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Complexation of Methylparathion and Bis(2-hydroxyethyl)sulfide by the Tridentate Lewis Acid $[(o\text{-}C_6F_4Hg)_3]$

Mitsukimi Tsunoda and François P. Gabbaï

Department of Chemistry, Texas A&M University, College Station, Texas 77843

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ABSTRACT: *The interaction of trimeric perfluoro-ortho-phenylene mercury (**1**) with bis(2-hydroxyethyl)sulfide ($S((CH_2)_2OH)_2$) in dichloromethane and methylparathion ($SP(OMe)_2(p\text{-}C_6H_4NO_2)$) in 1,2-dichloroethane leads to the crystallization of [**1** $\cdot$ ($S((CH_2)_2OH)_2$)] and [**1** $\cdot$ (μ_3-$SP(OMe)_2(p\text{-}C_6H_4\text{-}NO_2))_2$], respectively. These two adducts have been characterized by elemental analysis and single crystal X-ray diffraction. The structure of [**1** $\cdot$ $S((CH_2)_2OH)_2$] shows that the bis(2-hydroxyethyl)sulfide molecule interacts with the mercury centers of **1** by formation of a Hg–S interaction of 3.138(4) Å. Association of the two components is further strengthened by the coordination of one of the oxygen atoms of the bis(2-hydroxyethyl)sulfide molecule. This oxygen atom interacts simultaneously with three mercury centers of **1** with Hg–O distances ranging from 2.889(8) to 3.142(9) Å. In the lattice, molecules of [**1** $\cdot$ ($S((CH_2)_2OH)_2$)] associate with compact cofacial dimers with Hg–Hg metallophilic contacts of 3.794 Å and 4.076 Å. The structure of [**1** $\cdot$ (μ_3-$SP(OMe)_2(p\text{-}C_6H_4NO_2))_2$] is that of a 2:1 complex in which two molecules of methylparathion are triply coordinated via their sulfur atom to the mercury centers of **1** on either side of the molecular plane. The Hg–S contacts fall within the range of 3.278 and 3.651 Å.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:292–297, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20125

INTRODUCTION

Polyfunctional organomercurials constitute a remarkable class of Lewis acidic hosts which have been widely investigated in the domain of molecular recognition [1–7] and catalysis [8–10]. Fluorinated polyfunctional organomercurials such as pentameric perfluoroisopropylidenemercury [11], trimeric perfluoro-*ortho*-phenylene mercury ($[(o\text{-}C_6F_4Hg)_3]$, **1**),[5,6,12] and 1,2-bis(chloromercurio)tetrafluorobenzene [13–18] have attracted a great deal of attention because the electron withdrawing capacity of the fluorinated ligands leads to an increase in the Lewis acidity of the mercury centers. The trinuclear derivative **1** is one of the most studied examples of fluorinated polyfunctional organomercurials. It has been extensively employed for the complexation of anions and serves as a receptor for neutral organic substrates such as carbonyls [19–22], nitriles [23,24], sulfoxide [21], and aromatic substrates [25–28]. Recently, we also reported the formation of [**1** $\cdot$ μ_6-$Me_2S]_n$, a polymeric dimethyl sulfide adduct in which the sulfur is concomitantly coordinated to six mercury atoms provided by neighboring molecules of **1** [29]. Because of the possible use of polyfunctional Lewis acids as molecular recognition units for harmful sulfur-containing compounds, we have decided to study the interaction of **1** with

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Correspondence to: François P. Gabbaï; e-mail: francois@tamu.edu.

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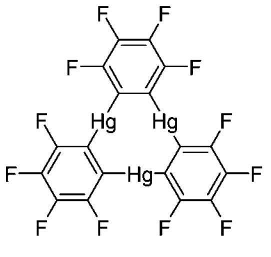
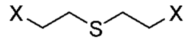
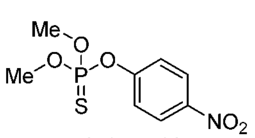
methylparathion, an acetylcholinesterase inhibitor, and bis(2-hydroxyethyl)sulfide, a structural surrogate for the blistering agent mustard gas.



1



X = OH, bis(2-hydroxyethyl)sulfide
X = Cl, mustard gas



methylparathion

EXPERIMENTAL SECTION

General Considerations

Great caution should be exercised when handling **1** *and methylparathion!* Because of the toxicity of the compounds, all experiments were carried out in a fume hood. The elemental analyses were performed by Atlantic Microlab (Norcross, GA). The infrared spectra were recorded as KBr pellets or nujol mulls on a Mattson Genesis series FTIR. The luminescence spectra were recorded with a SLM/AMINCO, model 8100 spectrofluorimeter equipped with a xenon lamp. Low-temperature measurements were made in a cryogenic device of local design. The samples were attached to the holder with collodion powder. The solvents were from EMD (Merck), and chemicals were purchased from Aldrich Chemical and used as received. The methyl parathion was a gift from AS Cheminova (80% technical grade) and used as received. Compound **1** was prepared according to the published procedure [12].

Single-Crystal X-ray Analysis

X-ray data was collected on a Bruker Smart 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å) at 50 kV, 40 mA. For each sample, a crystal of suitable size and quality was selected and mounted on a glass fiber with Apiezon grease. The structure was solved by direct methods that allowed for the location of the heavy atoms. Subsequent refinement on F^2 using the SHELXTL/PC version 5.1 (Bruker) located the remaining non-hydrogen atoms. Further crystallographic details can be found in the Table 1. CCDC 261406 and 261407 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Synthesis of $[\mathbf{1}\cdot(S((CH_2)_2OH)_2)]$

Compound **1** (80.0 mg, 76 μmol) was combined with an excess of bis(2-hydroxyethyl)sulfide (20.0 mg, 163 μmol) in dichloromethane (5.0 mL) at room temperature. Slow evaporation of the reaction mixture over 1 week at room temperature yielded a crop of clear colorless crystals of $[\mathbf{1}\cdot(S((CH_2)_2OH)_2)]$ (62.0 mg, 53 μmol, 69% yield). The use of an excess of bis(2-hydroxyethyl)sulfide led to higher yield of the adduct. Analytical data: calculated for $C_{22}H_{10}O_2F_{12}Hg_3S$: C, 22.62%; H, 0.86%. Found: C, 23.12%; H, 0.81%.

Synthesis of $[\mathbf{1}\cdot(\mu_3\text{-}SP(OMe)_2(p\text{-}C_6H_4NO_2))_2]$

Compound **1** (44.1 mg, 42 μmol) was combined with methylparathion (64.2 mg, 258 μmol) in 1,2-dichloroethane (4.0 mL) at room temperature. The mixture was allowed to evaporate at room temperature to about half the initial volume and then cooled, yielding clear colorless crystals of $[\mathbf{1}\cdot(\mu_3\text{-methylparathion})_2]$ (30.0 mg, 19.5 μmol, 46% yield). The crystals are stable at room temperature. Analytical data: calculated for $C_{34}H_{20}F_{12}Hg_3N_2O_{10}P_2S_2$: C, 25.98%; H, 1.28%; N, 1.78%. Found: C, 26.35%; H, 1.23%; N, 1.85%.

RESULTS AND DISCUSSION

Interaction of **1** with Bis(2-hydroxyethyl)sulfide

The addition of bis(2-hydroxyethyl)sulfide to a saturated solution of **1** in dichloromethane led to the slow crystallization of the adduct $[\mathbf{1}\cdot(S((CH_2)_2OH)_2)]$ which could be isolated in 69% yield. This adduct is stable at room temperature and loses the sulfide at 100°C as indicated by TGA analysis. It crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell (Table 1). The molecule of bis(2-hydroxyethyl)sulfide is tightly bound to the molecule of **1** by multiple contacts (Fig. 1). The Hg(2)—S distance of 3.138(4) Å is well within the sum of the van der Waals radii for sulfur ($r_{\text{vdw}} = 2.03$ Å) [30] and mercury ($r_{\text{vdw}} = 1.73$–2.00 Å) [31,32] and indicates the presence of a donor/acceptor interaction between these two atoms. This Hg—S distance is shorter than those observed in $[\mathbf{1}\cdot\mu_6\text{-}Me_2S]_n$ (3.543(7) and 3.571(3) Å) which probably results from the terminal rather than μ_6-bridging coordination of the sulfur center [29]. Further examination of the structure of $[\mathbf{1}\cdot S((CH_2)_2OH)_2]$ indicates

TABLE 1 Crystal Data, Data Collection, and Structure Refinement for [**1** · $(S((CH_2)_2OH)_2)$] and [**1** · $(\mu_3\text{-}SP(OMe)_2(p\text{-}C_6H_4NO_2))_2$]

Crystal data	[**1** · $(S((CH_2)_2OH)_2)$]	[**1** · $(\mu_3\text{-}SP(OMe)_2(p\text{-}C_6H_4NO_2))_2$]
Formula	$C_{22}H_{10}F_{12}Hg_3O_2S$	$C_{34}H_{20}F_{12}Hg_3N_2O_{10}P_2S_2$
M_r	1168.13	1572.37
Crystal size (mm^3)	0.23 × 0.20 × 0.12	0.22 × 0.12 × 0.11
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	10.120(2)	10.6245(9)
b (Å)	12.894(3)	11.0307(9)
c (Å)	19.840(4)	21.1700(17)
β(°)	97.76(3)	81.31.50(10)
V (Å^3)	2565.2(9)	2135.9(3)
Z	4	2
ρ_{calc} (g cm^{-3})	3.025	2.445
μ (Mo $K\alpha$) (mm^{-1})	18.100	11.037
F(000) (e)	2088	1456
Data Collection		
T (K)	293(2)	293(2)
Scan mode	ω	ω
hkl range	$-11 \rightarrow 11, -14 \rightarrow 14, -22 \rightarrow 22$	$-12 \rightarrow 12, -12 \rightarrow 12, -22 \rightarrow 24$
Measured reflections	22,172	12,557
Unique reflections, (R_{in})	4035 [0.0329]	6662 [0.0246]
Reflections used for refinement	4035	6662
Absorption correction	SADABS	SADABS
T_{min}/T_{max}	0.52	0.63
Refinement		
Refined parameters	365	586
$R1^a$, $wR2^b$ [$I>2\sigma(I)$]	0.0404, 0.0907	0.0418, 0.1022
ρ_{fin} (max/min) (eÅ^{-3})	1.726 and −1.154	2.645 and −0.959

[a] $R1 = \Sigma(F_o - F_c)/\Sigma F_o$.

[b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.04$, $b = 35$ for [**1** · $(S((CH_2)_2OH)_2)$]; $a = 0.065$; $b = 4$ for [**1** · $(\mu_3\text{-}SP(OMe)_2(p\text{-}C_6H_4NO_2))_2$].

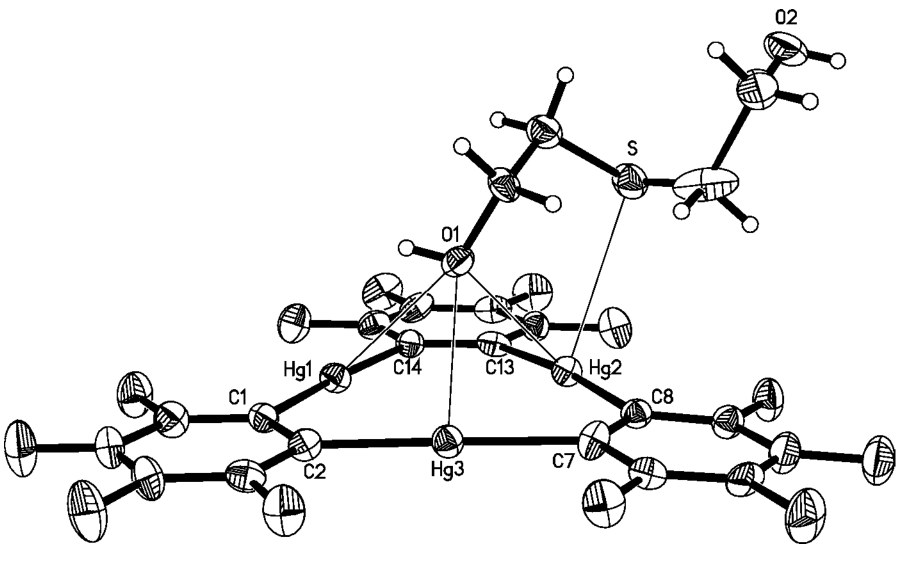


FIGURE 1 ORTEP view of [**1** · $(S((CH_2)_2OH)_2)$] (20% ellipsoids). Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)–C(1) 2.081(12), Hg(1)–C(14) 2.084(12), Hg(2)–C(8) 2.088(12), Hg(2)–C(13) 2.094(12), Hg(3)–C(2) 2.070(13), Hg(3)–C(7) 2.110(12), Hg(1)–O(1) 3.142(9), Hg(2)–O(1) 2.889(8), Hg(3)–O(1) 2.950(8), Hg(2)–S 3.138(4); C(1)–Hg(1)–C(14) 175.0(5), C(8)–Hg(2)–C(13) 173.3(5), C(2)–Hg(3)–C(7) 175.7(5), Hg(2)–O(1)–Hg(3) 76.21(19), Hg(2)–O(1)–Hg(1) 74.08(19), Hg(3)–O(1)–Hg(1) 73.05(18), O(1)–Hg(2)–S 66.64(18).

the simultaneous coordination of one of the oxygen atoms of the substrate to the mercury centers of **1**. The resulting Hg—O distances fall within the narrow range of 2.889(8)–3.142(9) Å. As a result, the oxygen atom is approximately equidistant from the three Lewis acidic sites and sits at 2.133 Å from the plane defined by the three mercury atoms. The Hg—O bond distances in $[\mathbf{1}\cdot(S((CH_2)_2OH)_2)]$ are within the sum of the van der Waals radii for oxygen ($r_{\text{vdw}} = 1.54$ Å) [30] and mercury ($r_{\text{vdw}} = 1.73$–2.00 Å) [31,32] and reflect the presence of secondary Hg—O interactions. These distances are close to those observed in adducts of **1** with organic carbonyls such as $[\mathbf{1}\cdot\mu_3$-acetone] [20]. Finally, the oxygen atom O(2) interacts with the mercury center Hg(1) of a neighboring molecule with which it forms a weak interaction of 3.126 Å.

In the crystal, molecules of $[\mathbf{1}\cdot(S((CH_2)_2OH)_2)]$ associate with compact cofacial dimers with a centroid distance of 3.498 Å (Fig. 2). In these dimers, the molecules of the trinuclear mercury complex adopt a staggered arrangement. It is interesting to note that, as a result of this arrangement, relatively short intramolecular Hg—Hg distances are observed between the mercury atoms (Hg(1)—Hg(2A) 3.794, Hg(1)—Hg(3A) 4.339, and Hg(2)—Hg(3A) 4.076 Å). The Hg(1)—Hg(2A) and Hg(2)—Hg(3A) distances are remarkably similar to those observed in the crystal structure of pure **1** which also adopt a cofacial dimeric structure (3.811 < Hg—Hg < 4.093 Å) [26]. These relatively short distances possibly reflect the presence of weak metallophilic interactions which have often been observed in the structural chemistry of **1** [20,26,27]. As in the case of pure **1** and $[\mathbf{1}\cdot\mu_3$-acetone], compound $[\mathbf{1}\cdot(S((CH_2)_2OH)_2)]$ luminesces. Its emission spectrum features a broad emission band which stretches from 400 to 500 nm with a maximum at 415 nm ($\lambda_{\text{ex}} = 350$).

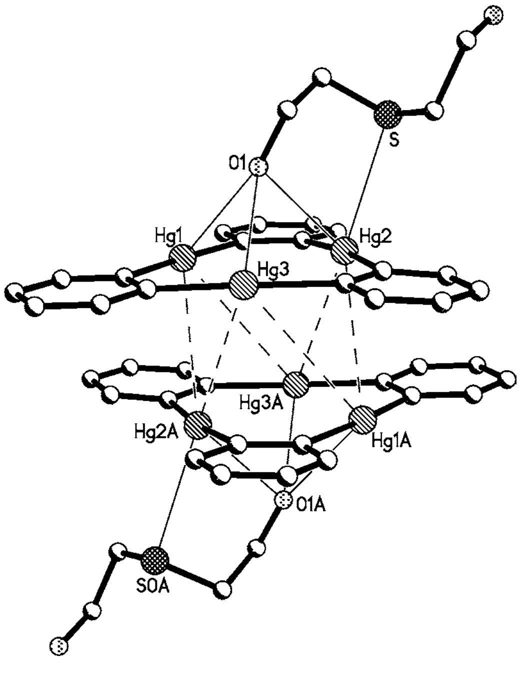


FIGURE 2 Stick and ball view of the cofacial dimers formed in the structure of $[\mathbf{1}\cdot(S((CH_2)_2OH)_2)]$. Hydrogen and fluorine atoms omitted for clarity. Intramolecular Hg–Hg distances (Å): Hg(1)–Hg(2A) 3.794, Hg(1)–Hg(3A) 4.339, Hg(2)–Hg(3A) 4.076.

Interaction of **1** *with Methylparathion*

Slow evaporation of a mixture containing an excess of methylparathion and **1** in 1,2-dichloroethane affords $[\mathbf{1}\cdot(\mu_3\text{-}SP(OMe)_2(p\text{-}C_6H_4NO_2))_2]$ as a crystalline product in 46% isolated yield. This adduct is stable at room temperature, and its composition has been confirmed by elemental analysis. A single-crystal X-ray diffraction study of $[\mathbf{1}\cdot(\mu_3\text{-}SP(OMe)_2(p\text{-}C_6H_4NO_2))_2]$ indicates that the adduct crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell (Table 1, Fig. 3). The structure of **2** is that of a 2:1 complex in which two molecules of methylparathion are triply coordinated to the mercury centers of **1**. The core of this molecule is reminiscent of a spinning-top. It resembles that encountered in other 2:1 adducts involving **1** and various donor ligands such as acetonitrile [23] or acetophenone [19]. The Hg—S contacts fall within the range of 3.278 and 3.651 Å and are also within the sum of the van der Waals radii of the two elements [30–32]. These distances indicate the presence of secondary Hg—S donor/acceptor interactions and are comparable to those observed in $[\mathbf{1}\cdot(\mu_6\text{-}Me_2S)]_n$ [29], $[(\mathbf{1})_2\cdot\text{TTF}]$ [24] or $[\mathbf{1}\cdot\text{SCN}]^-$ [33]. The P=S bonds (P(1)—S(1) 1.899(4), P(2)—S(2) 1.903(5) Å) do not appear significantly elongated when compared to the distance of 1.894 Å measured for pure methylparathion [34]. Finally, we also note the presence of a π-stacking interaction between the p-nitrophenyl ring at C(31) and the tetrafluorophenylene ring at C(7) whose centroids are separated by 3.63 Å.

CONCLUSION

The formation of $[\mathbf{1}\cdot(S((CH_2)_2OH)_2)]$ and $[\mathbf{1}\cdot(\mu_3\text{-}SP(OMe)_2(p\text{-}C_6H_4NO_2))_2]$ reflect the thiophilic character of mercury and suggests that appropriately designed mercury-based metalloreceptors could be used for the molecular recognition of harmful sulfur compounds. However, such a task will necessitate receptors with increased selectivity. In the case of **1**,

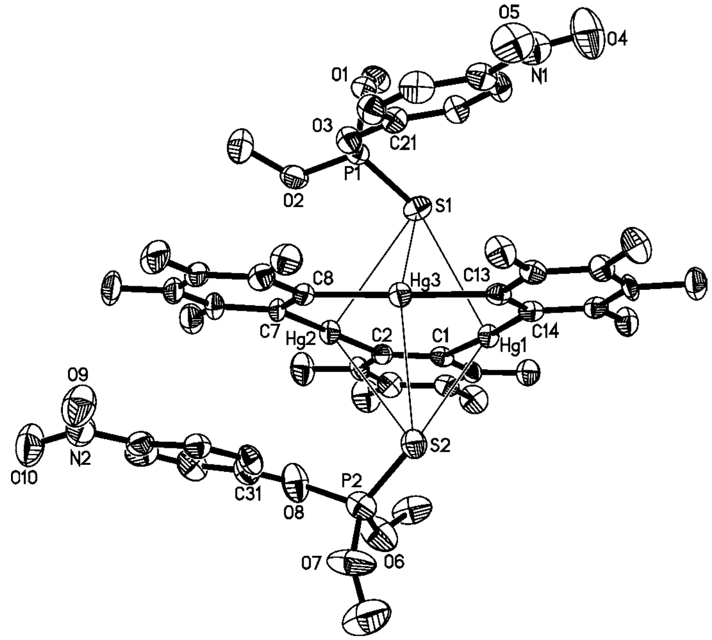


FIGURE 3 ORTEP view of [**1** · (μ_3-SP(OMe)$_2$(p-C$_6$H$_4$NO$_2$))$_2$] (20% ellipsoids). Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)–C(1) 2.077(9), Hg(1)–C(14) 2.066(9), Hg(1)–S(1) 3.278(3), Hg(1)–S(2) 3.375(3), Hg(2)–C(2) 2.062(10), Hg(2)–C(7) 2.064(11), Hg(2)–S(1) 3.428(4), Hg(2)–S(2) 3.651(3), Hg(3)–C(8) 2.061(10), Hg(3)–C(13) 2.075(11), Hg(3)–S(1) 3.398(3), Hg(3)–S(2) 3.410(3), P(1)–S(1) 1.899(4), P(2)–S(2) 1.903(5); C(14)–Hg(1)–C(1) 175.2(4), C(2)–Hg(2)–C(7) 177.0(4), C(8)–Hg(3)–C(13) 175.9(4), P(1)–S(1)–Hg(1) 154.32(18), P(1)–S(1)–Hg(3) 90.55(14), P(1)–S(1)–Hg(2) 97.58(16), P(2)–S(2)–Hg(1) 129.81(18), P(2)–S(2)–Hg(3) 137.71(19), P(2)–S(2)–Hg(2) 90.02(17), Hg(1)–S(1)–Hg(3) 65.34(6), Hg(1)–S(1)–Hg(2) 64.49(6), Hg(3)–S(1)–Hg(2) 63.04(6), Hg(1)–S(2)–Hg(3) 64.18(6), Hg(1)–S(2)–Hg(2) 61.11(6), Hg(3)–S(2)–Hg(2) 60.60(6).

which binds many Lewis basic substrates, the accessibility of the mercury centers and the absence of specific steric requirements around the binding sites are responsible for the lack of selectivity.

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