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Characterisation of the first authenticated organo-mercury hydroxide,

4-Me$_2$NC$_6$H$_4$HgOH.

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Synopsis

4-Me$_2$NC$_6$H$_4$HgOH has been characterised spectroscopically and crystallographically as a true organomercury hydroxide.

Abstract.

4-Me$_2$NC$_6$H$_4$HgOH was prepared from 4-Me$_2$NC$_6$H$_4$HgOAc. Full characterisation showed that it crystallises as discrete molecules, the first example of a true organomercury hydroxide in the solid state. The structures of 4-Me$_2$NC$_6$H$_4$HgOAc and (4-Me$_2$NC$_6$H$_4$)$_2$Hg are also discussed.

1. Introduction.

Despite their apparent simplicity, the chemistry of organomercury hydroxides, RHgOH, has a complicated history. Slotta and Jacobi first reported "methyl mercuric hydroxide" in 1929. [1] However subsequent investigations gave wildly differing physical properties with melting points ranging from 95-137°C for apparently the same compound. Grdenic and Zado resolved this system when they concluded that "MeHgOH" does not exist as a discrete compound, but is better formulated as an oxonium species [(MeHg)$_3$O]OH. [2] This salt has mp 88°C, and is readily dehydrated to the oxide (MeHg)$_2$O which has mp 137°C.

The [(MeHg)$_3$O]$^+$ oxonium cation can form stable salts with a variety of anions and has been structurally characterised in the solid state as the [ClO$_4$]$^-$ and [NO$_3$]$^-$ salts [3,4]. These show a flattened trigonal pyramidal structure with Hg-O-Hg angles of 116°.

In aqueous solution, spectroscopic studies [5] show that "MeHgOH" is involved in a pH-dependent equilibrium to give species [MeHgOH$_2$]$^+$, [(MeHg)$_2$OH]$^+$ and [(MeHg)$_3$O]$^+$. Only the last of these has been isolated and characterised as a crystalline species, despite being a minor component in solution.

Related onium cations are also established for the heavier chalcogenides, namely [(MeHg)$_3$S]$^+$, [(MeHg)$_3$Se]$^+$ and also for the halogen species [(ClHg)$_3$O]$^+$ [6-8].

While the methyl-mercury system has been well-studied because of the implications in bio-methylation of mercury in aqueous environments, the corresponding aryl-mercury chemistry is under-developed, with little crystallographic data. Bloodworth reported a supposedly true hydroxide "PhHgOH" which underwent dehydration to a

stable oxide (PhHg)$_2$O [9]. However an infrared spectroscopic study by Green suggested that the compound of empirical formula PhHgOH was more complicated than the simple stoichiometry would indicate since there were three IR bands which were assigned to Hg-O stretches, inconsistent with isolated simple molecules [11]. A more recent EXAFS study suggested that the material is better formulated as [(PhHg)$_2$OH]OH, containing the bis-mercury oxonium cation [(PhHg)$_2$OH]$^+$. This particular cation has been structurally characterised as the [BF$_4$]$^-$ and [NO$_3$]$^-$ salts [12,13], which show an Hg-O-Hg angle of 125°C. The same bis-oxonium cation has also been implicated in a variety of "basic phenyl mercury" salts, [PhHgOH.PhHgX] [X = NO$_3^-$, BF$_4^-$, 0.5(CO$_3^{2-}$), 0.5(SO$_4^{2-}$)] [11]. Although the tris-mercury oxonium species [(PhHg)$_3$O]$^+$ has been shown to exist in aqueous solution by electrospray mass spectrometry (ESMS) [11], no solid compounds incorporating this cation have yet been characterised.

The reason for the tendency for RHg$^+$ groups to aggregate about the oxygen centre to form bis- and tris-oxonium species is not clear; there are no apparent Hg...Hg intramolecular metallophilic attractions in these Hg(II) species corresponding to the well-established aurophilic interactions that account for the formation of analogous Au(I) oxonium cations such as [(Ph$_3$PAu)$_3$O]$^+$ [14].

The study of the phenyl-mercury hydroxides and oxides has been limited by the tendency for the compounds to form powders or very thin crystals unsuitable for X-ray diffraction studies, and by the absence of clear spectroscopic characteristics. We have therefore now examined the corresponding chemistry of the aryl mercury compounds formed by the 4-Me$_2$NC$_6$H$_4$Hg- moiety. This was chosen because the Me$_2$N- group is readily protonated allowing neutral, as well as cationic, species to be detected by

electrospray mass spectrometry; this concept of using "electrospray friendly" ligands has been succesfully utilised in other areas [15].

2. Experimental Section

2.1 General

Electrospray mass spectra were recorded on a VG Platform II spectrometer, operated as detailed elsewhere [16]. Assignments were confirmed by simulation of the characteristic isotope patterns using the ISOTOPE program [17]. The peaks reported are the most intense in the isotopic envelope. NMR were obtained on a Bruker AC300 instrument operating under standard conditions, with ^{199}Hg shifts referenced to PhHgOAc in dmso at 816 ppm [18].   IR spectra were recorded on a Digilab FTS-40 instrument; only the peaks 1000-400 cm^{-1} are listed in the experimental section since this is the diagnostic region. DSC was performed on a Perkin-Elmer DSC 6 instrument.

2.2.1 Preparation of 4-Me$_2$NC$_6$H$_4$HgOAc (1).

N,N-dimethylaniline (12.7 mL, 12.1 g, 0.100 mol) was added to a stirred slurry of mercury(II) acetate (31.9 g, 0.100 mol) in EtOH (150 mL). The mixture was stirred overnight and the insoluble crude product was collected by filtration. This solid was recrystallised from hot acetone to give colourless needles. The supernatant was concentrated and stored at -20°C to give a second crop of crystals, combined yield of 4-Me$_2$NC$_6$H$_4$HgOAc was 28.5 g, 75%. Mp, from acetone, 155°C (lit. [19,20], from ethanol, 165°C); Found: C 31.76, H 3.38, N 3.58%; C$_{10}$H$_{13}$NO$_2$Hg requires C 31.62, H 3.45, N 3.67%; NMR (CDCl$_3$): ^{1}H δ 2.08 (s, CC*H*$_3$), 2.95 (s, NC*H*$_3$), 7.12, 6.69 (two d, J 8.8 Hz, H$_{aryl}$); ^{13}C δ 23.5 (C*C*H$_3$), 40.3 (N*C*H$_3$), 113.0 (C3, ^{3}J$_{C\text{-}Hg}$ 212 Hz), 128.5 (C1), 136.8 (C2, ^{2}J$_{C\text{-}Hg}$ 142 Hz), 151.0 (C4), 177.5 (*C*=O); ^{199}Hg δ 930. ESMS (MeOH, HPF$_6$) m/z 382

$[M+H]^+$. IR (KBr, cm^{-1}) 945m, 926m, 803vs, 794sh, 752w, 690s, 650w, 614w, 570w, 509m, 476w.

*2.2.2 Preparation of 4-Me$_2$NC$_6$H$_4$HgCl (**2**).*

4-Me$_2$NC$_6$H$_4$HgOAc was dissolved in hot acetone and treated with excess of a saturated aqueous solution of LiCl. After the solution was stirred for a few minutes, the resulting solid was collected by filtration and air-dried to give a quantitative yield of 4-Me$_2$NC$_6$H$_4$HgCl. Mp 219-222°C, dec (lit. [20,21] 223-5°C, dec); Found: C 25.59, H 2.64, N 3.67%; C$_8$H$_{10}$NClHg requires C 26.97, H 2.82, N 3.93%; NMR (dmso-d^6): ^{1}H δ 2.87 (s, NCH$_3$), 7.23, 6.67 (two d, J 7.8 Hz, H$_{aryl}$); ^{13}C δ 40.5 (NCH$_3$), 113.0 (C3), 137.4 (C2), 150.7 (C4) (C1 not observed); ^{199}Hg insufficient solubility. ESMS (MeOH) m/z 358 $[M+H]^+$. IR (KBr, cm^{-1}) 943m, 805vs, 752w, 702w, 572w, 515m.

*2.2.3 Preparation of 4-Me$_2$NC$_6$H$_4$HgOH (**3**).*

An aqueous solution of NaOH (8%, 7.5 mL) was added to a slurry of 4-Me$_2$NC$_6$H$_4$HgOAc (1.90 g, 5 mmol) in MeOH (2 mL) and the mixture was heated under reflux for 30-60 min. After cooling, the crude product was collected by filtration. This solid was recrystallised from boiling water to give colourless needles of 4-Me$_2$NC$_6$H$_4$HgOH, 50-60% yield. Mp 177-182°C (with rapid heating, *c.f.* lit. [19] 152-156°C or 180°C); Found: C 28.53, H 3.35, N 4.00%; C$_8$H$_{11}$NOHg requires C 28.44, H 3.28, N 4.14%; NMR (CDCl$_3$): ^{1}H δ 1.6-2.1 (broad, OH), 2.98 (s, NCH$_3$), 7.18, 6.67 (two d, J 8.0 Hz, H$_{aryl}$); ^{13}C δ 40.3 (NCH$_3$), 112.8 (C3, ^{3}J$_{C-Hg}$ 142 Hz), 137.8 (C2, ^{2}J$_{C-Hg}$ 125 Hz), 151.1 (C4), (C1 not observed); ^{199}Hg δ 1140 (CDCl$_3$), 1044 (dmso-d^6). ESMS (MeOH/H+) m/z 340 $[M+H]^+$; 659 [(RHg)$_2$O + H]$^+$; 978 [(RHg)$_3$O]$^+$; ESMS

(MeOH/NaOH) m/z 362 [M+Na]$^+$; 394 [M+Na+MeOH]$^+$. IR (KBr, cm^{-1}) 3552 (ν_{O-H}), 944m, 886m (δ_{M-O-H}), 804vs, 753w, 707w, 528s (ν_{Hg-O}), 515s, 473w.

2.2.4 Preparation of (4-Me$_2$NC$_6$H$_4$Hg)$_2$O (4).

A small sample of 4-Me$_2$NC$_6$H$_4$HgOH was powdered and then heated to 120°C at 1 mm Hg for 4-5 h. The residue was dissolved in dichloromethane and diethyl ether was allowed to slowly diffuse, to give very fine crystals which were collected by filtration and air-dried to give (4-Me$_2$NC$_6$H$_4$Hg)$_2$O. Mp >230°C; Found: C 29.37, H 3.23, N 4.10%; C$_{16}$H$_{20}$N$_2$OHg$_2$ requires C 29.23, H 3.07, N 4.25%; NMR (dmso-d^6): ^{1}H δ 2.85 (s, NCH_3), 7.17, 6.67 (two d, J 7.8 Hz, H$_{aryl}$); ^{13}C δ 40.4 (NCH$_3$), 113.1 (C3), 137.7 (C2), 150.7 (C4) (C1 not observed); ^{199}Hg δ 1000. IR (KBr, cm^{-1}) 945m, 797vs, 752w, 708w, 667sh, 647s ($\nu_{Hg-O-Hg}$), 570w, 515m, 451w.

2.2.5 Preparation of (4-Me$_2$NC$_6$H$_4$)$_2$Hg (5).

A small sample of 4-Me$_2$NC$_6$H$_4$HgOH was dissolved in hot acetone and the solution was boiled, evaporating the solvent, until the solution turned yellow. Upon slow cooling to room temperature a few straw-coloured crystals of (4-Me$_2$NC$_6$H$_4$)$_2$Hg formed. Mp 163-165°C (lit. [19, 22] 167-168°C); Found: C 43.49, H 4.62, N 6.34%; C$_{16}$H$_{20}$N$_2$Hg requires C 43.58, H 4.58, N 6.35%; NMR (CDCl$_3$): ^{1}H δ 3.00 (s, NCH_3), 7.35, 6.88 (two d, J 8.2 Hz, H$_{aryl}$); ^{13}C δ 40.5 (NCH$_3$), 113.1 (C3, ^{3}J$_{C-Hg}$ 103 Hz), 138.2 (C2, ^{2}J$_{C-Hg}$ 95 Hz), 150.4 (C4), 158.7 (C1). ESMS (MeOH) m/z 443 [M+H]$^+$. IR (KBr, cm^{-1}) 945s, 816m, 799vs, 752w, 707w, 520m, 477w

2.3 X-ray crystallography

X-ray intensity data were collected on a Siemens SMART CCD diffractometer using standard procedures and software. Empirical absorption corrections were applied

(SADABS [23]). Structures were solved by direct methods and developed and refined on F^2 using the SHELX programmes [24]. Hydrogen atoms were included in calculated positions

2.3.1 Structure of Me₂NC₆H₄HgOAc

Colourless needle crystals of **1** were obtained from warm acetone.

Crystal data: $C_{10}H_{13}NO_2Hg$, M = 379.80, triclinic, space group P-1, a = 9.771(13), b = 9.630(13), c = 13.733(20) Å, α = 84.28(4), β = 69.02(5), γ = 62.84(4)°, U 1070(2) Å³, T 168 K, Z = 4, D_{calc} = 2.357 g cm⁻³, μ(Mo-K$_α$) = 14.35 mm⁻¹, F(000) = 704; 6732 reflections collected with 2° < θ < 26.5°, 4031 unique (R_{int} 0.0346) used after correction for absorption ($T_{max,\ min}$ 0.328, 0.0307). Crystal dimensions 0.80 x 0.15 x 0.10 mm³. Refinement on F^2 gave R_1 0.0440 [I > 2σ (I)] and wR_2 0.1134 (all data). The structure of **1** is illustrated in Figure 1, with selected bond parameters included in the caption to the figure.

2.3.1 Structure of Me₂NC₆H₄HgOH

Colourless needle crystals of **3** were obtained from hot water.

Crystal data: $C_8H_{11}NOHg$, M = 337.77, monoclinic, space group P2₁/c, a = 6.272(2), b = 6.962(3), c = 19.001(7) Å, β = 99.463(4)°, U 818.4(5) Å³, T 158 K, Z = 4, D_{calc} = 2.741 g cm⁻³, μ(Mo-K$_α$) = 18.74 mm⁻¹, F(000) 616; 8389 reflections collected with 2° < θ < 26°, 1463 unique (R_{int} 0.0474) used after correction for absorption ($T_{max,\ min}$ 0.454, 0.048). Crystal dimensions 0.41 x 0.30 x 0.05 mm³. Refinement on F^2 gave R_1 0.0514 [I > 2σ (I)] and wR_2 0.1387 (all data), GoF 1.047. A number of residual peaks (±4-5 e Å⁻³) close to the Hg atom probably reflect the difficulty of carrying out a reliable absorption correction

on a thin crystal with a high μ value. The structure of **3** is illustrated in Figure 2, with

selected bond parameters included in the caption to the figure.

2.3.3 Structure of (Me₂NC₆H₄)₂Hg

Colourless needle crystals of **5** were obtained from warm acetone.

Crystal data: $C_{16}H_{20}N_2Hg$, M = 440.93, triclinic, space group P-1, a = 11.5095(2), b =

11.8614(3), c = 12.2134(3) Å, α = 112.69(1), β = 97.91(1), γ = 97.64(1)°, U 1491.77(6)

Å^3, T 150 K, Z = 4, D_{calc} = 1.963 g cm^{-3}, μ(Mo-K$_\alpha$) = 10.31 mm^{-1}, F(000) = 840; 13353

reflections collected with 2° < θ < 25.5°, 5459 unique (R_{int} 0.0411) used after correction

for absorption ($T_{max, min}$ 0.739, 0.462). Crystal dimensions 0.42 x 0.10 x 0.02 mm^3.

Refinement on F^2 gave R_1 0.0338 [I > 2σ (I)] and wR_2 0.0758 (all data), GoF 0.997. The

structure of **5** is illustrated in Figure 3, with selected bond parameters included in the

caption to the figure.

3 Results and discussion

3.1 Syntheses and spectroscopy.

The compounds discussed here have all been reported in earlier literature, though

details are not readily accessible in some cases. They were all readily prepared using

standard routes. Scheme 1 summarises the reactions carried out.

The starting material was 4-Me₂NC₆H₄HgOAc (**1**) which was obtained in good

yield by direct mercuration of dimethylaniline [20, 21], a reaction that apparently was

first carried out by Pesci in 1893 [25]. The acetate was characterised by elemental

analysis, ^{1}H, ^{13}C and ^{199}Hg NMR spectroscopy, all of which were unremarkable. The

electrospray mass spectrum of the acetate **1** gave the expected [M+H]$^+$ ion at m/z 382

when run in acidified MeOH or H₂O. Other peaks in the spectrum can be assigned to

species arising from displacement of the acetate, such as m/z 354 [R*Hg(MeOH)]$^+$, m/z 673 [(R*Hg)$_2$OMe]$^+$, and 701 [(R*Hg)$_2$OAc]$^+$. When water was present a weak peak at m/z 978 [(R*Hg)$_3$O]$^+$ was occasionally observed. (R* = Me$_2$NC$_6$H$_4$-).

The corresponding chloride **2** was prepared from the acetate **1** by metathesis with LiCl in acetone. NMR spectra were difficult to obtain because of the low solubility, but sufficient dissolved in MeOH for ESMS which showed an ion at m/z 358 corresponding to [M+H]$^+$. This illustrates the usefulness of the electrospray-friendly Me$_2$N- group which allows chemical ionisation for detection by ESMS.

Conversion of the acetate **1** to the hydroxide **3** was by adaptation of Bloodworth's route to PhHgOH [9]. This gave the product as a poorly-soluble white powder. The melting point of this depended on the rate of heating, presumably because of dehydration to the oxide (c.f. the DSC results discussed below, see also ref. 19). The ^{1}H and ^{13}C NMR spectra were complicated by poor solubility. The observed peaks in an initial spectrum were consistent with the expected pattern, but with time other signals developed suggesting that the hydroxide slowly forms other species in solution, such as the oxide or possibly an oxonium species. The ^{199}Hg NMR signal of **3** was solvent dependent, δ 1139 ppm in CDCl$_3$ and 1043 ppm in dmso.

In the ESMS spectrum in acidified MeOH, the [M+H]$^+$ ion for **3** at m/z 340 was always weak. More intense ions at m/z 659 and 978 were readily assignable by their distinctive isotope patterns to [(R*Hg)$_2$O+H]$^+$ and [(R*Hg)$_3$O]$^+$. However in MeOH made alkaline with NaOH, significant ions attributable to [R*HgOH + Na]$^+$ and [R*HgOH + Na + MeOH]$^+$ at m/z 362 and 394 respectively were found. These results are consistent with the initial presence of **3** with a labile OH group which can be

displaced to generate R*Hg$^+$ moieties which then react *in situ* to generate a number of different ions.

The infrared spectrum of **3** as a KBr disk shows three extra peaks compared to the spectrum of the chloride **2**, at 528 cm^{-1}, 886 cm^{-1} and at 3552 cm^{-1}. The first of these is in the region assigned by Green to Hg-O stretching [10], and the pattern is much simpler than that in the corresponding region for "PhHgOH", which is consistent with a hydroxide formulation for **3** and an oxonium structure for the phenyl example. The second of the peaks is in the region expected for δ(M-O-H) [26], while the third sharp peak at 3552 cm^{-1} is consistent with a non-hydrogen bonded -OH group, as found in the crystal structure.

Overall, the spectroscopic data are in full agreement with formulation of **3** as a true hydroxide, but interpretation is not unambiguous, so characterisation depended mainly on the X-ray crystal structure determination discussed below.

A DSC/DTA investigation of the effect of heating the hydroxide **3** showed a sharp endothermic peak at 121°C, with a corresponding weight loss of 2.7%. This corresponds exactly to the process in eqn 1.

$$2 \ Me_2NC_6H_4HgOH \rightarrow (Me_2NC_6H_4Hg)_2O + H_2O \ \dots\dots\dots\dots\dots\dots\dots(1)$$

On a preparative scale, the hydroxide **3** when heated at 120°C under vacuum for several hours gave a white solid which could be recrystallised as very small needles from CH_2Cl_2/Et_2O. This was characterised as the oxide **4**. The ^1H and ^{13}C NMR details are similar to those of the other compounds studied, while the ^{199}Hg NMR spectrum showed a peak at δ 1000 ppm in dmso, near but distinct from that of the hydroxide **3**. In an infrared spectrum, the peaks assigned to ν(O-H), ν(M-O) and δ (M-O-H) for **3** had

disappeared, to be replaced by a strong broad peak for **4** at 647 cm^{-1}, which can be assigned to a ν(Hg-O-Hg) vibration (c.f 675 cm^{-1} for (PhHg)$_2$O [9]).

On one occasion, while attempting to recrystallise the hydroxide **3** from boiling acetone, straw-coloured crystals were obtained. These were characterised as the symmetrical **5**, based on NMR and elemental analysis results and an ESMS signal at m/z 443 assigned to [M+H]$^+$. Whitmire et al reported this compound earlier from a similar reaction [19], though without full characterisation. The formation of **5** is not unexpected since symmetrisation reactions (eqn 2) are well-known for organo-mercury compounds [20, 27].

$$2RHgX \leftrightarrow R_2Hg + HgX_2 \text{.........................(2)}$$

This identity of **5** was confirmed by a structural characterisation, see below.

3.2 Structural determinations.

4-Me$_2$NC$_6$H$_4$HgOAc: Despite the importance of aryl-mercury acetates as reagents in synthesis, the only structural characterisations appear to be imprecise determinations of PhHgOAc and (p-tolyl)HgOAc [28, 29]. The present determination of **1** is therefore the first accurate report. The crystals contain two independent molecules, differing mainly in the relative orientation of the acetate group. The dihedral angles between the aryl plane, and the acetate plane defined by the atoms C(8), C(9), O(1) and O(2), are 74.7(4)° and 42.7(5)° respectively for molecules A and B. The structure of molecule A is illustrated in Figure 1. It contains the expected linear coordination about the Hg atom (175.9(3)° and 177.0(3)° in the two molecules). The Hg-O bonds (av. 2.098(7) Å) are longer than the Hg-C ones (av. 2.035(10) Å) which is the opposite of what would be expected based on the covalent radii of O and C. This anomaly has been observed before [11] but has yet to

be explained. The intramolecular Hg....O=C distances, 2.787 and 2.873 Å are less than the sum of the Van der Waals radii (ca 2.9-3.1) which suggests a weak interaction. Similar Hg...O distances have been interpreted in terms of secondary coordination in other compounds. The stacking within the crystal gives aggregates of four molecules linked by a network of eight inter-molecular Hg...O interactions of 2.7- 2.8 Å.

4-Me$_2$NC$_6$H$_4$HgOH: The crystal structure shows that **2** is the first authenticated example of an organomercury hydroxide, as illustrated in Figure 2. The molecule is essentially planar, with a linearly-coordinated Hg atom (175.9(3)°). In this example the Hg-C distance (2.08(1) Å) appears greater than the Hg-O one (2.04(1) Å), in contrast to the trend in **1**, but the accuracy of the determination precludes more definite discussion.

A surprising feature of the structure is the absence of intermolecular H-bonding between the -O-H group and either of the acceptor sites (the Me$_2$N group or the O atom) of an adjacent molecule. Instead the packing is organised into pairs of molecules about an inversion centre, held together by relatively short Hg...O interactions (2.680 Å), Fig. 3a. These pairs are then stacked in a zigzag herring-bone manner, Fig. 3b. The H atom of the hydroxyl group could not be reliably located in the X-ray experiment, but the position of the oxygen atom is such that the O-H bond is probably directed towards an adjacent aryl ring, giving weak O-H...π hydrogen bonding [30]. It appears that in this compound the need to maintain Hg$^{\delta+}$...O$^{\delta-}$ intermolecular interactions dominates over normal H-bonding possibilities. (An alternative interpretation of the structure in terms of a zwitterion, $^+$HMe$_2$NC$_6$H$_4$HgO$^-$ can be discounted since the sum of the C-N-C angles around the N atom is 353°, and anyway this too would be expected to have N-H ....O hydrogen bonding). The presence of an essentially free Hg-OH group is also consistent

with the infrared spectrum, as discussed earlier. The dimeric head-to-tail units with Hg...O intermolecular interactions explains the ready elimination of H_2O on heating to form the corresponding oxide.

(4-Me$_2$NC$_6$H$_4$)$_2$Hg: The asymmetric unit of crystals of **5** consist of one whole molecule and two half-molecules lying on inversion centres. However there are no chemically significant differences between them. The Hg-C distances average 2.062(7) Å, and the C-Hg-C angles are constrained to exactly 180° for two of the independent molecules, and is 176.6(2) in the unconstrained molecule. One interesting observation is that all three independent molecules are essentially planar, when there appears to be no particular reason why this should be so since there would be free rotation about the Hg-C bonds. Indeed this phenomenon appears to be general for most of the bis-aryl-mercury compounds for which structures are known [31], except for those examples with bulky ortho substituents [32] and for fluoro-substituted rings. [33]. There is no obvious explanation for this. One possibility is the need to arrange efficient π-stacking type interactions (or alternatively $Hg^{\delta+}...C^{\delta-}$ intermolecular attractions), but neither of these seems to be involved in the crystal structure of **5**. It may simply be a consequence of the tendency of these symmetrical molecules to occupy crystallographic inversion centres.

4. Conclusions.

This study has shown that a true organomercury hydroxide does exist. It is unlikely that the Me$_2$N substituent confers any particular stability for a hydroxide rather than an oxonium form. It appears RHgOH compounds undergo ready equilibria in solution involving the free hydroxide and the $[(RHg)_2OH]^+$ and $[(RHg)_3O]^+$ ions (as shown here for the 4-Me$_2$NC$_6$H$_4$- derivative, and previously for the phenyl example, by electrospray

mass spectrometry) and that the form that crystallises is the one with the most favourable lattice packing.

5. Supplementary material.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no XXXXXXXX. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Rd., Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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Captions to figures.

Figure 1. The structure of one of the independent molecules of $Me_2NC_6H_4HgOAc$.

Parameters include bond lengths (Å): Hg(1)-C(10) 2.036, Hg(2)-C(20)

2.033(10), Hg(1)-O(11) 2.081(7), Hg(2)-O(21) 2.116(7), C(18)-O(11)

1.289(11), C(28)-O(21) 1.280(11), C(18)-O(12) 1.224(11), C(28)-O(22)

1.238(11); bond angles (degrees) O(11)-Hg(1)-C(10) 175.9(3), O(21)-

Hg(2)-C(20) 177.0(3).

Figure 2. The structure of $Me_2NC_6H_4HgOH$. Parameters include bond lengths (Å):

Hg(1)-C(1) 2.081(12), , Hg(1)-O(1) 2.039(9); bond angle O(1)-Hg(1)-C(1)

176.2(3)°.

Figure 3. The crystal packing for $Me_2NC_6H_4HgOH$; (a) the Hg...O bonded dimers; (b)

the herring-bone packing of dimers.

Figure 4. The structure of one of the independent molecules of $(Me_2NC_6H_4)_2Hg$. The

average Hg-C distance is 2.065(7)Å.