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Mercury(II) and Organomercury(II) Complexes of Thiols and Dithiols, Including British Anti-Lewisite

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The dithiols 2,3-dimercapto-1-propanol (British anti-Lewisite) and 1,3-dimercapto-2propanol form complexes RHgS~SHgR (R = Me, Ph). The PhHg(II) complexes decompose in benzene and methanol at ambient temperature to form diphenylmercury. A 1:1 complex of Hg(II) with 1,3-dimercapto-2-propanol is dimeric in pyridine. Infrared, Raman, and ^1H *NMR spectra of RHg(II) and Hg(II) dithiol complexes are compared with those of PhHgSR (R = Me, Et,* Pr^i*,* Bu^t*, Ph,* CH_2CH_2OH*) and* $Hg(SR')_2$ *(R' = Me, Et,* Bu^t*, Ph,* CH_2CH_2OH*). Phenylmercury(II) thiolates have the coupling constant* $J(^{ortho}H-^{199}Hg)$ *within the range 144–155 Hz. The complexes PhHgSR and* $Hg(SR'')_2$ *(R'' = Et,* Bu^t*, Ph) are monomeric in chloroform; the chloroform insoluble complexes* $Hg(SR''')_2$ *(R''' = Me,* CH_2CH_2OH*) and organomercury(II) dithiolates are monomeric in pyridine. Aspects of the use of British anti-Lewisite as an antidote for mercury poisoning are discussed.*

Introduction

Several chelating agents have been used to treat mercury poisoning [1, 2]. Of these agents British anti-Lewisite ('dimercaprol', 2,3-dimercapto-1-propanol, $BALH_3$†) is particularly successful for poisoning by inorganic mercury [1, 2] and is the most satisfactory antidote for phenylmercury(II) poisoning (animal experiments only to date [2]), but has no therapeutic effect for methylmercury(II) poisoning in humans or animals [2]. For PhHg(II) poisoning $BALH_3$ greatly increases the amount of mercury in the brain compared with the bodily distribution in the absence of $BALH_3$ treatment, [2–5], and for MeHg(II) poisoning it merely hastens the distribution of mercury [3, 4] and may increase the amount of mercury in the brain [2]. An increased mercury content in the brain is undesirable, as it attacks the central nervous system. $BALH_3$ also increases the amount of mercury in the brain following its administration for inorganic mercury poisoning [6–8], but this effect has been explained in terms of the timing and dosage of $BALH_3$ [8]. Even with the above difficulties $BALH_3$ may still have an important role in treatment of organomercury poisoning as it increases biliary excretion of mercury [9], possibly allowing increased faecal excretion of mercury bound to deprotonated sulphydryl groups of indigestible polymers eaten with food [10].

In order to understand some of these phenomena we have studied the chemistry of $BALH_3$ with Hg(II), PhHg(II), and MeHg(II). Isolation of Hg(BALH) [11–13] and evidence for the formation of $[Hg(BALH)_2]^{2-}$ [11], $(PhHg)_2BALH$ [12], and $(RHg)_nBALH_{3-n}$ [n = 1 [14], 2 [12]; R = $CH_2CH(OMe)CH_2R'$] in solution has been documented. To assist with interpretation of physical and spectroscopic data for complexes isolated we have studied related complexes of Hg(II) and RHg(II) with thiols and dithiols. A communication of part of this work has been published [15].

Experimental

Reagents

Phenylmercuric acetate and MeHgX (X = Cl, O_2CMe) are commercially available (Alfa Inorganics) and were recrystallized from ethanol. Mercury(II) salts and thiols were used as received. Analytical reagent grade solvents were used: benzene was dried over sodium and distilled, methanol was dried and distilled from magnesium, and pyridine was dried and distilled from potassium hydroxide. Unless stated otherwise all complexes were dried over phosphorus pentoxide *in vacuo*.

Physical Measurements

Infrared spectra (4000–400 cm^{-1}) of complexes in Nujol and hexachlorobutadiene mulls were recorded with a Perkin–Elmer 577 spectrometer. Far IR spectra of complexes in Nujol mulls between polyethylene plates were recorded with a Perkin–Elmer

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†Usual abbreviation 'BAL' [1–9, 11, 12]. $BALH_3$ is used here to indicate loss of thiol protons on reactions with metal ions, *e.g.* Hg(BALH).

TABLE I. Analytical Data for the New Complexes[a]

Complex	Found %				Calcd. %			
	C	H	S	Hg	C	H	S	Hg
$(PhHg)_2BALH$[b]	25.9	2.5	9.6	59.1	26.5	2.4	9.5	59.2
$(PhHg)_2DMPH$	26.1	2.5	9.3	59.0	″	″	″	″
$(PhHg)_2DMPH \cdot C_5H_5N$[c]	30.9	2.8	8.8	52.7	31.7	2.8	8.5	53.0
$(MeHg)_2DMPH$	11.2	2.2	11.5	72.0	10.9	2.2	11.6	72.5
Hg(DMPH)	11.1	1.9	19.7	61.0	11.2	1.6	19.9	62.1
Hg(DMPH)[d]	11.4	1.6	19.6	61.5	″	″	″	″

[a] $(MeHg)_2BALH$, an oil, has microanalyses indicating contamination with $BALH_3$, also a viscous oil. Found: C, 12.25; H, 2.29; S, 14.1; Hg, 72.4. $(MeHg)_2BALH$ requires C, 10.9; H, 2.2; S, 11.6, Hg, 72.5%. Satisfactory integration is present in ^1H NMR spectra (Figure 2), and vibrational spectra are as expected. [b] BALH,DMPH = $C_3H_6OS_2$. [c] N 1.6, Calcd. 1.9%. [d] Recrystallized from pyridine N < 0.5%.

577 spectrometer (600–200 cm^{-1}) and, for Hg(II) complexes only, with a Perkin–Elmer 180 spectrometer (500–50 cm^{-1}). Raman spectra were measured with a Cary 82 laser Raman spectrometer over the range 4000–100 cm^{-1} using 514.5 nm excitation. Complexes giving poor spectra with this excitation were re-examined with a Coherent Radiation dye laser Model 590 using Rhodamine 6G dye, and for these complexes the wavelength of excitation is given with the listing of spectra. Maximum errors are considered to be 4 cm^{-1} for both IR and Raman spectra. ^1H NMR spectra at 100 MHz were measured on a Jeol-JNM-4H-100 spectrometer with tetramethylsilane as internal reference. Molecular weights were determined in chloroform (37 °C) and pyridine (60 °C) with a Knauer vapour pressure osmometer. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. Analytical data for new complexes are given in Table I. Conductivities were measured with a Philips PW 9504/00 conductivity meter in pyridine and water, and are reported as ohm^{-1} mol^{-1} cm^2 (X 10^4 mol dm^{-3}, solvent), *e.g.* [pyridineH]ClO_4 has molar conductivity 98 (27.9, py).

Preparation of Complexes

poly-[(2,3-dimercapto-1-propanolato-S,S'-)mercury(II)], Hg(BALH)

2,3-Dimercapto-1-propanol (0.266 g, 2.14 mmol) dispersed in water (5 ml) was added to mercuric chloride (0.582 g, 2.14 mmol) in water (15 ml). A white precipitate which formed immediately was collected and washed with water and ethanol (0.687 g, 99%), m.p. 160 °C (dec.). (Found: C, 11.4; H, 2.1; Hg, 60.6; S, 19.6. $C_3H_6HgOS_2$ requires C, 11.2; H, 1.9; Hg, 62.1; S, 19.9%). Infrared and Raman spectra are reported elsewhere [13]. A similar preparation using mercuric acetate gave an identical product (i.r. identification).

Reaction of mercuric acetate with 2,3-dimercapto-1-propanol in pyridine

2,3-Dimercapto-1-propanol (0.467 g, 3.76 mmol) in pyridine (5 ml) was added to mercuric acetate (1.20 g, 3.76 mmol) in pyridine (10 ml). A white precipitate which formed immediately was collected and washed with pyridine (0.621 g) (*1*), m.p. 130 °C (dec.). (Found: C, 14.7; H, 2.1; Hg, 55.7; N, 1.0%). A similar reaction with $Hg(O_2CMe)_2$:$BALH_3$ ratio 1:2 gave a clear solution during addition of the second mole of dithiol. Addition of acetone gave a white precipitate. The solid was collected, dissolved in pyridine, and reprecipitated by addition of acetone (*2*), m.p. 90 °C (dec.). (Found: C, 14.7; H, 2.2; Hg, 49.1; S, 19.9%). Molar conductivity: 6.2 (24.1, py), '8.6' ('12.4' (water) and with one mole equivalent of $BaLH_3$ added, 12.4(py) and '12.0' (water). $BALH_3$ has molar conductivity 0.1 (307, py) and '0.2' ('838', saturated solution in water, concentration of dissolved $BALH_3$ much lower than 838 X 10^{-4} mol dm^{-3}).

poly-[(1,3-dimercapto-2-propanolato-S,S')Mercury(II)], Hg(DMPH)

1,3-Dimercapto-2-propanol (0.34 g, 2.74 mmol) dispersed in water (2 ml) was added to mercuric chloride (0.706 g, 2.60 mmol) in water (18 ml). A white precipitate which formed immediately was collected and washed with water and ethanol (0.812 g, 97%), m.p. 120 °C (dec.). Infrared absorption: 3330 s(br), 2956 vw, 2910 w, 1409 s, 1334 vw, 1290 vw, 1258 vw, 1226 vw, 1180 vw, 1063 m(sh) and 1027 s, 974 w, 934 vw, 832 vw, 740 w, 680 vw, 551 vw, 509 vw, 459 vw and 431 vw(sh), 353 m(vbr), 200–90 w (extremely broad) cm^{-1}. Raman bands (589.2 nm): 2953 m(sh) and 2912 vs, 1414 w, 1325 vw, 1263 vw, 1191 vw, 1073 vw, 1031 vw, 979 vw, 933 vw, 863 vw and 836 vw, 778 w and 753 w(sh) and 723 vw(sh), 683 w, 564 vw, 325 vs and 275 w(sh), 179 vw(vbr) cm^{-1}. Molar conductivity: 1.81 (7.1, py), '12.3' ('12.4', water) and, with one mole equivalent of DMPH$_3$ added, 9.74 (py), '53.4' ('9.3', water). DMPH$_3$ has molar conductivity 0.1 (187, py), and '1.7' ('592', saturated solution in water).

Recrystallization of Hg(DMPH) from pyridine

Hg(DMPH) (0.375 g, 1.16 mmol) in pyridine (20 ml) deposited colourless crystals over 14 hours. The crystals were collected, but not washed or dried (0.138 g, 13%). [Found: py (by weight loss at ambient temperature) 26.7. Hg(DMPH)py$_{1.5}$ requires py 26.9%]. Raman spectrum (sealed tube): 3064 m, 2970 m, 2957 m, 2924 vs and 2917 vs, 1596 vw, 1576 vw, 1421 w, 1388 vw, 1325 vw, 1300 vw, 1224 w, 1200 vw, 1173 vw, 1152 vw, 1076 vw, 1038 m, 1009 m, 997 w, 927 w, 874 vw, 840 vw, 787 vw(sh) and 771 w(sh) and 760 m, 669 s, 580 w, 365 m, 343 vs, 269 m, 254 w, 182 m, 152 m cm^{-1}.

On loss of pyridine the white powder formed has analysis consistent with Hg(DMPH) (Table I), m.p. 202 °C. Infrared absorption: 3274 m(br), 2954 w, 2916 w, 1417 w and 1407 m, 1383 w, 1327 m, 1297 w, 1251 m, 1221 w, 1196 w, 1169 m, 1041 m(sh) and 1029 s, 917 vw, 864 w, 835 w, 755 m, 722 vw, 662 w, 572 w, 519 w(br), 425 m, 373 m, 351 w, 261 w, 243 w, 229 w, 181 w(sh) and 173 w, 142 w, 87 m cm^{-1}. Raman bands: 2970 w, 2953 w, 2920 s, 1417 vw and 1409 vw(sh), 1383 vw, 1323 vw, 1296 vw, 1250 vw, 1220 vw, 1196 vw, 1168 vw, 1042 vw(sh) and 1032 vw, 1004 vw, 919 vw, 866 vw, 833 vw, 753 w, 663 w, 575 vw, 435 vw, 360 w, 339 s, 263 w, 247 vw, 223 vw, 176 w, 146 m cm^{-1}. Molar conductivity 2.9 (19.5) in pyridine.

Bis(benzenethiolato)mercury(II)

On addition of benzenethiol (0.480 g, 4.36 mmol) in ethanol (5 ml) to mercuric acetate (0.637 g, 2.0 mmol) in ethanol (15 ml) a white precipitate formed immediately. It was collected and washed with ethanol (0.795 g, 95%), m.p. 150 °C (lit. 150–152° [16], 152.5–153.5° [17]). (Found: C, 34.8; H, 2.4; Hg, 47.7; S, 15.2 $C_{12}H_{10}HgS_2$ requires C, 34.4; H, 2.4; Hg, 47.9; S, 15.3%). Infrared absorption: 3070 w and 3060 w, 3049 w, 3017 vw, 2998 vw, 1949 vw, 1877 vw, 1747 vw, 1578 m, 1476 m, 1437 s, 1385 vw, 1333 vw, 1319 vw, 1303 m, 1272 vw, 1164 w, 1084 m, 1069 m, 1023 s, 1002 m, 905 m, 845 vw, 750 m(sh) and 739 s, 689 s, 614 vw, 485 s, 424 w, 365 s(br), 270 w, 204 w, 96 s cm^{-1}. Raman bands: 3152 vw and 3138 vw, 3057 s, 3015 vw, 2997 vw, 2986 vw, 1579 vs, 1480 vw, 1437 vw, 1382 vw(br), 1337 vw(br), 1303 vw, 1275 vw, 1186 vw(sh), 1164 w, 1122 w, 1085 vs and 1072 vw(sh), 1025 s, 1000 vs, 991 vw, 976 vw(br), 910 vw, 848 vw, 748 vw, 742 vw, 698 m, 616 w, 486 vw, 425 s and 413 w, 344 s, 253 s, 182 vs, 122 s(br) cm^{-1}.

Bis(1-mercapto-2-ethanolato-S)mercury(II)

On addition of 1-mercapto-2-ethanol (0.743 g, 9.51 mmol) to mercuric cyanide (1.077 g, 4.26 mmol) in ethanol (10 ml) a white precipitate formed immediately. It was collected and washed with ethanol (1.436 g, 95%), m.p. 122 °C (lit. [18] 119–121°). (Found: C, 13.9; H, 3.1; S, 18.3. $C_4H_{10}HgO_2S_2$ requires C, 13.5; H, 2.8; S, 18.1%). Infrared absorption: 3200 s(br), 3077 s(br), 2933 s, 2879 s, 2789 m, and 2565 w(sh) as part of very broad absorption 3400–2200 cm^{-1}, 1483 vw, 1471 w, 1441 s, 1395 m, 1367 w, 1282 w, 1222 s, 1175 w, 1155 w, 1048 vs, 1018 vs and 1004 w(sh), 847 vw, 776 w, 746 s, 721 m, 424 w, 371 s(br), 222 m, 196 m, 177 m, 163 m, 140 m. 97 s, 82 s, 53 s cm^{-1}. Raman bands (589.2 nm): 2969 w, 2933 w, 2907 w, 2883 w, 2849 w, 2716 vw, 1471 w, 1441 m, 1289 w, 1222 m, 1052 w, 1019 m, 1007 w, 774 vw, 746 s, 424 vw, 352 m, 198 s, 139 vw cm^{-1}.

Preparations, analytical data, infrared, and Raman spectra for Hg(SR)$_2$ (R = Me, Et, Bu^t) have been given previously [13].

μ-(2,3-Dimercapto-1-propanolato-S,S')di[phenylmercury(II)], (PhHg)$_2$BALH

2,3-Dimercapto-1-propanol (0.185 g, 1.49 mmol) was added to a solution of phenylmercuric acetate (1.002 g, 2.98 mmol) in water (200 ml) with stirring. A white precipitate formed immediately, and after several hours of stirring was collected and washed with water (0.707 g, 70%), m.p. 66 °C. Infrared absorption: 3528 vw(br, sh), 3346 w(vbr), 3064 w and 3051 w, 2906 vw and 2866 vw(sh), 1573 w, 1475 w, 1429 m, 1300 vw, 1263 vw, 1228 vw, 1188 vw, 1154 vw, 1060 w, 1021 m, 996 m, 963 vw, 892 vw, 864 vw, 729 s, 699 s, 658 vw, 552 vw, 460 vw(sh) and 447 m, 335 s(vbr), 256 w, 232 vw, 207 vw cm^{-1}. Raman bands: 3141 vw and 3130 vw, 3036 s, 2977 vw, 2940 w(sh) and 2900 m, 1574 m and 1567 s, 1478 w, 1430 vw, 1414 vw, 1330 vw, 1305 vw, 1261 vw, 1190 vw, 1158 w, 1074 w, 1023 m, 1000 s, 985 w, 906 vw, 855 vw, 728 vw, 701 vw, 657 s, 617 w, 564 vw, 453 vw, 338 m(vbr) and 318 w(sh), 234 s, 215 w(sh), 209 m, 185 m and 165 m(sh) cm^{-1}.

μ-(2,3-Dimercapto-1-propanolato-S,S')di[methylmercury(II)], (MeHg)$_2$BALH

2,3-Dimercapto-1-propanol (0.162 g, 1.30 mmol) in benzene (5 ml) was added dropwise to a solution of methylmercuric acetate (0.716 g, 2.61 mmol) in benzene (20 ml). After 15 min a 'gluey' solid was collected and washed with benzene (10 ml) twice by decanting off the solvent. Infrared absorption(thin film of gluey solid): 3340 s(vbr), 2985 m(sh) and 2903 s and 2867 m(sh) and 2792 w(sh), 1708 vw(br), 1452 w, 1409 m, 1296 w(sh, br) and 1262 m, 1227 w, 1176 m and 1140 w(sh), 1040 s(vbr) and 1000 m and 936 w(sh), 892 m, 863 w, 770 s, 680 w and 656 vw(sh), 555 vw(sh) and 530 m [ν(Hg–C)], 451 vw, 408 vw, 328 m(vbr) cm^{-1}. Raman bands (589.2 nm): 2990 w, 2908 s, 1460 vw, 1418 vw, 1304 vw(br), 1268 vw, 1179 s, 995 w, 898 vw, 873 vw, 769 vw, 733 vw, 662 vw, 627 vw, 537 vs [ν(Hg–C)], 457 vw, 418 vw, 328 s(br) cm^{-1}.

μ-(1,3-Dimercapto-2-propanolato-S,S')di[phenylmercury(II)], (PhHg)$_2$DMPH

1,3-Dimercapto-2-propanol (0.230 g, 1.85 mmol) was added to a suspension of phenylmercuric acetate (1.251 g, 3.71 mmol) in water (200 ml) with stirring. A white precipitate formed immediately, and after several hours of stirring was collected and washed with water (1.01 g, 80%), m.p. 62–66 ℃. Infrared absorption: 3500 w(br, sh), 3294 w(br), 3061 m, 3046 w, 2909 w, 1573 w, 1475 w, 1428 s and 1412 w(sh), 1330 vw, 1258 vw, 1220 vw,1180 vw(br), 1153 vw, 1060 m, 1021 s, 997 m, 971 w, 932 vw, 906 vw, 853 vw, 830 vw, 814 vw, 726 vs, 697 vs, 567 w(br), 504 w(br), 460 w(sh), 447 s, 343 s(br), 256 w, 234 w cm^{-1}. Raman bands: 3143 w and 3132 w, 3040 vs, 2944 w, 2910 s, 2815 vw, 1575 m and 1568 m, 1479 w, 1430 w, 1419 w, 1330 w, 1263 w, 1223 vw, 1190 w, 1159 w, 1075 w, 1024 m, 1001 vs and 986 w(sh), 909 vw(br), 853 vw(br), 778 w, 659 s and 645 vw(sh), 617 w, 451 vw, 343 s(br), 237 vs, 213 w(sh), 187 s cm^{-1}.

μ-(1,3-Dimercapto-2-propanolato-S,S')di[phenylmercury(II)]·pyridine, (PhHg)$_2$DMPH·py

(PhHg)$_2$DMPH dissolved in pyridine forms colourless crystals during several days. These were collected and washed with pyridine (52%), m.p. 74–75 ℃. Infrared absorption: 3065 m and 3047 m and 3026 w(sh) and 2986 w, 2918 w, 2892 m, 2870 w, 2806 w, 2691 w, and 2604 as part of very broad absorption 3200–2580 cm^{-1}, 1594 m, 1575 w, 1475 m, 1440 m, 1428 m, 1413 w, 1307 m, 1248 vw, 1220 vw and 1213 w, 1182 vw, 1160 vw, 1148 w, 1066 m, 1043 m, 1033 m, 1022 m, 1003 m and 997 w(sh), 906 vw, 852 w, 751 m, 773 m(sh) and 726 s, 707 m(sh) and 698 s, 666 w(sh), 660 w(sh) 620 w, 575 m, 463 w(sh), 452 m, 408 w, 343 s(br), 257 m cm^{-1}. Raman bands: 3150 vw, 3134 vw, 3068 w(sh) and 3044 s, 2956 vw, 2940 vw, 2921 w, 2894 w, 2872 vw, 1593 vw, 1575 m, 1568 w, 1479 vw, 1414 vw, 1330 vw, 1311 vw, 1216 vw, 1192 vw, 1160 vw, 1077 vw, 1038 w, 1025 w, 1006 m(sh) and 1000 vs, 988 vw, 925 vw, 865 vw, 726 vw, 673 vw(sh), 662 w, 621 vw, 578 vw, 361 vw, 344 m, 238 s, 212 vw, 196 w and 184 vw(sh), 153 w cm^{-1}.

μ-(1,3-Dimercapto-2-propanolato-S,S')di[methylmercury(II)], (MeHg)$_2$DMPH

1,3-Dimercapto-2-propanol (0.138 g, 1.11 mmol in ethanol (5 ml) was added to a solution of methylmercuric acetate (0.579 g, 2.11 mmol) in ethanol (30 ml). After 24 hr a colourless crystalline precipitate was collected and washed with ethanol (0.518 g, 89%), m.p. 103–104 ℃. Infrared absorption: 3306 w(br), 2990 vw, 2905 w, 2884 w, 1415 w, 1384 w, 1333 w, 1301 w, 1264 m, 1225 w, 1190 w, 1180 m and 1173 m, 1137 w, 1069 s, 1019 w, 976 m, 842 m, 777 s(br), 684 m, 559 w(sh) and 540 s(sh) and 533 s [ν(Hg–C)], 491 s, 458 m, 341 s and 329 m(sh), 304 m, 271 w cm^{-1}. Raman bands (608.8 nm); 2958 w, 2918 m and 2908 w(sh), 2884 w, 1427 w, 1388 vw, 1305 vw, 1269 w, 1225 vw, 1200 vw, 1184 vs and 1179 s(sh), 1142 vw, 1070 w, 1021 vw, 980 w, 839 vw, 779 s, 687 w, 543 s(sh) and 537 vs [ν(Hg–C)], 461 vw, 342 vs, 313 s, 275 vw, 172 s, 132 s cm^{-1}.

Phenylmercury(II) complexes PhHgSR (R = Me, Et, Pr^i, Bu^t, Ph, CH$_2$CH$_2$OH)

These complexes were prepared by addition of thiol to an equimolar amount of phenylmercuric acetate in ethanol. Characterization data for each complex are given.

Methanethiolato(phenyl)mercury(II), m.p. 83 ℃. (Found: C, 25.4; H, 2.6; Hg, 62.2; S, 10.1. C_7H_8HgS requires C, 25.9; H, 2.5; Hg, 61.8; S, 9.9%). Infrared absorption: 3060 w and 3048 w, 3020 vw, 2980 vw, 2919 m, 2833 vw, 1573 w, 1471 w, 1425 m, 1326 vw, 1305 w, 1185 vw and 1172 vw(sh), 1152 vw, 1071 vw, 1060 w, 1020 m, 998 w, 948 m, 901 w, 771 vw, 723 s, 691 s, 446 m, 350 w(sh) and 335 m, 256 vw, 232 vw cm^{-1}. Raman bands: 3147 vw, 3136 vw, 3048 m(sh) and 3038 s, 3022 vw(sh), 2985 w, 2942 vw, 2920 s, 2834 vw, 1575 w, 1568 w, 1477 vw, 1429 vw, 1328 vw, 1306 vw, 1263 vw, 1188 vw, 1157 vw, 1076 vw, 1022 w, 999 vs, 988 vw, 957 vw, 909 vw, 852 vw, 697 m, 660 m, 620 vw, 451 vw, 337 vs, 236 s, 206 m, 185 w cm^{-1}.

Ethanethiolato(phenyl)mercury(II), m.p. 50 ℃ (recryst. ethanol/chloroform) (lit. 53–54 ℃ [19], 56° [20]). (Found: C, 28.7; H, 2.8; Hg, 59.5; S, 9.9. $C_8H_{10}HgS$ requires C, 28.4; H, 3.0; Hg, 59.2; S, 9.5%). Infrared absorption: 3067 w, 3056 w, 2955 w, 2918 w, 2858 vw, 1575 w, 1477 w, 1445 w, 1431 m, 1373 w, 1251 s and 1238 w(sh), 1187 vw, 1070 vw(sh) and 1061 vw(sh) and 1051 vw, 1018 m, 997 m, 965 w, 762 w, 723 s, 695 s, 651 w, 448 m, 387 w(br), 328 m(vbr), 226 w cm^{-1}. Raman bands: 3147 w, 3135 w, 3050 vs, 2987 vw, 2958 w, 2945 w, 2919 s, 2864 w, 2838 vw, 2718 vw, 1576 m, 1570 m, 1482 w, 1452 vw, 1430 w, 1331 w, 1254 w, 1239 vw, 1193 w, 1160 w, 1076 w, 1057 w, 1022 m, 1000 vs, 970 vw, 915 vw, 853 vw, 700 vw, 659 s, 619 w, 457 vw, 355 m(br), 231 s, 214 m, 195 m, 154 w cm^{-1}.

iso-Propanethiolato(phenyl)mercury(II), m.p. 54 °C (recryst. ethanol/chloroform). (Found: C, 30.4; H, 3.3; Hg, 56.1; S, 9.8. $C_9H_{12}HgS$ requires C, 30.6; H, 3.4; Hg, 56.8; S, 9.1%). Infrared absorption: 3060 w and 3048 w, 3012 vw, 2950 m, 2920 w, 2857 w, 1573 w, 1477 m, 1446 m, 1429 m, 1380 m, 1362 m, 1315 vw, 1297 vw, 1242 s, 1185 vw, 1144 m, 1072 vw, 1060 vw, 1045 m, 1021 m, 996 m, 923 vw, 903 vw, 884 vw, 724 s, 698 s, 611 m, 448 m, 388 m(vbr), 353 vw, 330 vw(vbr), 256 w cm^{-1}. Raman bands: 3154 vw, 3140 vw, 3068 m(sh) and 3046 s and 3022 vw(sh), 2992 vw(sh) and 2970 vw(sh) and 2954 vw(sh) and 2923 m and 2909 vw(sh), 2857 w, 2750 vw, 2713 vw, 1580 w, 1573 w, 1481 vw, 1454 vw and 1445 vw(sh) and 1436 vw(sh), 1334 vw, 1322 vw, 1247 w, 1194 vw, 1161 vw and 1153 vw(sh), 1112 vw, 1080 vw, 1052 vw, 1028 w, 1000 vs, 988 vw, 909 vw, 887 w, 661 m, 618 m, 444 vw, 399 w, 358 vw, 262 vw, 228 s, 216 m, 192 m, 134 m cm^{-1}.

tert-Butanethiolato(phenyl)mercury(II), m.p. 107–108 °C (recryst. ethanol/chloroform). (Found: C, 32.4; H, 4.0; Hg, 55.0; S, 9.0. $C_{10}H_{14}HgS$ requires C, 32.7; H, 3.8; Hg, 54.7; S, 8.7%). Infrared absorption: 3065 w and 3045 vw(sh) and 3025 vw, 2974 w(sh) and 2956 m, and 2938 m(sh), 2890 w, 2858 w, 1575 vw, 1478 w, 1453 m, 1431 m, 1366 m, 1303 vw, 1213 vw, 1162 m and 1142 w(sh), 1073 vw, 1061 vw, 1024 vw(sh) and 1021 w, 996 vw, 967 vw(br), 911 vw, 819 vw, 755 vw(br), 733 s, 727 s, 700 s, 574 w, 447 m, 434 w, 387 m, 359 m, 337 vw, 320 vw, 292 vw, 249 w, 221 vw, 203 w cm^{-1}. Raman bands: 3149 w, 3134 w, 3072 vw(sh) and 3047 vs and 3041 vs and 3025 vw(sh), 2989 vw(sh), 2972 w, 2958 m, 2930 m(br), 2893 m, 2855 w, 2774 vw, 2720 vw, 2707 vw, 1575 m, 1569 w, 1480 w, 1454 w, 1441 w, 1432 vw, 1334 w, 1261 vw, 1213 w, 1197 vw, 1161 w, 1078 w, 1025 w, 1000 vs. 988 w, 932 w, 915 vw, 824 w, 661 s, 620 w, 580 m, 451 vw, 439 w, 392 w, 362 w, 257 vw, 232 s, 208 s, 189 m, 170 vw(sh) cm^{-1}.

Benzenethiolato(phenyl)mercury(II), m.p. 102 °C (recryst. ethanol/chloroform) (lit. [20, 21] 105–106 °C). (Found: C, 37.5: H, 2.8; Hg, 51.4; S, 8.5. $C_{12}H_{10}HgS$ requires C, 37.3; H, 2.6; Hg, 51.9; S, 8.3%). Infrared absorption: 3061 w(sh) and 3043 w, 1577 m, 1473 m, 1437 m, 1431 m, 1333 vw, 1303 w, 1267 vw, 1193 vw(sh), 1183 w, 1155 vw(br), 1113 vw(br), 1083 m and 1070 vw(sh), 1023 m, 999 w, 983 vw, 905 w and 898 vw(sh), 850 vw and 843 vw, 739 s, 727 s, 693 s, 617 vw, 479 m, 453 m, 422 w and 408 w(sh), 382 vw(sh) and 367 m, 290 vw(br), 255 w and 247 vw(sh), 232 w, 208 w cm^{-1}. Raman bands: 3148 w, 3137 w, 3049 vw, 3014 vw, 2995 vw(sh) and 2987 vw, 2948 vw, 1577 vw, 1478 w, 1437 vw and 1431 vw(sh), 1385 vw(br), 1333 vw, 1305 vw, 1266 vw(br), 1183 w, 1157 w, 1117 w, 1085 s, 1025 s, 999 vs, 987 w(sh), 962 vw, 907 vw, 695 w, 660 s, 618 w, 428 vw, 455 vw, 430 w, 409 vw, 384 vw(sh) and 367 m, 295 vw, 260 vw(sh) and 249 vw(sh) and 233 s, 214 m, 193 s cm^{-1}.

(2-Mercapto-1-ethanolato-S)phenylmercury(II), m.p. 80 °C (recryst. Chloroform). (Found: C. 26.9; H, 2.8; Hg, 56.7; S, 9.0. $C_8H_{10}HgOS$ requires C, 27.1; H, 2.8; Hg, 56.5; S, 9.0%). Infrared abosrption: 3318 m(br) and 3260 m(br), 3069 vw, 3046 vw, 3028 vw, 2950 vw, 2925 vw, 2911 vw, 2866 vw, 1574 vw, 1476 w, 1433 m, 1413 w, 1371 vw, 1329 vw, 1296 w(sh) and 1284 w, 1223 w, 1192 vw, 1164 w and 1152 vw, 1072 vw(sh) and 1053 m, 1021 m, 1002 m, 987 vw, 968 vw, 935 vw, 907 vw, 828 w, 729 s, 699 m, 645 m(br), 478 w, 446 m, 343 s(br), 256 w, 240 w, 212 w cm^{-1}. Raman bands: 3152 m, 3136 m, 3077 w(sh) and 3066 w(sh) and 3050 vs(sh) and 3042 vs and 3024 w(sh), 2990 vw, 2978 w, 2934 vs, 2910 vs, 2870 m, 2807 vw, 2720 vw, 1577 s. 1570 m, 1480 w, 1455 w, 1433 w, 1412 w(br), 1376 vw, 1330 m, 1284 w, 1262 w, 1224 vw, 1192 w, 1164 w, 1076 m, 1064 vw, 1022 s, 999 vs, 985 w, 938 w, 912 w, 855 vw, 830 w, 729 vw, 660 vs, 651 s, 618 m, 478 w, 448 vw, 343 s, 302 vw, 240 s, 214 s, 190 m, 116 m(sh) cm^{-1}.

Stability of Phenylmercury(II) Complexes

The experimental procedure used in these reactions is given in the discussion and Table II, and is similar to that used in studying the stability of PhHg(II) amino-acid complexes [22].

Reactions between Ph_2Hg and Hg(LH), and between Ph_2Hg and LH_3 (LH_3 = $BALH_3$, $DMPH_3$), were carried out similarly, *e.g.* a solution of Ph_2Hg (0.399 g, 1.12 mmol) and $BALH_3$ (0.070 g, 0.56 mmol) in benzene (60 ml) was stirred in a closed vessel at ambient temperature for 7 d. A white insoluble solid (0.014 g, collected by filtration) has IR and Raman spectra indicating the presence of Hg(BALH), occluded benzene, and PhHg (very weak PhHg absorption). The filtrate was evaporated to dryness (rotary evaporator) at ambient temperature, giving a white solid (0.1385 g) with spectra similar to those of insoluble residues from decomposition of $(PhHg)_2BALH$ (Table II), and indicating the presence of Ph_2Hg.

Results and Discussion

Mercury(II) Complexes

Mercury(II) salts react with $BALH_3$ and 1,3-dimercapto-2-propanol ($DMPH_3$) in water to give highly insoluble complexes which are amorphous (absence of X-ray powder diffraction).

TABLE II. Decomposition Reactions of Some Phenylmercury(II) Complexes.[a]

Complex (mg)	Solvent (ml)	Time (hr)	Soluble Product(s) (mg)	Insoluble Product(s)[b] (mg)
$PhHgSCH_2CH_2OH$ (300)	benzene (60)	96	$PhHgSCH_2CH_2OH$, Ph_2Hg (219)	$Hg(SCH_2CH_2OH)_2$ (66)
$PhHgSCH_2CH_2OH$ (301)	methanol[c] (60)	168	$PhHgSCH_2CH_2OH$ (280)	None
$(PhHg)_2BALH$ (78)	acetone (30)	168	Ph_2Hg (39)	Hg(BALH) (30)
$(PhHg)_2BALH$ (300)	benzene (60)	168	Ph_2Hg (121)	Hg(BALH) (160)
$(PhHg)_2BALH$ (701)	benzene[c] (80)	73	Ph_2Hg (275)	[$(PhHg)_2BALH$, Hg(BALH), benzene][d,e] (444)
$(PhHg)_2BALH$ (502)	methanol[c] (80)	243	Ph_2Hg (187)	[$(PhHg)_2BALH$, Hg(BALH)][f] (283)
$(PhHg)_2DMPH$ (300)	benzene (60)	168	Ph_2Hg (130)	[$(PhHg)_2DMPH$, Hg(DMPH), benzene][d,g] (169)
$(PhHg)_2DMPH$ (300)	methanol (60)	113	Ph_2Hg (153)	[$(PhHg)_2DMPH$, Hg(DMPH)][h] (134)

[a] Solutions or suspensions at ambient temperature were stirred magnetically with metal-in-glass stirring bars unless otherwise stated. [b] Parentheses [ ] indicate uncertainty about the constitution of these products. Spectra are consistent with the presence of $(PhHg)_2LH$ and Hg(LH), (L = BALH, DMPH), but do not exclude the presence of a different complex. [c] Teflon stirrer, no interference observable in IR spectra. [d] An IR absorption due to occluded benzene occurs at 676 cm^{-1}. The only intense band in the Raman spectrum of benzene occurs at 992 cm^{-1} [23], and if present in spectra of disproportionation products is masked by a PhHg(II) band at *ca.* 1000 cm^{-1}. [e] Very broad bands at 346–332 cm^{-1} (IR) and 313 cm^{-1} (Raman, *ca.* 75 cm^{-1} wide at half-height). ^{1}NMR spectrum in pyridine (suspension): δ3.2–4.5 m (CH, CH_2 of BALH), δ4.93 (OH), 7–7.8 m (Ph), δ7.36 s (benzene). [f] Very broad bands at 338 (IR) and 313 cm^{-1} (Raman) (*ca.* 70 cm^{-1} wide at half-height). ^1H NMR spectrum in pyridine (suspension): δ3.5–4.5 m (CH, CH_2 of BALH), δ5.0 (OH), δ7.15–7.75 (Ph), absence of resonance associated with benzene[e]. [g] Broad absorption at 358–348 (IR) and 331 cm^{-1} (Raman). [h] Broad bands at 351 (IR) and 324 cm^{-1} (Raman).

$$HgX_2 + BALH_3 \rightarrow Hg(BALH) + 2HX \qquad (1)$$

$$(X = Cl, MeCO_2)$$

$$HgCl_2 + DMPH_3 \rightarrow Hg(DMPH) + 2HCl \qquad (2)$$

Hg(DMPH) is sufficiently soluble in pyridine for molecular weight and ^1H NMR studies. Hg(BALH) is insoluble, but an impure form of Hg(BALH), *2*, which is soluble in pyridine may be isolated from preparations in this solvent:

$$Hg(O_2CMe)_2 + BALH_3 \xrightarrow{\text{pyridine}} \mathit{1} \xrightarrow[\text{acetone}]{\text{pyridine, } BALH_3} \mathit{2} \qquad (3)$$

Solid *1* precipitates on addition of an equimolar amount of $BALH_3$ and has IR and Raman spectra indicating the presence of Hg(BALH), pyridine, and 'acetate'. Repeated washings with methanol or water removes both pyridine and acetate to give insoluble Hg(BALH). Solid *1* dissolves on addition of one mole equivalent of $BALH_3$, and *2* is precipitated on addition of acetone. Solid *2*, Hg(BALH) containing a small amount of pyridine, is sufficiently soluble for ^1H NMR spectra and conductivity studies. Pyridine is removed on washing with water to give insoluble Hg(BALH). Hg(DMPH) may be recrystallized from pyridine to give highly crystalline $Hg(DMPH)py_{1.5}$ which rapidly loses pyridine at ambient temperature.

Mercury–sulphur stretching frequencies in complexes $Hg(SR)_2$ are sensitive to coordination number in the expected way [13], *e.g.* $Hg(SMe)_2$ (linear SHgS, with weak intermolecular Hg•••S interactions [24]) has ν_{as}(SHgS) 337, ν_s(SHgS) 297 cm^{-1}, much higher than $Hg(SBu^t)_2$ (tetrahedral HgS_4 polymer, with bridging sulphur [25]) ν_{as}(SHgS) 172, ν_s(SHgS) 188 cm^{-1} [13]. It has been shown [13] that Hg-

TABLE III. Mercury–Sulphur Vibrations (cm^{-1})

Complex	IR	Raman
A. Mercury(II) Complexes		
	ν_{as}(SHgS)	ν_s(SHgS)
Hg(SMe)$_2$[a]	337 vs[b], 338 vs[c,d]	297 vs[b], 295 s[c], 298 m[d]
Hg(SEt)$_2$[e]	405 s, br or 268 s, br[b]; 268 s[d]	394 vs or 245 vs[b]; 246 s[d]
Hg(SBu^t)$_2$[f]	172 vs, vbr[b]	188 vs[b], 185 vs[d]
Hg(SCH$_2$CH$_2$OH)$_2$	371 s, br	352 m
Hg(SPh)$_2$	365 s, br	344 s
Hg(BALH)	*ca.* 348 m, vbr[b]	*ca.* 298 s, vbr[b]
Hg(DMPH)	353 m, vbr	325 vs
Hg(DMPH)[g]	373 m[h]	339 s
Hg(DMPH)py$_{1.5}$	-[i]	343 vs[j]
B. Organomercury(II) Complexes		
PhHgSMe	335 m	337 vs
PhHgSEt	328 m, vbr[k]	335 m, br
PhHgSPr^i	388 m (?)[l]	[l]
PhHgSBu^t	359 m (?) or 387 m (?)[m]	[m]
PhHgSPh	367 m	367 m
PhHgSCH$_2$CH$_2$OH	343 s, br	343 s
PhHgSCH$_2$CH(NH$_3$)CO$_2$[n]	346 m, br[o]	349 vs[o]
MeHgSMe	333 m[p], 329 m[c]	329 vs[p], 327 w[c]
MeHgSCH$_2$CH(NH$_3$)CO$_2\cdot$H$_2$O[q]	325 mw[r]	326 vs[r]
(PhHg)$_2$BALH	335 s, vbr	338 m, vbr
(PhHg)$_2$DMPH	343 s, br	343 s, br
(PhHg)$_2$DMPH·py	343 s, br	344 m
(MeHg)$_2$BALH	328 m, vbr[s]	328 s, br
(MeHg)$_2$DMPH	341 s	342 vs

[a] Linear structure [24]. [b] From reference [13]. [c] From reference [27]. [d] From reference [28]. [e] Linear strucutre [29]. [f] Tetrahedral 'HgS_4' [25]. [g] Recrystallized from pyridine. [h] Weak absorption at 351 cm^{-1} may also be a ν_{as}(SHgS) mode. [i] Spectrum shows both coordinated and free pyridine, with absorption in the region 300–400 cm^{-1} similar to that of Hg(DMPH) obtained on loss of pyridine (376 m, 354 w and 340 vw(sh) cm^{-1}). [j] Crystals in a sealed tube to prevent loss of pyridine. [k] Measured at *ca.* 20 °C, as PhHgSEt melts in the IR beam to give ν(Hg–S) 316 m, br. [l] Weak Raman band at 399 cm^{-1}. [m] Weak Raman bands at 392 and 362 cm^{-1}. [n] Linear structure [30]. [o] From reference [22]. [p] From reference [31]. [q] Linear structure [32, 33]. [r] From reference [33]. [s] As a thin film of gluey solid.

(BALH) has ν(SHgS) modes appropriate for the linear, polymeric structure (–Hg–S~S–)$_n$ (n > 1).

I

rather than alternative structures involving higher coordination numbers, or non-linear mercury in the cyclic, monomeric, structure usually drawn for Hg(BALH) [12, 26]. Mercury–sulphur stretching modes in IR and Raman spectra of Hg(SPh)$_2$, Hg(SCH$_2$CH$_2$OH)$_2$, and all three DMPH$_3$ complexes are also in the region found for Hg(SMe)$_2$ and Hg(BALH) (Table III).

Crystalline Hg(DMPH)py$_{1.5}$ has Raman spectra indicating coordination of pyridine*, but with ν_s(SHgS) similar to that of the other forms of Hg(DMPH). Pyridine is readily lost from the complex (above), and is assumed to be weakly coordinated with presence of a polymeric structure similar to that of Hg(DMPH). On loss of pyridine Hg(DMPH) has sharp IR and Raman spectra, unlike amorphous Hg(DMPH) and Hg(BALH) which have broad bands with spectra poorly resolved below *ca.* 200 cm^{-1}.

The only soluble dithiol complexes suitable for molecular weight studies are those of DMPH$_3$ (Table IV). The complex isolated from pyridine is dimeric in pyridine, and may have a ring structure S–Hg–S~S–Hg–S to maintain HgS$_2$ geometry, or a structure with

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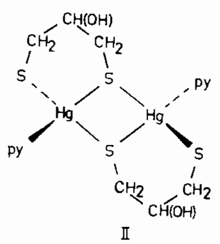
*Crystals of the complex in a sealed tube, to prevent loss of pyridine, have bands of pyridine shifted from values for the free ligand, *e.g.* bands of pyridine at 1028 and 990 cm^{-1} are raised to 1038 and 1009 cm^{-1} respectively. Pyridine is lost on forming Nujol mulls for measurement of IR spectra (4000–200 cm^{-1}): *e.g.* absorptions of pyridine occur at 992 and 600 cm^{-1} (pyridine as a thin film has absorptions at 990 and 601 cm^{-1}) together with absorptions raised in the usual manner [34] on coordination at 998 and 616 cm^{-1}.

TABLE IV. Molecular Weight Data[a].

Complex	Solvent	Calcd.	Found	Found/Calcd.
$Hg(SMe)_2$	pyridine[b]	295	303 (1.27), 303 (0.95)	1.03, 10.3
$Hg(SEt)_2$	chloroform pyridine	323	328 (0.97), 319 (0.32) 330 (0.83), [327][c]	1.02, 1.00 1.02
$Hg(SBu^t)_2$	chloroform pyridine	379	387 (0.64), 371 (0.35) 383 (0.71), [371][c]	1.02, 0.98 1.01
$Hg(SPh)_2$	chloroform	419	422 (0.54), 415 (0.64)	1.01, 0.99
$Hg(SCH_2CH_2OH)_2$	pyridine[b]	355	342 (0.63), 335 (0.84)	0.96, 0.94
Hg(DMPH)	pyridine[b]	323	567 (0.96), 540 (1.04), 517 (1.15), 474 (0.91), 454 (0.88), 445 (1.18)	1.76, 1.67, 1.60, 1.47, 1.41, 1.38
Hg(DMPH)[d]	″ [b]	323	652 (1.22), 646 (1.14), 633 (0.75)	2.02, 2.00, 1.96
PhHgSMe	chloroform	325	330 (0.81), 329 (0.77)	1.02, 1.01
PhHgSEt	″	339	348 (0.87), 347 (0.84)	1.03, 1.02
$PhHgSPr^i$	″	353	359 (1.13), 346 (0.78)	1.02, 0.98
$PhHgSBu^t$	″	367	369 (0.81), 366 (0.75)	1.00, 1.00
PhHgSPh	″	387	408 (0.77), 398 (0.83)	1.05, 1.03
$PhHgSCH_2CH_2OH$	″ pyridine	355	371 (1.30), 370 (0.70) 368 (0.62), 364 (0.89)	1.04, 1.04 1.04, 1.02
$(PhHg)_2BALH$	pyridine[b]	678	678 (4.70), 649 (0.76)	1.00, 0.96
$(PhHg)_2DMPH$	″ [b]	678	696 (0.55), 675 (0.40) 631 (0.50), 610(0.44)	1.03, 1.00 0.93, 0.90
$(PhHg)_2DMPH{\cdot}py$	pyridinc[b]	757[e]	784 (0.45), 717 (0.40)	1.04, 0.95
$(MeHg)_2DMPH$	″ [b]	554	535 (0.71), 532 (0.95)	0.97, 0.96

[a] Osmometric in chloroform (37 °C) and pyridine (60 °C). Concentrations in mol $dm^{-3} \times 10^2$, based on monomeric molecular weights, are given in parentheses ( ). [b] Insoluble in chloroform. As pyridine is a non-ideal solvent accurate molecular weights are not expected. However, complex formation with pyridine, *e.g.* $(PhHg)_2DMPH{\cdot}py$, as one form of non-ideal behaviour is not expected to affect the accuracy of determinations, as the colligative property determined is the number of molecules formed in solution per solid complex added, and this will not be altered by interaction with the solvent which is present in vast excess. [c] From reference [28]. [d] Recrystallized from pyridine. [e] The calculated molecular weight is that expected for dissolution of a 1:1 mixture of $(PhHg)_2DMPH$ and pyridine in pyridine.

higher coordination number for mercury, *e.g.* II, related to solid $Hg(SBu^t)_2$.



II

¹H NMR spectra are consistent with a dimeric structure (II) as there is a single CH resonance, but very broad methylene resonance (Table V). Several samples of amorphous Hg(DMPH) have molecular weights intermediate between monomeric and dimeric values, suggesting the presence of a monomer–dimer equilibrium, and NMR spectra have a single CH resonance and two broad methylene resonances. Although amorphous and crystalline Hg(DMPH) have different vibrational spectra in the metal–ligand region they are expected to adopt identical structures in solution, and thus lower molecular weights for the amorphous form may result from the presence of impurities.

The pyridine soluble form of Hg(BALH), *2*, has poor elemental analysis and is thus unsuitable for molecular weight determinations. ¹H NMR spectra are as expected for presence of 'BALH' but provide no indication of structure, although a dimeric structure and/or a monomeric structure $Hg(BALH)py_x$ is possible.

TABLE V. ^{1}H NMR Data for the complexes[a].

Complex	Solvent	RHg[b]	$\lvert J(^1H-^{199}Hg)\rvert$[c]	Thiol Protons[d]
A. Phenylmercury(II) Complexes				
PhHgSMe	$CDCl_3$	7.1–7.6 m	149	2.47 s
	C_5D_5N	7.2–7.7 m	148	2.45 s
PhHgSEt	$CDCl_3$	7.1–7.6 m	148	1.41 t (Me, J 7.5 Hz) 3.08 q (CH_2, J 7.5 Hz)
	C_5D_5N	7.2–7.7 m	148	1.40 t (Me, J 7.5 Hz) 3.06 q (CH_2, J 7.5 Hz)
$PhHgSPr^i$	$CDCl_3$	7.1–7.7 m	146	1.43 d (Me, J 7 Hz), 3.77 s (CH, J 7 Hz)
	C_5D_5N	7.2–7.7 m	144	1.48 d (Me, J 7 Hz), 3.75 s (CH, J 7 Hz)
$PhHgSBu^t$	$CDCl_3$	7.1–7.5 m	148	1.57 s
	C_5D_5N	7.15–7.7. m	145	1.60 s
PhHgSPh	$CDCl_3$	7.05–7.5 m	155	7.12 m
	C_5D_5N	7.1–7.7 m	158	7.15 m
$PhHgSCH_2CH_2OH$	$CDCl_3$	7.1–7.65	149[e]	2.74 br (OH), 3.08 t (CH_2S, J 5 Hz), 3.78 m (CH_2O)
	C_5D_5N	7.1–7.7 m	150	3.29 t (CH_2S, J 5 Hz), 4.06 t (CH_2O, J 5 Hz), 4.9 br (OH)[f]
$(PhHg)_2BALH$	C_5D_5N	7.1–7.7 m	~150[g]	3.83 m(2H), 4.17 m(3H), 6.99 s(OH)[f]
$(PhHg)_2DMPH$	C_5D_5N	7.1–7.7 m	147	3.6 br (CH_2), 4.38 br (CH), 6.3 vbr (OH)[f]
$(PhHg)_2DMPH{\cdot}py$	C_5D_5N	7.1–7.7 m	149	3.61 m (CH_2), 4.41 t [CH, J (CH, CH_2) 5 Hz]
Ph_2Hg	$CDCl_3$	7.2–7.6 m	101	–
	C_5D_5N	7.0–7.8 m	105	–
B. Methylmercury(II) Complexes				
$(MeHg)_2BALH$	C_5D_5N	0.73 s	169	3.65 m [2H], 4.1 m [3H], 6.35 br [OH][f]
$(MeHg)_2DMPH$	C_5D_5N	0.68 s	161	3.58 d [CH_2, J(CH, CH_2) 5 Hz], 4.28 t [CH, J(CH, CH_2) 5 Hz], 6.77 br (OH)[f]
C. Mercury(II) Complexes				
		Thiol Protons		
$Hg(SMe)_2$	C_5D_5N	2.44 s		
$Hg(SEt)_2$	$CDCl_3$	1.43 t (J 7 Hz), 3.11 q (J 7 Hz)		
	C_5D_5N	1.42 t (J 7 Hz), 3.06 q (J 7 Hz)		
$Hg(SBu^t)_2$	$CDCl_3$	1.55 s		
	C_5D_5N	1.67 s		
$Hg(SPh)_2$	$CDCl_3$	7.19 m ($^{m,p}H$), 7.39 m (^oH)		
	C_5D_5N	7.12 m ($^{m,p}H$), 7.78 m (^oH)		
$Hg(SCH_2CH_2OH)_2$	C_5D_5N	3.28 t (CH_2S, J 6 Hz), 4.07 t (CH_2O, J 6 Hz), 7.1 br (OH)[f]		
Hg(BALH)[h]	C_5D_5N	3.65 mb (2H)[i], 4.1 mb (3H)[i], 6.7 s (OH)[f]		
Hg(DMPH)	C_5D_5N	3.4 br and 4.15 br (CH_2), 4.38 (CH), 6.73 (OH)[f]		
Hg(DMPH)	C_5D_5N	3.2–3.8 m (CH_2), 4.35 m (CH), 4.96 (OH)[f]		

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[a] Measured at 100 MHz with tetramethylsilane as internal reference, chemical shifts are p.p.m. downfield from TMS. Integrated intensities are approximately as expected for formulae presented (chloroform and pyridine overlap with aromatic resonances). [b] Ph resonances are broad multiplets and resemble the spectrum of PhHgCl drawn in reference 35. [c] For PhHg(II) complexes

(Continued overleaf)

TABLE V *(continued)*.

coupling occurs between ^{199}Hg and the *ortho* protons. The sign of the coupling constant is assumed to be positive for $J(^{ortho}H-^{199}Hg)$ [36], and negative for $J(^{1}H-^{199}Hg)$ for the MeHg(II) group [37]. $J(^{ortho}H-^{meta}H)$ 6–8 Hz, resolved only for the sideband furthest downfield, except for Ph_2Hg which has both resolved. [d]$HSCH_2CH_2OH$ (in pyridine): 1.43 s (SH), 2.85 t [CH_2S, J 6 Hz], 3.95 m (CH_2O), 6.61 t [OH, J(OH, CH_2O) 5 Hz]; $BALH_3$ (pyridine): 2.5 br (SH), 3.12 br (CH_2S), 3.25 br (CH), 4.05 m (CH_2O), 6.63 br (OH); $DMPH_3$ (pyridine): 2.15 br (SH), 2.88 br (CH_2), 3.95 m (CH), 6.8 br (OH). [e]$PhHgSCH_2CH_2OH$ dissolves in $CDCl_3$, and then deposits a fine precipitate of $Hg(SCH_2CH_2OH)_2$ (IR identification) in the NMR tube. A spectrum of the solution shows the presence of *ca.* equal amounts of $PhHgSCH_2CH_2OH$ and Ph_2Hg [estimated from relative intensities of $J(^{ortho}H-^{199}Hg)$]. Ph_2Hg, in this solution, has $J(^{ortho}H-^{199}Hg)$ 102 Hz, $J(^{ortho}H-^{meta}H)$ 7 Hz. [f]Hydroxyl resonances are sensitive to the presence of water, and values given are those observed furthest downfield. On addition of D_2O these resonances shift upfield to 5.7–5.8 p.p.m. [g]The sideband of lowest chemical shift is obscured by the OH resonance. On addition of D_2O both sidebands are visible, but broad, allowing an estimate of $J(^{ortho}H-^{199}Hg)$. [h]Complex *2* prepared from mole ratio $Hg(O_2CMe)_2:BALH_3$ of 1:2 in pyridine. [i]Overlapping, broad, ligand resonances have intensity ratios 1:4 ($CH:CH_2O$, CH_2S) on addition of D_2O. [j]Recrystallized from pyridine.

All of the thiolates $Hg(SR)_2$, except insoluble $Hg(SMe)_2$ and $Hg(SCH_2CH_2OH)_2$, are monomeric in the non-coordinating solvent chloroform (Table IV). Monomeric behaviour is consistent with the linear structure of solid $Hg(SEt)_2$, but is surprising for $Hg(SBu^t)_2$ which has tetrahedral mercury with a polymeric structure in the solid state.

In water at pH 7.5 Hg(BALH) dissolves on addition of excess $BALH_3$, suggesting [11] formation of $[Hg(BALH)_2]^{2-}$. The pyridine soluble form of Hg(BALH), *2*, and Hg(DMPH) form very weakly conducting solutions in pyridine, having molar conductivities 6.2 and 1.81 ohm^{-1} mol^{-1} cm^2 respectively ([pyH] [ClO_4], 98 ohm^{-1} mol^{-1} cm^2). Addition of one mole equivalent of dithiol results in small increases in conductivity (*2* + $BALH_3$, 8.6; Hg(DMPH) + $DMPH_3$, 12.4 ohm^{-1} mol^{-1} cm^2) and, on addition of ligand to aqueous *suspensions* of *2* and Hg(DMPH) conductivities also increase (*2*, '8.6', increases to '12.0'; Hg(DMPH), '12.3', increases to '53.4 ohm^{-1} mol^{-1} cm^2')*. These results indicate that some ionization is occurring on addition of excess ligand, presumably *via*

$$[Hg(LH)py_x]_n + LH_3 \rightleftharpoons [Hg(LH)_2]^{2-} + 2[pyH]^+ + (x-2)\,py \qquad (4)$$

$$(n = 2 \text{ for } LH_3 = DMPH_3)$$

in pyridine, and

$$Hg(LH)(solid) + LH_3 \rightleftharpoons [Hg(LH)_2]^{2-} + 2H^+ \qquad (5)$$

in water. As blood has pH ~7.4 ionic complexes may be formed more readily *in vivo*; and neutral complexes $[Hg(BALH)L_x]_n$, related to $[Hg(DMPH)py_x]_2$ in pyridine, may be formed in less polar media, *e.g.* lipid tissue.

Organomercury(II) Complexes

Phenylmercuric acetate reacts with the dithiols in water to give solid complexes $(PhHg)_2LH$

$$2PhHgO_2CMe + nBALH_3 \xrightarrow{H_2O} (PhHg)_2BALH + (n-1)BALH_3 + 2MeCO_2H \qquad (6)$$

$$(n = 1, 2)$$

$$2PhHgO_2CMe + DMPH_3 \xrightarrow{H_2O} (PhHg)_2DMPH + 2MeCO_2H \qquad (7)$$

$(PhHg)_2DMPH$ crystallizes from pyridine as an adduct of composition $(PhHg)_2DMPH \cdot py$. The dithiols react similarly with methylmercuric acetate. $(MeHg)_2DMPH$ is crystalline from ethanol; $(MeHg)_2BALH$ is initially formed as a 'gluey white solid' from benzene, but after washing with benzene a white powder is obtained which slowly changes to a colourless oil within 24 hr. Both the powdered and oily forms have identical NMR and vibrational spectra, and are insoluble in water, benzene, and chloroform but soluble in pyridine and dimethylsulphoxide.

The related model thiol complexes PhHgSR (R = Me, Et, Pr^i, Bu^t, Ph, CH_2CH_2OH) crystallize from ethanol solutions of $PhHgO_2CMe$ and RSH; the colligative and spectroscopic properties of these simple complexes have not been reported to date.

Absence of ν(S–H) and presence of ν(O–H) absorption in IR spectra of dithiol complexes establishes the loss of two protons on complex formation and the presence of mercury–sulphur bonding. The complexes may have linear C–Hg–S coordination (III–V) as found in crystallographic studies of related complexes $MeHgSCH_2CH(NH_3)CO_2 \cdot H_2O$ [32, 33], $PhHgSCH_2CH(NH_3)CO_2$ [30], and $PhCH_2HgSCPh_3$ [38], although higher coordination numbers are possible, *e.g.* related alkoxides form dimers (VI) in boiling benzene [39] and PhHg(S-2,6-Me_2Ph) has

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*As these values are for saturated solutions the concentration of Hg(II) in solution is much lower than that used in calculation of 'molar conductivities', and hence the conductivities per mole of Hg(II) *in solution* are much higher.

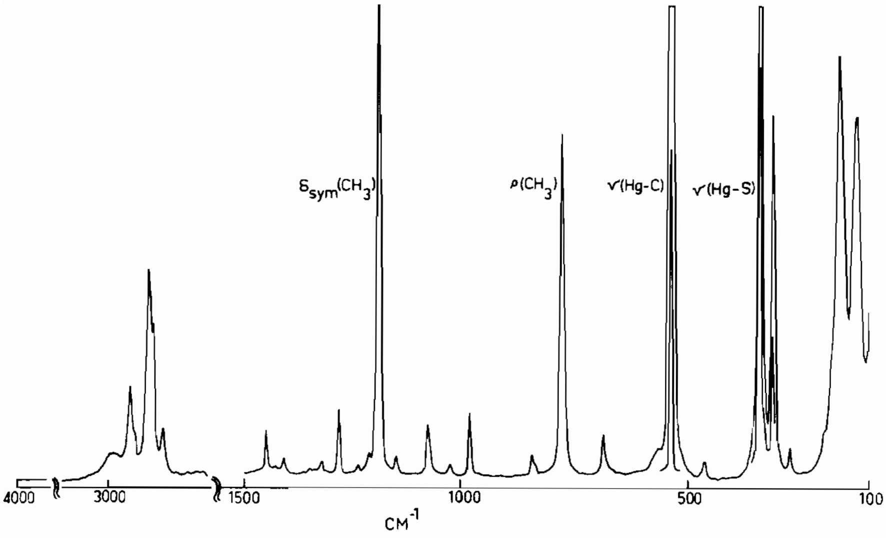
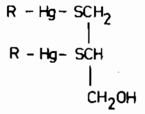


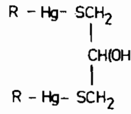
Figure 1. Raman spectrum of $(MeHg)_2DMPH$, $MeHgSCH_2CHOHCH_2SHgMe$, with assignment of ν(Hg–S) and the most intense bands of the MeHg(II) group by comparison with the assignment for MeHgSMe [27, 31].

weak intermolecular Hg···S bonding* with reduction of the C–Hg–S angle to 172° [40].



III

$(RHg)_2BALH (R = Me, Ph)$

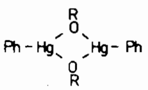


IV

$(RHg)_2DMPH (R = Me, Ph)$

R – Hg – SR′

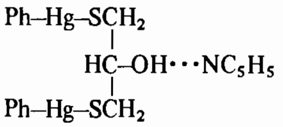
V



VI

Assignment of ν(Hg–S) is fairly straightforward for most of the complexes on comparison of IR and Raman spectra (Table III, Figure 1). All of the RHg(II) derivatives, except for $PhHgSPr^i$ and $PhHgSBu^t$, have medium to high intensity Raman bands attributable to ν(Hg–S) in the region 250–400 cm^{-1}, and IR spectra have absorption within experimental error of these Raman bands (as required for structures III–V). The similarity between ν(Hg–S) values for these complexes and values for $MeHgSCH_2CH(NH_3)CO_2 \cdot H_2O$ and $PhHgSCH_2CH(NH_3)CO_2$ indicate structures III–V for the solid state. However, all of the PhHg(II) complexes have Raman bands attributable [43] to 'X-sensitive' modes of the PhHg(II) group in the ranges 240–226, 216–206, and 196–185 cm^{-1} which could obscure Hg–S modes for structures involving higher coordination numbers for mercury. This is particularly so for $PhHgSPr^i$ and $PhHgSBu^t$ which have weak Raman bands in the region expected for linear geometry.

The pyridine adduct, $(PhHg)_2DMPH \cdot py$, has ν(Hg–S) unaltered from that of $(PhHg)_2DMPH$ suggesting that pyridine is not coordinated to mercury, even though IR absorptions of pyridine are shifted on adduct formation in a manner characteristic [34] of coordination of pyridine to metal ions and formation of pyH^+*. Hydrogen-bonding as in VII is also expected to cause similar shifts in absorptions of pyridine, and consistent with this possible structure ν(O–H) is lowered *ca.* 300 cm^{-1} on adduct formation to *ca.* 3200–2800 cm^{-1}.



$$\begin{array}{l} Ph{-}Hg{-}SCH_2 \\ \quad\quad\quad | \\ \quad\quad HC{-}OH \cdots NC_5H_5 \\ \quad\quad\quad | \\ Ph{-}Hg{-}SCH_2 \end{array}$$

VII

With the hydroxyl group deuterated, by crystallization of the adduct from pyridine/D_2O, ν(O–D) occurs at 2200 cm^{-1}.

The complexes PhHgSR (R = Me, Et, Pr^i, Bu^t, Ph, CH_2CH_2OH) dissolve in chloroform to give

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*Hg···S 3.18 Å, sum of van der Waals radii 3.35 (Hg 1.5 [41], S 1.85 [42]) or 3.58 Å using Grdenić's upper limit of 1.73 Å for the radius of mercury [41].

**E.g.* Absorptions of pyridine at 601 and 403 cm^{-1} (thin film) are raised to 620 and 408 cm^{-1} on adduct formation.

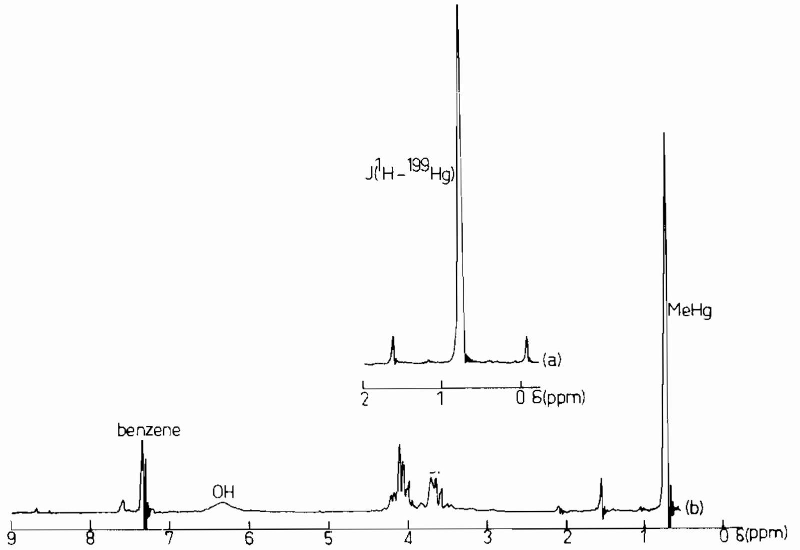

Figure 2. ^1H NMR spectrum of $(MeHg)_2BALH$, $MeHgSCH_2CH(SHgMe)CH_2OH$, in C_5D_5N. (a) Without TMS. (b) With TMS as internal reference.

monomers at 37 °C (Table IV). In contrast PhHg(II) alkoxides form dimers in boiling benzene [39],

$$2PhHgOR \rightleftharpoons (PhHgOR)_2 \qquad (8)$$

e.g. mol wt. found/mol wt. calcd for monomer: 1.99 (R = Me), 1.75 ($R = Pr^i$).

Organomercury(II) derivatives of $BALH_3$ and $DMPH_3$ are insoluble in common organic solvents, but soluble in pyridine and dimethylsulphoxide. The PhHg(II) complexes and $(MeHg)_2DMPH$ are monomeric in pyridine at 60 °C.

Coupling constants $J(^1H–^{199}Hg)$ for the MeHg(II) group in $BALH_3$ and $DMPH_3$ derivatives, 169 (Figure 2) and 161 Hz(py) respectively, are within the range previously noted for MeHg(II) thiolates (155–196 Hz) [44, 45] and are similar to that of the closely related cyclohexyl thiolate, 157 Hz(py) [44] (Table V). For the PhHg(II) thiolates coupling constants $J(^{ortho}H–^{199}Hg)$ have not been previously reported, and we find that they occur in the range 144–155 Hz, lower than in the corresponding alkoxides (174–190 Hz) [39]. A similar trend occurs for MeHg(II) thiolates and alkoxides [44].

Stability of Phenylmercury(II) Thiolates

Early attempts to prepare a PhHg(II) derivative of $BALH_3$ in benzene, methanol, or ethanol were frustrated by isolation of insoluble, amorphous, products of analytical composition intermediate between the expected complex, $(PhHg)_2BALH$, and Hg(BALH). $BALH_3$ has low solubility in water but it was only on use of this solvent to more closely simulate biological media that $(PhHg)_2BALH$ was isolated.

The stability of $(PhHg)_2BALH$ under mild conditions was studied by stirring a slurry of the complex in acetone, benzene, or methanol for long periods of time at ambient temperature*. The reaction

$$(PhHg)_2BALH \longrightarrow Ph_2Hg + Hg(BALH) \qquad (9)$$

occurs in acetone and benzene, and apparently in methanol, but is incomplete in methanol and often incomplete in benzene, even after 1 week (Table II).

A similar reaction occurs for $(PhHg)_2DMPH$, and the soluble model complex, $PhHgSCH_2CH_2OH$, partially decomposes in benzene but not in methanol.

$$2PhHgSCH_2CH_2OH \xrightarrow{\text{benzene}} Ph_2Hg + Hg(SCH_2CH_2OH)_2 \qquad (10)$$

Reaction products from $PhHgSCH_2CH_2OH$ are readily identified by IR and Raman spectroscopy, and solvent soluble Ph_2Hg is isolated in pure form from reactions of the dithiol complexes on filtration and evaporation of solvents. As all products are obtained as crystals (Ph_2Hg) or fine white powders, absence of decomposition to metallic mercury is assumed.

The relative intensities of 'PhHg(II)' absorptions in spectra of insoluble products from incomplete decompositions indicate that the extent of decomposition to form Ph_2Hg varies. IR and Raman spectra above *ca.* 400 cm^{-1} are identical with that expected for a mixture of $(PhHg)_2LH$ and Hg(LH) (LH = BALH, DMPH), and absorptions attributable to Hg–S stretching (<400 cm^{-1}) often differ from

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*Metal-in-glass magnetic stirrers were used as we have found that on stirring for long periods in benzene Teflon stirrers give rise to additional absorption in IR spectra of insoluble products at ~1240 m (br), 1156 s, 638 w, 625 w, and 501 m cm^{-1}.

that of $(PhHg)_2LH$ and Hg(LH) but are broad enough to be consistent with the presence of both. Solids with similar spectra precipitate immediately on addition of the dithiols to solutions of phenylmercuric acetate in benzene or ethanol. These solids have variable microanalyses (C,H,S,Hg) but correspond to *ca.* 1:1 ratio of $(PhHg)_2LH$:Hg(LH), and thus the possibility that these insoluble products contain intermediate complexes such as '$(PhHg–S{\sim}S–)_2Hg$' cannot be eliminated. The decomposition reactions are irreversible, as there is no reaction between Ph_2Hg and Hg(LH) in benzene (1 week).

Berlin *et al.* [4] suggested that formation of a complex between MeHg(II) and British anti-Lewisite is responsible for redistribution of mercury on $BALH_3$ treatment. They assumed that the complex would have low polarity, allowing penetration of the blood–brain barrier to give higher mercury content of the brain [4]. Consistent with this view we find that complexes $(RHg)_2BALH$ (R = Me, Ph) are formed under very mild conditions, and are insoluble in water but soluble in polar organic solvents (pyridine and dimethylsulphoxide).

The relevance of Ph_2Hg formation from $(PhHg)_2$-BALH is difficult to assess. Apart from uncertainty in estimation of *in vivo* behaviour of $(PhHg)_2BALH$ from chemical studies, the toxicity, bodily distribution on poisoning, and stability of Ph_2Hg *in vivo* are unknown. Preliminary results in our laboratories indicate that Ph_2Hg, when injected intraperitoneally into rats, adopts a different bodily distribution initially (5–20 min) than $HgCl_2$ or $PhHgO_2CMe$, with a much higher mercury content in the brain [46], presumably resulting from its lower polarity and higher lipid solubility. PhHg(II) complexes of L-cysteine, and the antidote D-penicillamine, also decompose to Ph_2Hg so that *in vivo* decomposition of PhHg(II) toxins to Ph_2Hg may be a general phenomenon [22]. The rate of decomposition of $(PhHg)_2$-BALH in various bodily organs, if decomposition occurs *in vivo*, is also important as PhHg(II) compounds are degraded to inorganic mercury in a few days after administration to animals [47]. In addition, we have found that Ph_2Hg reacts slowly with $BALH_3$ and $DMPH_3$ to give Hg(LH), together with residues having similar spectra to those obtained on decomposition of $(PhHg)_2LH$. However, for both Ph_2Hg and $(PhHg)_2BALH$ physical properties, *e.g.* solubility and polarity, are assumed to be more important than *in vivo* stability towards decomposition to inorganic mercury, as bodily distribution of chemicals may be rapid, *e.g.* different bodily distributions of mercury from $HgCl_2$, $PhHgO_2CMe$, and Ph_2-Hg 5 min after injection into rats [46]; and mercury vapour is oxidized to Hg(II) in *ca.* 30 sec in blood, but this is sufficient time for mercury (from vapour) to achieve a *ca.* ten-fold higher accumulation in the brain than from inorganic mercury poisoning [48,49].

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