

## PREPARATION AND X-RAY STRUCTURE OF BIS(PHENYLMERCURIC)OXONIUM TETRAFLUOROBORATE HYDRATE, $[(\text{PhHg})_2\text{OH}][\text{BF}_4] \cdot \text{H}_2\text{O}$

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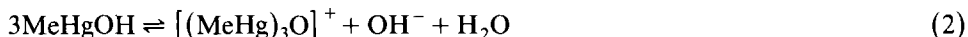
(Received November 13th, 1985)

### Summary

The reaction of  $\text{PhHgOH}$  or  $(\text{PhHg})_2\text{O}$  with strong acids gives  $[(\text{PhHg})_2\text{OH}]^+$ , which has been fully characterised as the  $[\text{BF}_4]^-$  salt. The X-ray structure of  $[(\text{PhHg})_2\text{OH}][\text{BF}_4] \cdot \text{H}_2\text{O}$  shows the cation to have an  $\text{Hg}-\text{O}-\text{Hg}$  angle of  $126^\circ$  and a  $\text{Hg} \cdots \text{Hg}$  distance of 3.639 Å, which precludes an intramolecular  $\text{Hg}-\text{Hg}$  bonding interaction.

### Introduction

Subsequent to the first report of “methyl mercuric hydroxide” by Slotta and Jacobi [1] in 1929, much controversy surrounded this substance, with differing physical properties being attributed to it. The enigma was resolved by Grdenic and Zado [2,3] when they recognised that solid “methyl mercuric hydroxide” does not exist as such, but undergoes ready loss of water to give a mixture of the oxide,  $(\text{MeHg})_2\text{O}$ , and the oxonium hydroxide,  $[(\text{MeHg})_3\text{O}][\text{OH}]$  (eqs. 1,2).



In solutions of “ $\text{MeHgOH}$ ” additional species  $[\text{MeHgOH}_2]^+$  and  $[(\text{MeHg})_2\text{OH}]^+$  are strongly indicated by spectroscopic means in a pH dependent equilibrium [4]; however only the tris(methylmercuric)oxonium cation has been isolated, despite being a minor component at all pH's, because it forms stable salts with a wide variety of anions [2,3,5].

The crystal structures of  $[(\text{MeHg})_3\text{O}][\text{X}]$  ( $\text{X} = \text{ClO}_4^-, \text{NO}_3^-$ ) have been determined, although only brief details have been published [6]. The cation consists of a flattened pyramidal  $\text{Hg}_3\text{O}$  skeleton, with an  $\text{Hg}-\text{O}-\text{Hg}$  angle of  $116^\circ$ , although spectroscopic data in solution indicated a  $D_{3h}$  planar geometry [7]. Related species include the mixed  $[(\text{MeHg})_2\text{O}(\text{HgR})]^+$ , ( $\text{R} = \text{Et}, \text{Pr}, \text{Ph}$ ) [8], and the heavier con-

geners  $[(\text{MeHg})_3\text{S}]^+$  [5–7] and  $[(\text{MeHg})_3\text{Se}]^+$  [9]. The neutral  $(\text{MeHg})_3\text{N}$  is also known [9]. The same oxonium-type structure is also found for the mercuric oxychloride  $[(\text{HgCl}_2)_2 \cdot \text{HgO}]$ , which is better formulated as  $[(\text{ClHg})_3\text{O}]\text{Cl}$  [10].

In contrast to the well studied methyl-mercury system the corresponding aryl-mercury chemistry is relatively undeveloped. Bloodworth [11,12] concluded that the true hydroxide  $\text{PhHgOH}$  exists, and that it can be dehydrated to the oxide  $(\text{PhHg})_2\text{O}$ . No tris(phenylmercuric)oxonium species, analogous to  $[(\text{MeHg})_3\text{O}]^+$  was detected. However Grdenic has shown that “basic phenyl mercuric nitrate”, prepared by reaction of  $\text{Ph}_2\text{Hg}$  with  $\text{Hg}(\text{NO}_3)_2$ , is actually bis(phenylmercuric)oxonium nitrate,  $[(\text{PhHg})_2\text{OH}][\text{NO}_3]$  [6,13].

We report herein our studies on the interconversion of phenyl-mercuric oxygen species, including the full characterisation of  $[(\text{PhHg})_2\text{OH}]^+$  as the hydrated  $[\text{BF}_4]^-$  salt.

## Experimental

$\text{PhHgOH}$  and  $(\text{PhHg})_2\text{O}$  were prepared by Bloodworth's method [11,12], and characterised by m.p., IR spectra and Hg analysis. Infrared spectra were recorded on a Shimadzu IR27G spectrometer, while NMR spectra were run on a JEOL FX90Q machine;  $^{199}\text{Hg}$  NMR shifts are reported relative to  $\text{Me}_2\text{Hg}$ .

### *Reaction of PhHgOH with HBF<sub>4</sub>*

A suspension of  $\text{PhHgOH}$  (0.5 g, 1.7 mmol) in  $\text{H}_2\text{O}$  (20 ml) was treated with  $\text{HBF}_4$  (0.09 ml of a 40% solution, 0.6 mmol). A homogeneous solution resulted. Evaporation under vacuum left a white powder of  $[(\text{PhHg})_2\text{OH}][\text{BF}_4] \cdot \text{H}_2\text{O}$  (0.39 g, 80%), m.p.  $170^\circ\text{C}$  (decomp). Found: C, 21.69; H, 2.20;  $\text{C}_{12}\text{H}_{13}\text{BF}_4\text{Hg}_2\text{O}_2$  calcd.: C, 21.28; H, 1.94%.  $^1\text{H}$  NMR (DMSO)  $\delta$  4.74 (br, s OH), 7.48 (br, m phenyl protons).  $^{199}\text{Hg}$  NMR  $\delta$  (DMSO)  $-1466$  (s);  $\delta$  ( $\text{D}_2\text{O}$ )  $-1495$  (s). IR (KBr disc): 3600 s, 3200s, br, 1660 s, 1580 m, 1480 s, 1430 s, 1295 m, 1050 vs, br, 910 m, 730 s, br, 690 s, 550 s, 515 m, 450 m.

An identical product was also obtained from the reaction of  $(\text{PhHg})_2\text{O}$  or  $\text{PhHgOH}$  with  $\text{HBF}_4$  in acetone.

### *Reaction of (PhHg)<sub>2</sub>O and PhHgCl with TlBF<sub>4</sub>*

A mixture of  $(\text{PhHg})_2\text{O}$  (0.5 g, 0.88 mmol),  $\text{PhHgCl}$  (0.27 g, 0.88 mmol) and  $\text{TlBF}_4$  were refluxed together in acetone for 2 h. The solution was filtered while hot and cooled to deposit white crystals, identified as  $\text{Ph}_2\text{Hg}$  by comparison with an authentic sample.

### *Reaction of (PhHg)<sub>2</sub>O with HNO<sub>3</sub>*

$(\text{PhHg})_2\text{O}$  (0.9 g, 1.58 mmol) in acetone was treated with excess  $\text{HNO}_3$  (1.0 ml, 16 mmol). Evaporation and recrystallisation of the residue from ethanol gave off-white crystals which were identified as “basic phenyl mercuric nitrate” by comparison with published infra-red data [14].

The same product was produced from  $\text{PhHgOH}$  (0.70 g, 2.37 mmol) and  $\text{HNO}_3$  (0.15 ml, 2.4 mmol) in acetone under the same conditions.

TABLE 1  
REFINED ATOM COORDINATES FOR  $[(\text{PhHg})_2\text{OH}][\text{BF}_4] \cdot \text{H}_2\text{O}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Hg(1)	0.8855(1)	0.6433(1)	0.9935(1)
O(1)	0.879(3)	0.75	0.107(4)
C(1)	0.883(3)	0.538(2)	0.890(4)
C(2)	0.801(4)	0.483(3)	0.940(4)
C(3)	0.801(3)	0.412(2)	0.869(5)
C(4)	0.885(3)	0.390(2)	0.741(4)
C(5)	0.962(3)	0.441(2)	0.693(4)
C(6)	0.964(3)	0.518(2)	0.752(4)
B(1)	0.147(5)	0.75	0.738(8)
F(1)	0.074(5)	0.75	0.858(6)
F(2)	0.268(4)	0.75	0.763(5)
F(3)	0.122(3)	0.694(2)	0.639(6)
O(2)	0.413(3)	0.75	0.055(4)

*Crystal structure of  $[(\text{PhHg})_2\text{OH}][\text{BF}_4] \cdot \text{H}_2\text{O}$*

Large colourless diamond-shaped plates were obtained by slow evaporation of an acetone solution. These were partially redissolved to give a more regular, elliptical shape to reduce absorption effects. Crystal parameters and intensity data were collected on an Enraf–Nonius CAD4 diffractometer using Mo- $K_\alpha$  monochromated X-rays ( $\lambda$  0.7107 Å).

*Crystal data.*  $\text{C}_{12}\text{H}_{11}\text{O}_2\text{BF}_4\text{Hg}_2$ ,  $M = 657.2$ . Orthorhombic, space group  $Pnma$ ,  $a$  11.096(4),  $b$  17.048(2),  $c$  8.099(1) Å,  $U$  1532 Å<sup>3</sup>,  $D_m$  2.90,  $D_c$  2.93 g cm<sup>-3</sup> for  $Z = 4$ ,  $F(000) = 1200$ ,  $\mu(\text{Mo-}K_\alpha)$  205 cm<sup>-1</sup>,  $T$  23°C.

A total of 1245 unique reflections in the range  $0^\circ < \theta < 28^\circ$  were collected by  $\omega$ - $2\theta$  scans. After data reduction and correction for absorption (based on azimuthal scans, maximum and minimum transmission factors 0.99 and 0.90 respectively) 718 had  $I > 2\sigma(I)$  and were used in all calculations.

The structure was solved in  $Pn2_1a$  by a combination of direct and Patterson methods to give the mercury atom positions. Remaining non-hydrogen atoms,

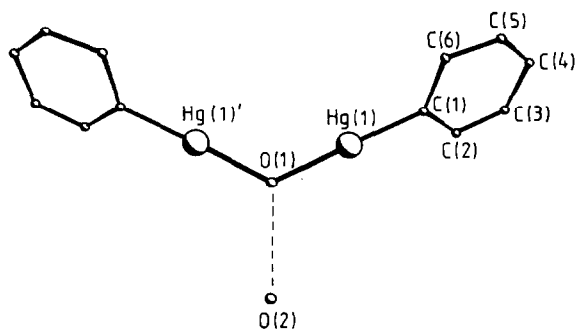


Fig. 1. A view of the hydrated  $[(\text{PhHg})_2\text{OH}]^+$  cation showing atom labelling; hydrogen atoms are not shown. Bond parameters include Hg(1)–C(1) 1.98 Å, Hg(1)–O(1) 2.04 Å, O(1)⋯O(2) 2.77 Å; Hg(1)–O(1)–Hg(1) 126°.

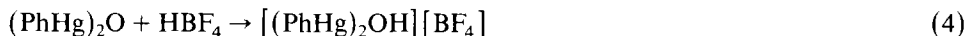
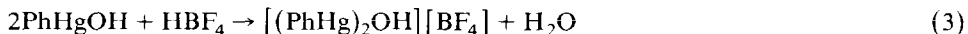
including the O of the unanticipated H<sub>2</sub>O of solvation, were located in subsequent difference maps. The mirror symmetry of both ions suggested the higher symmetry space group and subsequent convergence of the full-matrix least squares refinement in *Pnma* with anisotropic temperature factors for Hg and F atoms, and isotropic treatment for other atoms, gave  $R = 0.058$ ,  $R_w = 0.062$ . Hydrogen atoms were not included, since they did not appear in a final difference map. All calculations were performed with SHELX76 [15].

Final atomic coordinates are given in Table 1, while Fig. 1 illustrates the cation and gives the main bond parameters. Full lists of bond lengths and angles, temperature factors, and structure factors are available from the authors.

## Discussion

The preparation of PhHgOH is straightforward, as previous workers have shown [11,12]. Bloodworth [11] concluded on the basis of thermogravimetric methods that it existed as a true hydroxide, rather than as a [(PhHg)<sub>3</sub>O]<sup>+</sup> hydroxide analogous to that found for the methyl-mercury system. We note however that it would not be possible to distinguish between PhHgOH and a [(PhHg)<sub>2</sub>OH][OH] formulation on the basis of the analytical data, and it has been noted by Green [14] that the infra-red spectrum of PhHgOH has more bands (possibly four) in the Hg–O stretching region than expected for the simple hydroxide. This can be explained in terms of an oxonium-type structure, or in terms of a polymeric structure involving bridging OH groups. We would favour the latter rationalisation, since the infra-red spectrum of the [(PhHg)<sub>2</sub>OH]<sup>+</sup> cation, as the [BF<sub>4</sub>]<sup>−</sup> or [NO<sub>3</sub>]<sup>−</sup> salts, (vide infra) is quite different in the 650 to 500 cm<sup>−1</sup> region to that of PhHgOH; furthermore the <sup>199</sup>Hg NMR spectrum of PhHgOH in CH<sub>2</sub>Cl<sub>2</sub> shows a single peak at  $\delta -806$  which is characteristic of a simple PhHgX species in solution [16]. Similarly (PhHg)<sub>2</sub>O gives a single resonance under the same conditions at  $\delta -756$  ppm, whereas [(PhHg)<sub>2</sub>OH]<sup>+</sup> gives a resonance at  $\delta -1495$  ppm.

The addition of aqueous HBF<sub>4</sub> to PhHgOH gave a product shown to be [(PhHg)<sub>2</sub>OH]<sup>+</sup>; there was no indication of a tris-mercuric-oxonium cation analogous to that found in the methyl system. Under a variety of conditions of stoichiometry and solvent the bis-oxonium appeared to be the only product on acidification of either PhHgOH or (PhHg)<sub>2</sub>O (eqs. 3,4).



The [(PhHg)<sub>2</sub>OH]<sup>+</sup> cation has been previously identified as the [NO<sub>3</sub>]<sup>−</sup> salt from the reaction of Ph<sub>2</sub>Hg with Hg(NO<sub>3</sub>)<sub>2</sub> [6,13]; not surprisingly a more logical synthesis involving PhHgOH or (PhHg)<sub>2</sub>O with HNO<sub>3</sub> gives this nitrate in high yield.

An alternative route to a tris complex by stoichiometric reaction of (PhHg)<sub>2</sub>O, PhHgCl and TIBF<sub>4</sub> gave Ph<sub>2</sub>Hg as the only isolable organometallic product via a complicated symmetrisation reaction.

It was not apparent from the infra-red spectra of [(PhHg)<sub>2</sub>OH][BF<sub>4</sub>] and [(PhHg)<sub>2</sub>OH][NO<sub>3</sub>] (see Experimental) that they contained the same cation so a full X-ray crystal structure of the former was carried out. Crystals of [(PhHg)<sub>2</sub>OH]·[BF<sub>4</sub>]<sup>−</sup>·H<sub>2</sub>O contain discrete [BF<sub>4</sub>]<sup>−</sup> ions and hydrated cations [(PhHg)<sub>2</sub>OH·H<sub>2</sub>O]<sup>+</sup>

(see Fig. 1). The hydrogen atoms of the oxonium cation were not located directly but are required for neutrality. The cation lies on a crystallographic mirror plane through O(1) and O(2), and contains planar PhHg fragments with a dihedral angle between the plane of the phenyl ring and the plane defined by Hg(1)O(1)Hg(1)' of 45°, indicating little steric interaction between the adjacent phenyl rings. The Hg(1)–O(1)–Hg(1)' angle of 126° in [(PhHg)<sub>2</sub>OH][BF<sub>4</sub>]·H<sub>2</sub>O is slightly less than the 130° found for the corresponding nitrate [6] (possibly because of the hydration of the former) and the Hg···Hg distance is 3.639 Å. While this is probably within the sum of the Van der Waals' radii of the mercury atoms there is no indication in any of the parameters of an attractive interaction between the Hg atoms in [(PhHg)<sub>2</sub>OH]<sup>+</sup>. This is also true for the [(MeHg)<sub>2</sub>O]<sup>+</sup> cation [6]. It is interesting to contrast this with the [(Ph<sub>3</sub>PAu)<sub>3</sub>O]<sup>+</sup> ion where short Au···Au distances (3.03–3.21 Å) and compressed Au–O–Au angles (103°) clearly point to Au–Au attraction between adjacent, formally non-bonded atoms [17]. Similar features are found in a number of related gold species. There is obviously a major difference in the long-distance bonding tendencies for the superficially isolobal PhHg<sup>+</sup> and Ph<sub>3</sub>PAu<sup>+</sup> moieties.

The spectroscopic properties of [(PhHg)<sub>2</sub>OH][BF<sub>4</sub>] are given in the Experimental section. The main area of interest in the infra-red spectrum is between 700 and 400 cm<sup>-1</sup> where bands assignable to Hg–O stretches and/or O–H deformation can be seen. Unfortunately part of this region is obscured by the 540 cm<sup>-1</sup> band of the [BF<sub>4</sub>]<sup>-</sup> ion, but from comparisons with the spectrum of the nitrate it seems that a relatively simple pattern is characteristic of the bis(phenylmercuric)oxonium species; certainly there are fewer bands than for PhHgOH.

The <sup>199</sup>Hg NMR spectrum of [(PhHg)<sub>2</sub>OH][BF<sub>4</sub>]·H<sub>2</sub>O in DMSO or in acidified water gives only single resonances at δ –1467 or –1495 ppm respectively. This strongly indicates that the bis-oxonium structure observed in the solid is maintained in solution since resonances near δ –800 ppm would be expected if there was any dissociation to PhHgOH or (PhHg)<sub>2</sub>O.

It is clear that the [(PhHg)<sub>2</sub>OH]<sup>+</sup> cation is the favoured species in equilibria involving the phenylmercuric group, and that it can be isolated with a number of counter-ions, in contrast to the methylmercuric system where the tris compound is the only oxonium complex which has so far been crystallised.

### Acknowledgments

We thank the NZ Universities Grants Committee for financial support, Dr. C. Rickard of the University of Auckland for collection of X-ray data, and Mr. R. Thomson for recording NMR spectra. We are also grateful to Professor D. Grdenic for providing unpublished information concerning [(PhHg)<sub>2</sub>OH][NO<sub>3</sub>].

### References

- 1 K.H. Slotta and K.R. Jacobi, *J. Prakt. Chem.*, 120 (1929) 249.
- 2 D. Grdenic and F. Zado, *Croat. Chem. Acta*, 29 (1957) 425.
- 3 D. Grdenic and F. Zado, *J. Chem. Soc.*, (1962) 521.
- 4 D.L. Rabenstein, *Acc. Chem. Res.*, 11 (1978) 100, and refs. therein; D.L. Rabenstein, C.A. Evans, M.C. Tourangeau and M.T. Fairhurst, *Anal. Chem.*, 47 (1975) 338.
- 5 D. Grdenic and B. Markusic, *J. Chem. Soc.*, (1958) 2434.

- 6 D. Grdenic and B. Kamenar, *Acta Cryst.*, 34A (1978) S127.
- 7 J.H.R. Clarke and L.A. Woodward, *Spectrochim. Acta*, 23A (1967) 2077.
- 8 W. Thiel, F. Weller, J. Lorbeth and K. Dehnicke, *Z. Anorg. Allgem. Chem.*, 381 (1971) 57.
- 9 D. Breitingner and W. Morell, *Inorg. Nucl. Chem. Letters*, 10 (1974) 409.
- 10 A. Weiss, G. Nagorsen and A. Weiss, *Z. Anorg. Allgem. Chem.*, 274 (1953) 152; K. Aurivillius, *Acta Chimica Scand.*, 8 (1954) 523.
- 11 A.J. Bloodworth, *J. Organomet. Chem.*, 23 (1970) 27.
- 12 A.J. Bloodworth, *J. Chem. Soc. (C)*, (1970) 2051.
- 13 D. Grdenic, personal communication.
- 14 J.H.S. Green, *Spectrochim. Acta*, 24A (1968) 863.
- 15 SHELX76-Program for Crystal Structure Determination, G. Sheldrick, University of Cambridge, 1976.
- 16 *NMR and The Periodic Table*, R.K. Harris and B.E. Mann (Eds.), Academic Press, London, 1978.
- 17 A.N. Nesmayanov, E.G. Perevalova, Yu.T. Struchkov, M.Y. Antipin, K.I. Grandberg and V.P. Dyadchenko, *J. Organomet. Chem.*, 201 (1980) 343.