] thus indicating the presence of a donor interaction. A similar conclusion can be reached by inspecting the IR spectrum of this adduct, which reveals a weakened carbonyl stretching vibration ($\nu_{\text{CO}} = 1706$ vs 1726 cm^{-1} in pure acetaldehyde). Related structures are also observed with ketones including acetone and benzophenone.^[22, 26]

Non-covalent interactions

Although it is sometimes difficult to differentiate between the occurrence of covalent and non-covalent interactions, the formation of adducts involving **1** and both neutral and anionic electron-rich substrates apparently results from weak dative bonds. Such bonds have often been observed in the chemistry of organomercury compounds and are typically referred to as secondary interactions. Yet, in several other instances, the structural chemistry of **1** points to the existence of non-covalent interactions. We were able to isolate crystals of pure **1** by slow evaporation of a CS₂ solution.^[27] Analysis of the crystals reveals the formation of staggered cofacial dimers in which the monomeric units are spaced by only 3.38 Å (Figure 4). This arrangement places the monomeric units in close contact and results in intermolecular Hg⋯C distances

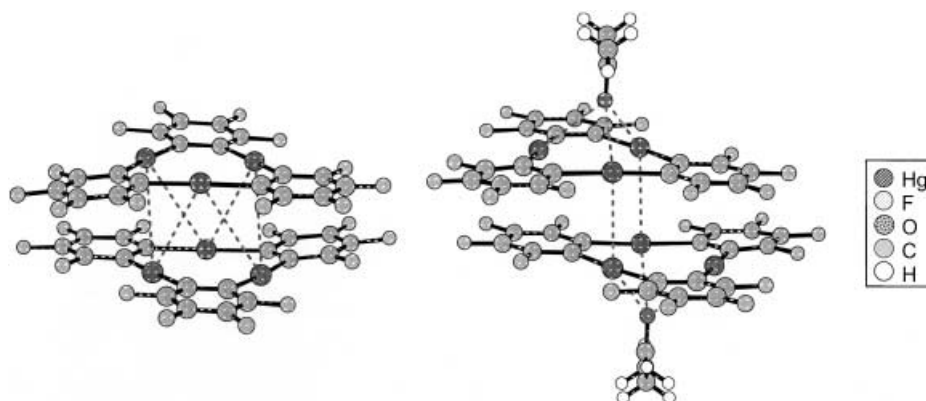


Figure 4. View of the cofacial dimers formed in the structure of **1** and [**1** · μ₃-acetone].^[26, 27]

of 3.443–3.650 Å and Hg⋯Hg distances of 3.811–4.093 Å. While the Hg⋯C distances might reflect the formation of polyhapto-π interactions, 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 atoms. Hence, other interactions are probably responsible for the observed arrangement. In particular, it appears acceptable to invoke the participation of dispersion forces between these largely aromatic molecules. Moreover, relativistic effects at mercury cause a contraction of the s and p orbitals followed by an increased shielding of the nuclear charge. As a result, the d electrons and especially the 5d¹⁰ shell experience a greater radial extension accompanied by an increase in polarizability.^[28] This effect, which also permits the occurrence of metallophilic interactions,^[29] contributes to the general polarizability of **1** thereby adding to its ability to engage in dispersion interactions. Further evidence for this type of effect has been observed in the structure of the acetone adduct [**1** · μ₃-((CH₃)₂CO)], which also forms

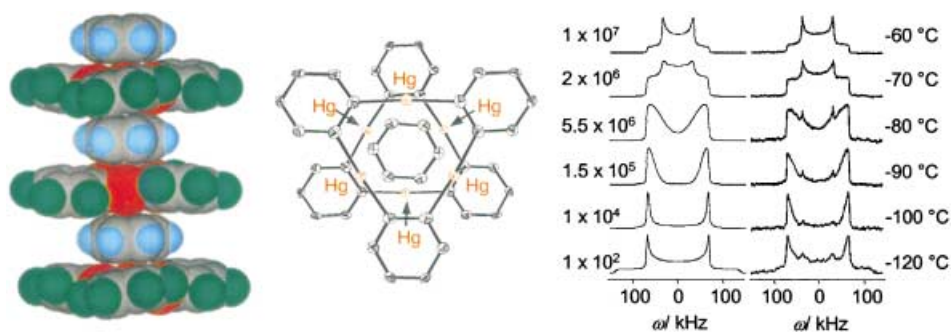


Figure 5. Left: Side and top view of a portion of a stack in the structure of [**1** · C₆H₆]; F and H atoms are omitted from top view.^[39] Right: simulated and observed ²H NMR line shapes of [**1** · C₆D₆]. Color code: Hg, red; C, grey; F, green; H, light blue.

cofacial dimers (Figure 4). In this case, however, the parallel trinuclear mercury units are separated by 3.46 Å from one another and adopt an offset arrangement. Both components are held by mercuriphilic interactions of 3.51 Å, which is only slightly larger than the mercuriphilic interaction distance calculated for the perpendicular (HgMe₂)₂ dimer.^[25] As demonstrated by Fackler, metallophilic interactions are also responsible for the formation of supramolecules involving **1** and trinuclear gold complexes.^[30]

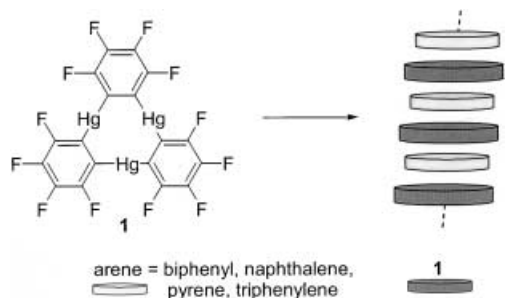
Complexation of arenes

Arene mercurations constitute a common set of reactions. They follow an electrophilic substitution mechanism and substantiate the strong interactions that can occur between Hg^{II} ions and aromatic substrates. This chemical characteristic is supported by the isolation and structural characterization of arene–mercury π-complexes involving either Hg^{I[31]} and Hg^{II} ions.^[32–35] In these complexes, the arene is typically η²-coordinated to the mercury center through Hg–C_{arene} bonds ranging from 2.3 to 2.7 Å. Weaker interactions are observed between aromatic substrates and the mercury center of neutral organomercurial derivatives. With Hg–C_{arene} distances in the range of 3 to 3.4 Å, these interactions are inherently weak^[36] and occur mainly in an intramolecular fashion.^[37] However, recent reports indicate that unsupported examples of such complexes can be isolated in the case of fluorinated organomercurials.^[38]

We found that compound **1** crystallizes from benzene to afford [**1** · C₆H₆].^[39] This adduct is very stable and can be kept for months at room temperature. It starts losing benzene at 70 °C as shown by TGA. X-ray analysis reveals the formation of extended stacks that consist of nearly parallel, yet staggered molecules of **1** that sandwich benzene molecules (Figure 5). These stacks are rather compact (centroid distance of 3.24 Å) so that secondary π-interactions occur between the

benzene molecule and the mercury centers. Each of the six C–C bonds of the benzene molecule interacts with one of the six mercury centers of the two juxtaposed molecules of **1**. The resulting Hg–C_{benzene} distances of 3.408 and 3.457 Å are within the sum of the van der Waals radius of mercury ($r_{\text{vdw}} = 1.73 - 2.00$ Å)^[24, 25] and that usually accepted for carbon in aromatic system ($r_{\text{vdw}} = 1.7$ Å).^[40] As a result, the benzene is hexacoordinated in a $\mu_6\text{-}\eta^2:\eta^2:\eta^2:\eta^2:\eta^2:\eta^2$ fashion. In an effort to account for the Lewis acid character of **1**, we have proposed that the cohesion of this supramolecule results from the donation of electrons from the benzene π -orbitals into sets of empty 6p orbitals of the mercury atoms. To further probe the nature of the interactions present in this supramolecule, we have measured and analyzed the static solid-state wide-line deuterium NMR spectrum of [**1**·C₆D₆] at different temperatures. As shown by the spectra (Figure 5), the line shape already features some distortion arising from molecular reorientation at -120°C . Line narrowing occurs at higher temperature indicating that the guest molecule enters the intermediate motional regime. These spectra could be satisfactorily simulated on the basis of an in-plane 60° reorientation of the benzene guest and yielded, after an Arrhenius analysis, an activation energy of 52 ± 4 kJ mol⁻¹. To our knowledge, this is the highest activation energy measured for the in-plane 60° reorientation of an enclathrated or complexed benzene molecule.^[41–44] In turn, this observation suggests the presence of directional interactions between the mercury atoms of **1** and the benzene molecules.

In a continuation of these studies, we extended our investigations to larger aromatic substrates such as biphenyl, naphthalene, pyrene, and triphenylene and found that these arenes readily form binary adducts with **1** in CH₂Cl₂ (Scheme 2).^[27, 45] In all cases, the 1:1 stoichiometry of the



Scheme 2. Formation of binary stacks by interaction of **1** with arenes.

resulting adducts has been confirmed by elemental analysis as well as X-ray structural studies (Figures 6 and 7). The solid state structure of these compounds consists of extended stacks in which eclipsed molecules of **1** alternate with the aromatic substrate. While the orientation of the arene with respect to the mercury centers of **1** appears random, it is important to note the presence of short Hg–C_{arene} contacts which range from 3.25 to 3.55 Å. As in [**1**·C₆H₆], these contacts possibly reflect the presence of secondary polyhapto- π interactions occurring between the electron-rich aromatic molecules and the acidic mercury centers. These interactions, including those observed in [**1**·C₆H₆], must, however, be relatively weak as no

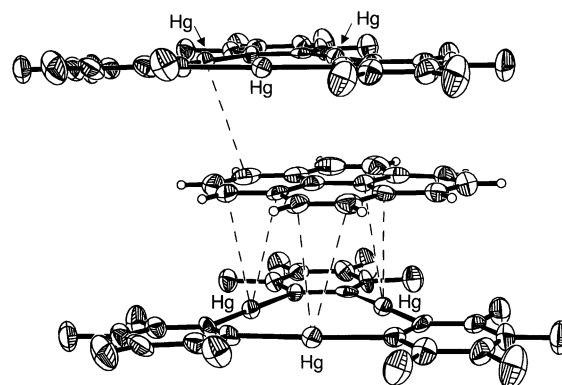


Figure 6. Portion of a stack observed in the structure of [**1**·pyrene] showing the short contacts between the carbon atoms and the mercury centers.^[45]

lengthening could be detected in the C–C bonds of the aromatic molecule. Hence, both electrostatic and dispersion forces probably contribute to the cohesion of these assemblies.

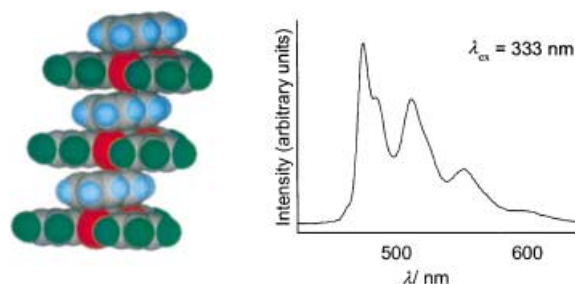


Figure 7. Left: Space-filling models of the binary stacks observed in the structures of [**1**·naphthalene]. Right: emission spectrum for [**1**·naphthalene] recorded at room temperature.^[27] Color code: Hg, red; C, grey; F, green, H, light blue.

The biphenyl, naphthalene, pyrene, and triphenylene compounds display an intense room temperature photoluminescence in the visible part of the spectrum.^[27, 45] As shown by their emission spectra, the energy of the bands present in the luminescence spectrum correspond very closely to that expected for the $T_1 \rightarrow S_0$ phosphorescence of the aromatic substrates (Figure 7). While the excitation mechanism remains to be elucidated, these observations indicate the occurrence of a mercury heavy-atom effect, which promotes population of the T_1 state of the aromatic derivative. Time-resolved measurements obtained in collaboration with Omary indicate excited state lifetimes ranging from 0.3 to 1 ms depending on the temperature of the measurement. These excited state lifetimes are longer than those typically measured for singlet excited state lifetimes, adding further support to the triplet nature of the emitting state. They are, however, shorter than those reported for the monomer phosphorescence of the free arenes (0.7, 2.3, and 4.4 s for pyrene, naphthalene, and biphenyl in frozen glasses, respectively); this substantiates the strong mercury heavy atom effect that makes the $T_1 \rightarrow S_0$ phosphorescence transition a more allowed transition.

Conclusion

In conclusion, trimeric perfluoro-*ortho*-phenylene mercury constitutes a remarkably versatile derivative that can serve as a tridentate Lewis acid. While the complexation of anions and basic organic substrates has been previously investigated, we have been able to show that **1** has an affinity for weakly coordinating organic substrates, such as aldehydes and ketones. Our work also points to the propensity of this trinuclear derivative to engage in non-covalent interactions including mercuriphilic interactions and dispersion interactions. The combination of these properties possibly accounts for the rich supramolecular chemistry that **1** exhibits with aromatic substrates. It is noteworthy that no thermodynamic data accounting for the stability of the complexes is currently available. Current efforts in our laboratory center on the incorporation **1** in sensors and light emitting materials.

Acknowledgement

The donors of the American Chemical Society Petroleum Research Fund (Grant ACS PRF# 38143 -AC 3) and The National Science Foundation (Grant CAREER CHE-0094264) are gratefully acknowledged for supporting the investigations carried out in our laboratory.

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