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PHENYLMERCURY DITHIOLATES. THE CRYSTAL AND MOLECULAR STRUCTURES OF $(C_6H_5)Hg(S_2COR)$ (R = Me; ^iPr AND $(C_6H_5)Hg(S_2CNEt_2)$)

EDWARD R.T. TIEKINK

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, South Australia, 5001 (Australia)

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Summary

The preparation, spectroscopic characterization, and X-ray structures of a number of phenylmercury dithiolates (xanthate and dithiocarbamate) are reported. The solid state structures feature monodentate dithiolate ligands and approximate linear geometries about the mercury atoms. The Hg–S distances fall within the relatively narrow range of 2.374(4)–2.388(2) Å in these compounds. The presence of additional Hg $\cdots$ S contacts also characterize these structures; the number and strength of these interactions depending on the nature of the dithiolate ligand. Crystals of $PhHg(S_2COMe)$ are monoclinic, space group $C2/c$ with unit cell dimensions a 37.73(2), b 4.825(1), c 12.686(1) Å, β 101.21(2)° with $Z = 8$; $PhHg(S_2CO^iPr)$ crystallizes in the monoclinic space group $P2_1/a$ with a 13.678(5), b 21.347(7), c 14.570(6) Å, β 114.99(2)° and $Z = 12$; and crystals of $PhHg(S_2CNEt_2)$ are triclinic, $P\bar{1}$, with cell parameters a 9.959(2), b 12.359(4), c 13.098(2) Å, α 65.53(2), β 65.81(2), γ 81.26(2)° and $Z = 4$. Refinement on 777 reflections [with $I \geq 3.0\sigma(I)$] converged with final R 0.096 and R_w 0.090 for $PhHg(S_2COMe)$; 2888 reflections [$I \geq 2.5\sigma(I)$], R 0.033, R_w 0.038 for $PhHg(S_2CO^iPr)$; 2675 reflections [$I \geq 2.5\sigma(I)$], R 0.033, R_w 0.038 for $PhHg(S_2CNEt_2)$.

Introduction

The 1,2-phenylenedimercury dixanthate compound, $Ph[Hg(S_2COMe)]_2$, was recently isolated and characterized by X-ray crystallography as an unexpected product of the 1:1 reaction between PhHgCl and the potassium salt of $^-S_2COMe$ [1]. Further studies of this reaction are now reported herein. The original interest in these dithiolate compounds focussed on the mode of coordination adopted by the dithiolate ligands. In addition to the common bidentate and monodentate coordination modes of the xanthate ligand, an intermediate or asymmetric mode has also been noted in a number of organometallic derivatives of the Main Group elements [1]. In order to determine whether the observed coordination modes found in these

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systems can be related to stereochemical or electronic effects, a number of organometallic derivatives containing the xanthate ligand have been prepared and structurally characterized. The phenylmercury xanthates form one such series and the closely related dithiocarbamate complex has been included for comparison.

Experimental

Preparations

The procedure employed to prepare each of the compounds was similar and thus only details of the preparation of PhHg(S_2COMe) will be given. To a stirred solution of PhHgCl (0.5 g, 50 ml CH_2Cl_2) was added the stoichiometric quantity of K^+ $^-S_2$COMe (20 ml H_2O). After 1 h of stirring the organic layer was separated and dried over Na_2SO_4; crystals were deposited as the volume was reduced. In each case the bulk product was recrystallized from CH_2Cl_2 solution. This procedure yielded crystals suitable for the diffraction studies for the xanthate derivatives and crystals of PhHg(S_2CNEt_2) were obtained from the slow evaporation of a benzene/(80–100 °C) petroleum spirit solution of the compound.

PhHg(S_2COMe). M.p. 120–121°C, characteristic C–O and C–S infrared absorptions: 1215, 1205 and 1050, 1020 cm^{-1} respectively; NMR measurements in $CDCl_3$ solution: ^1H δ (CH_3) 4.10, δ (Ph) 7.25–7.50 ppm.

PhHg(S_2COEt). M.p. 120–121°C, infrared absorptions: 1220, 1215 and 1035,

TABLE 1

CRYSTAL DATA

	PhHg(S_2COMe)	PhHg(S_2CO^{i}Pr)	PhHg(S_2CNEt_2)
Formula	$C_8H_8HgOS_2$	$C_{10}H_{12}HgOS_2$	$C_{11}H_{15}HgNS_2$
Formula wt.	384.9	412.9	426.0
Crystal system	monoclinic	monoclinic	triclinic
Space group	$C2/c$ (C_{2h}^6, No. 15)	$P2_1/a$ (C_{2h}^5, No. 14)	$P\bar{1}$ (C_i^1, No. 2)
a (Å)	37.73(2)	13.678(5)	9.959(2)
b (Å)	4.825(1)	21.347(7)	12.359(4)
c (Å)	12.686(1)	14.570(6)	13.098(2)
α (°)	90	90	65.53(2)
β (°)	101.21(2)	114.99(2)	65.81(2)
γ (°)	90	90	81.26(2)
V (Å^3)	2011.9	3855.9	1338.2
Z	8	12	4
D_x (g cm^{-3})	2.542	2.134	2.114
$F(000)$	1408	2304	800
μ(Mo-K_α) (cm^{-1})	156.20	122.26	117.41
Transmission factors	0.1865–0.0551	0.2605–0.0153	0.1322–0.0107
Reflections meas.	1656	4521	3765
Theta range, deg.	1–21	1–21	1–22.5
Unique reflections	1087	4150	3491
Criterion of obs.	$I \geq 3.0\sigma(I)$	$I \geq 2.5\sigma(I)$	$I \geq 2.5\sigma(I)$
Observed reflections	777	2888	2675
R	0.096	0.033	0.033
g	0.040	0.008	0.003
R_w	0.090	0.038	0.038

1020(sh), 1000 cm^{-1}; NMR: δ (CH_3) 1.48, δ(CH_2) 4.55, δ(Ph) 7.25–7.55 ppm.

PhHg(S$_2$CO^{i}Pr). M.p. 76–77°C, infrared absorptions: 1235, 1210 and 1020 cm^{-1}; NMR: δ (CH_3) 1.39, δ (CH) 5.50, δ (Ph) 7.25–7.50 ppm.

PhHg(S$_2$CNEt$_2$). M.p. 104–105°C, characteristic C–N and C–S infrared absorptions: 1490, 1470 and 995, 980 cm^{-1}; NMR: δ (CH_3) 1.35, δ (CH_2) 3.85, δ (Ph) 7.20–7.50 ppm.

Crystallography

Intensity data for the three compounds were measured at room temperature on an Enraf–Nonius CAD4F diffractometer, fitted with Mo-K_α radiation, with the use of the ω–2θ scan technique. No decomposition of the crystals was noted during

TABLE 2

FRACTIONAL ATOMIC COORDINATES FOR PhHg(S_2COMe)

Atom	x	y	z
Hg	0.11415(4)	0.19748(34)	0.24320(10)
S(1)	0.0629(3)	−0.1346(29)	0.1915(7)
S(2)	0.0958(3)	0.0007(29)	−0.0021(7)
C(1)	0.0647(9)	−0.1587(68)	0.0547(25)
O(1)	0.0345(7)	−0.2905(51)	0.0060(20)
C(2)	0.0286(10)	−0.3526(79)	−0.1151(29)
C(3)	0.1552(7)	0.5056(61)	0.2977(22)
C(4)	0.1769(10)	0.5615(96)	0.2208(29)
C(5)	0.2094(11)	0.7860(76)	0.2592(32)
C(6)	0.2170(12)	0.8735(88)	0.3695(35)
C(7)	0.1992(14)	0.7447(93)	0.4366(43)
C(8)	0.1667(11)	0.5780(94)	0.4037(30)

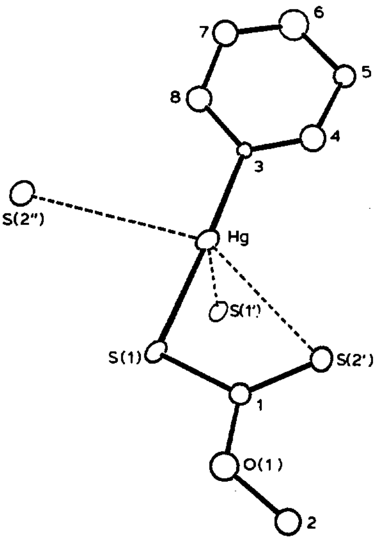

Fig. 1. The numbering scheme used for PhHg(S_2COMe); atoms otherwise not indicated are carbons.

their respective data collections. Corrections were applied for Lorentz and polarization effects and for absorption with the use of an analytical procedure [2]. Relevant crystal data are listed in Table 1.

The heavy-atom technique was used to solve the structures of PhHg(S_2COMe) and PhHg(S_2CNEt$_2$) and the direct-methods program MITHRIL [3] was employed for PhHg(S_2CO^{i}Pr). The structures were refined by a full-matrix least-squares

TABLE 3

FRACTIONAL ATOMIC COORDINATES FOR PhHg(S_2CO^{i}Pr)

Atom	*x*	*y*	*z*
Hg(1)	0.71290(4)	0.23303(2)	0.37030(4)
Hg(2)	0.47287(4)	0.43523(2)	0.38127(4)
Hg(3)	0.56146(4)	0.26164(2)	0.55232(4)
S(1)	0.8057(3)	0.2654(1)	0.5415(3)
S(2)	0.7138(3)	0.3802(2)	0.4163(3)
C(1)	0.7886(9)	0.3464(6)	0.5251(10)
O(1)	0.8431(7)	0.3731(4)	0.6132(7)
C(2)	0.8449(12)	0.4431(7)	0.6224(13)
C(3)	0.8613(15)	0.4557(9)	0.7287(16)
C(4)	0.9387(14)	0.4641(9)	0.5964(15)
S(3)	0.5462(3)	0.4172(2)	0.5593(3)
S(4)	0.3051(3)	0.4083(2)	0.4731(3)
C(5)	0.4248(10)	0.4054(6)	0.5679(10)
O(2)	0.4459(7)	0.3925(4)	0.6645(7)
C(6)	0.3552(11)	0.3810(7)	0.6936(11)
C(7)	0.4089(14)	0.3391(9)	0.7861(15)
C(8)	0.3217(15)	0.4438(8)	0.7156(16)
S(5)	0.4652(3)	0.2734(1)	0.3728(3)
S(6)	0.5170(3)	0.1399(2)	0.4334(3)
C(9)	0.4476(10)	0.1931(6)	0.3518(11)
O(3)	0.3703(7)	0.1828(4)	0.2606(7)
C(10)	0.3355(11)	0.1164(6)	0.2267(11)
C(11)	0.4007(14)	0.0933(8)	0.1762(15)
C(12)	0.2145(14)	0.1219(8)	0.1543(14)
C(13)	0.6418(10)	0.2028(6)	0.2251(11)
C(14)	0.5514(13)	0.2369(7)	0.1500(14)
C(15)	0.5041(14)	0.2133(9)	0.0501(14)
C(16)	0.5346(17)	0.1628(10)	0.0224(17)
C(17)	0.6210(14)	0.1268(9)	0.0913(16)
C(18)	0.6767(12)	0.1473(7)	0.1974(13)
C(19)	0.4216(9)	0.4485(5)	0.2299(10)
C(20)	0.3743(12)	0.5056(7)	0.1827(13)
C(21)	0.3404(17)	0.5116(10)	0.0769(17)
C(22)	0.3591(15)	0.4646(9)	0.0187(15)
C(23)	0.4040(15)	0.4114(9)	0.0651(16)
C(24)	0.4378(13)	0.4004(8)	0.1674(14)
C(25)	0.6309(10)	0.2530(6)	0.7103(11)
C(26)	0.6848(14)	0.3006(8)	0.7696(15)
C(27)	0.7241(16)	0.2914(10)	0.8760(17)
C(28)	0.7053(18)	0.2322(10)	0.9148(18)
C(29)	0.6591(18)	0.1866(11)	0.8550(19)
C(30)	0.6185(14)	0.1960(9)	0.7490(15)

TABLE 4

FRACTIONAL ATOMIC COORDINATES FOR $PhHg(S_2CNEt_2)$

Atom	*x*	*y*	*z*
Hg(1)	−0.00193(4)	0.33736(3)	0.00559(3)
Hg(2)	0.08161(4)	0.18200(3)	0.40595(3)
S(1)	0.2499(3)	0.3985(2)	−0.0799(2)
S(2)	0.0744(3)	0.5649(2)	−0.2127(2)
C(1)	0.2373(10)	0.5243(8)	−0.1997(8)
N(1)	0.3652(9)	0.5832(7)	−0.2847(8)
C(2)	0.3653(12)	0.6897(9)	−0.3942(10)
C(3)	0.3813(13)	0.6523(11)	−0.4938(12)
C(4)	0.4949(25)	0.5718(18)	−0.2473(19)
C(4′)	0.5148(26)	0.5247(18)	−0.2922(19)
C(5)	0.5978(30)	0.4989(20)	−0.3124(20)
C(5′)	0.5747(31)	0.5823(21)	−0.2349(22)
C(6)	−0.2078(10)	0.2710(8)	0.0620(8)
C(7)	−0.2846(12)	0.3276(10)	−0.0168(10)
C(8)	−0.4301(13)	0.2862(11)	0.0210(11)
C(9)	−0.4912(13)	0.1912(11)	0.1294(11)
C(10)	−0.4187(13)	0.1373(10)	0.2079(11)
C(11)	−0.2748(10)	0.1762(8)	0.1730(9)
S(3)	0.0571(3)	0.1363(2)	0.2542(2)
S(4)	0.2134(3)	−0.0443(2)	0.3994(2)
C(12)	0.1516(9)	0.0020(8)	0.2846(8)
N(2)	0.1684(8)	−0.0600(7)	0.2193(7)
C(13)	0.0946(12)	−0.0253(9)	0.1312(10)
C(14)	0.1976(14)	0.0377(11)	0.0049(12)
C(15)	0.2569(11)	−0.1679(8)	0.2345(9)
C(16)	0.4216(12)	−0.1387(10)	0.1698(11)
C(17)	0.1294(11)	0.2323(9)	0.5188(9)
C(18)	0.2250(12)	0.1620(10)	0.5735(11)
C(19)	0.2598(14)	0.1924(11)	0.6537(12)
C(20)	0.1918(16)	0.2899(13)	0.6776(13)
C(21)	0.0986(15)	0.3563(12)	0.6288(13)
C(22)	0.0683(13)	0.3304(11)	0.5466(11)

procedure in which the function $\Sigma w\Delta^2$ was minimized where $\Delta = \| F_o | - | F_c \|$ and w was the weight applied to each reflection [2]. The Hg and S atoms were refined with anisotropic thermal parameters and the remaining atoms were refined isotropi-

TABLE 5

INTERATOMIC BOND DISTANCES (Å) AND ANGLES (°) FOR $PhHg(S_2COMe)$

Hg–S(1)	2.388(10)	S(1)–Hg–S(2)	64.0(3)
Hg–S(2)	3.167(9)	Hg–S(1)–C(1)	97(1)
S(1)–C(1)	1.75(3)	Hg–S(2)–C(1)	74(1)
S(2)–C(1)	1.64(3)	S(1)–C(1)–S(2)	125(2)
C(1)–O(1)	1.31(4)	S(1)–C(1)–O(1)	107(2)
Hg–C(3)	2.05(3)	S(2)–C(1)–O(1)	127(2)
		C(1)–O(1)–C(2)	119(3)
		S(1)–Hg–C(3)	174.1(7)
		S(2)–Hg–C(3)	120.6(8)

TABLE 6

INTERATOMIC BOND DISTANCES (Å) AND ANGLES (°) FOR $\mathrm{PhHg(S_2CO^iPr)}$

Hg(1)–S(1)	2.374(4)	Hg(2)–S(3)	2.384(3)	Hg(3)–S(5)	2.394(4)
Hg(1)–S(2)	3.210(4)	Hg(2)–S(4)	3.160(3)	Hg(3)–S(6)	3.039(4)
S(1)–C(1)	1.75(1)	S(3)–C(5)	1.74(1)	S(5)–C(9)	1.74(1)
S(2)–C(1)	1.65(1)	S(4)–C(5)	1.64(1)	S(6)–C(9)	1.63(1)
C(1)–O(1)	1.31(2)	C(5)–O(2)	1.34(2)	C(9)–O(3)	1.32(2)
O(1)–C(2)	1.50(2)	O(2)–C(6)	1.49(2)	O(3)–C(10)	1.51(2)
C(2)–C(3)	1.49(3)	C(6)–C(7)	1.52(2)	C(10)–C(11)	1.46(2)
C(2)–C(4)	1.55(2)	C(6)–C(8)	1.50(2)	C(10)–C(12)	1.55(2)
Hg(1)–C(13)	2.03(1)	Hg(2)–C(19)	2.03(1)	Hg(3)–C(25)	2.10(1)
S(1)–Hg(1)–S(2)	62.8(1)	S(3)–Hg(2)–S(4)	63.7(1)	S(5)–Hg(3)–S(6)	65.3(1)
Hg(1)–S(1)–C(1)	99.4(5)	Hg(2)–S(3)–C(5)	97.3(5)	Hg(3)–S(5)–C(9)	93.5(5)
Hg(1)–S(2)–C(1)	73.7(5)	Hg(2)–S(4)–C(5)	73.6(4)	Hg(3)–S(6)–C(9)	74.6(5)
S(1)–C(1)–S(2)	123.9(8)	S(3)–C(5)–S(4)	125.4(8)	S(5)–C(9)–S(6)	124.3(9)
S(1)–C(1)–O(1)	108.0(9)	S(3)–C(5)–O(2)	108.5(9)	S(5)–C(9)–O(3)	109.5(9)
S(2)–C(1)–O(1)	128(1)	S(4)–C(5)–O(2)	126.0(9)	S(6)–C(9)–O(3)	126(1)
C(1)–O(1)–C(2)	120(1)	C(5)–O(2)–C(6)	120(1)	C(9)–O(3)–C(10)	120(1)
O(1)–C(2)–C(3)	105(1)	O(2)–C(6)–C(7)	102(1)	O(3)–C(10)–C(11)	108(1)
O(1)–C(2)–C(4)	105(1)	O(2)–C(6)–C(8)	106(1)	O(3)–C(10)–C(12)	105(1)
C(3)–C(2)–C(4)	115(1)	C(7)–C(6)–C(8)	114(1)	C(11)–C(10)–C(12)	113(1)
S(1)–Hg(1)–C(13)	176.6(4)	S(3)–Hg(2)–C(19)	175.6(3)	S(5)–Hg(3)–C(25)	174.3(3)
S(2)–Hg(1)–C(13)	119.2(4)	S(4)–Hg(2)–C(19)	120.4(3)	S(6)–Hg(3)–C(25)	116.1(4)

TABLE 7

INTERATOMIC BOND DISTANCES (Å) AND ANGLES (°) FOR $\mathrm{PhHg(S_2CNEt_2)}$

Hg(1)–S(1)	2.387(2)	Hg(2)–S(3)	2.388(2)
Hg(1)–S(2)	2.978(2)	Hg(2)–S(4)	2.923(3)
S(1)–C(1)	1.740(9)	S(3)–C(12)	1.756(9)
S(2)–C(1)	1.679(9)	S(4)–C(12)	1.705(9)
C(1)–N(1)	1.36(1)	C(12)–N(2)	1.32(1)
N(1)–C(2)	1.49(1)	N(2)–C(13)	1.50(1)
C(2)–C(3)	1.50(2)	C(13)–C(14)	1.48(2)
N(1)–C(4) [a]	1.53(2)	N(2)–C(15)	1.47(1)
C(4)–C(5) [a]	1.49(4)	C(15)–C(16)	1.53(1)
Hg–C(6)	2.047(9)	Hg(2)–C(17)	2.06(1)
S(1)–Hg(1)–S(2)	66.2(1)	S(3)–Hg(2)–S(4)	67.4(1)
Hg(1)–S(1)–C(1)	95.5(3)	Hg(2)–S(3)–C(12)	95.0(3)
Hg(1)–S(2)–C(1)	77.5(3)	Hg(2)–S(4)–C(12)	78.8(3)
S(1)–C(1)–S(2)	120.6(5)	S(3)–C(12)–S(4)	118.8(5)
S(1)–C(1)–N(1)	116.7(7)	S(3)–C(12)–N(2)	118.3(7)
S(2)–C(1)–N(1)	122.6(7)	S(4)–C(12)–N(2)	122.9(7)
C(1)–N(1)–C(2)	120.3(9)	C(12)–N(2)–C(13)	121.3(8)
C(1)–N(1)–C(4)	119(1)	C(12)–N(2)–C(15)	120.3(8)
C(2)–N(1)–C(4)	117(1)	C(13)–N(2)–C(15)	118.3(8)
N(1)–C(2)–C(3)	110.0(9)	N(2)–C(13)–C(14)	111.6(9)
N(1)–C(4)–C(5)	102(2)	N(2)–C(15)–C(16)	111.9(7)
S(1)–Hg(1)–C(6)	171.8(3)	S(3)–Hg(2)–C(17)	172.3(3)
S(2)–Hg(1)–C(6)	114.0(3)	S(4)–Hg(2)–C(17)	112.3(3)

[a] N(1)–C(4′) 1.54(3); C(4′)–C(5′) 1.54(4).

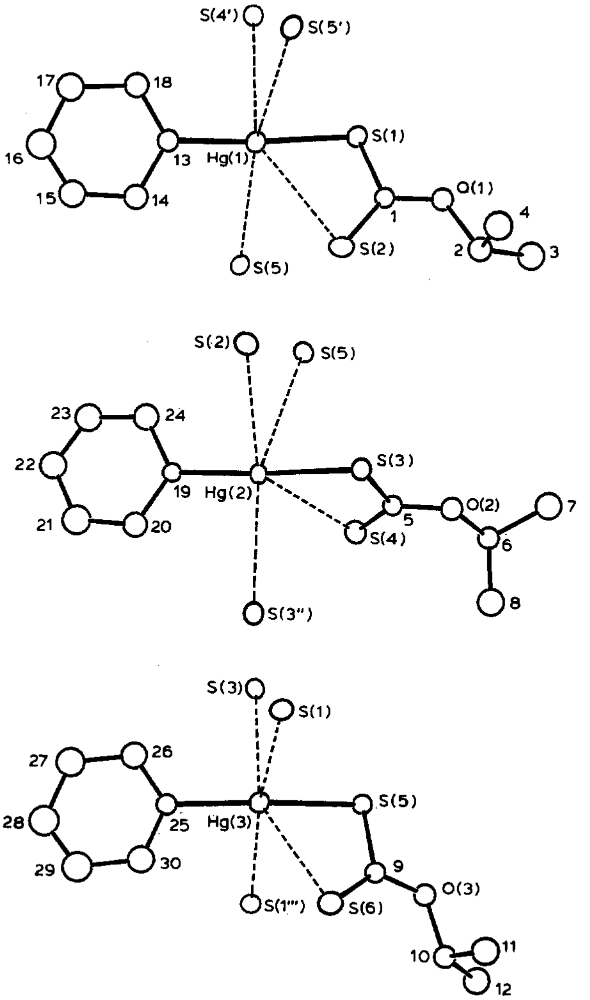

Fig. 2. The numbering scheme used for the three molecules constituting the asymmetric unit in $PhHg(S_2CO^iPr)$; atoms otherwise not indicated are carbons.

cally. Hydrogen atoms were not included in the models. For $PhHg(S_2CNEt_2)$, the terminal ethyl group C(4)–C(5) was found to be disordered over two sites; the occupancies were refined and found to be 0.52/0.48 for C(4)/C(4′) and 0.48/0.52 for C(5)/C(5′). After the inclusion of a weighting scheme, $w = [\sigma^2(F) + g|F|^2]^{-1}$, the refinements were continued until convergence; final refinement details are given in Table 1.

Scattering factors for C, H, N, O, and S were those incorporated in SHELX76 [2] and those for neutral Hg (corrected for f' and f'') were from ref. [4]. Fractional atomic coordinates are given in Tables 2–4 and the numbering schemes used are shown in Figs. 1–3. Interactomic bond angles and distances are listed in Tables 5–7. Tables of thermal parameters, phenyl-ring parameters and the observed and calculated structure factors are available from the author.

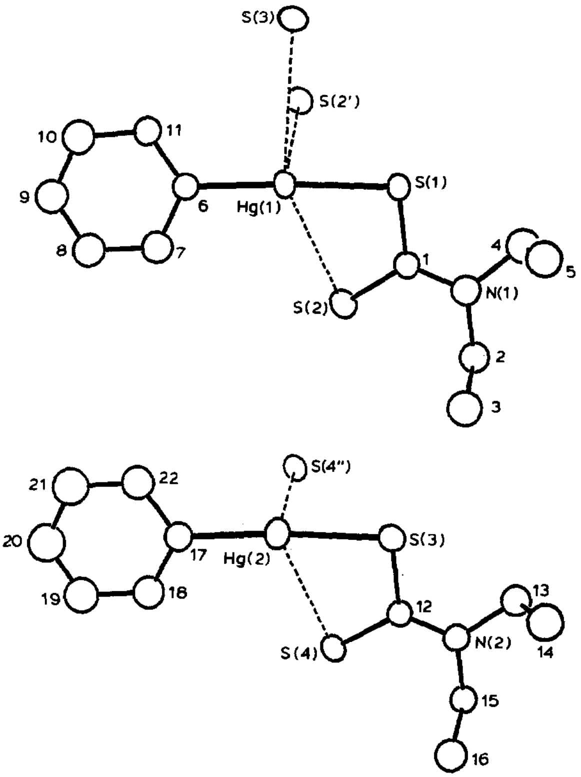

Fig. 3. The numbering scheme used for the two molecules constituting the asymmetric unit in $PhHg(S_2CNEt_2)$; atoms otherwise not indicated are carbons.

Results and discussion

The PhHg(dithiolate) compounds are formed by the facile reaction of PhHgCl and the dithiolate anion as described in the Experimental. The compounds are air-stable pale-yellow (colourless for the dithiocarbamate derivative) crystalline solids. The composition of each of the bulk products was confirmed by ^1H NMR spectra and the presence of strong and characteristic absorptions in the C–O (C–N) and C–S regions of their infrared spectra. In the mass spectra, the most abundant peaks (containing Hg) have been assigned to the ions $[PhHgS_2COR]^+$, $[PhHgS_2C]^+$, $[PhHgSC]^+$, $[PhHgS]^+$, $[PhHg]^+$, $[Hg]^+$, and $[Hg]^{2+}$ for the xanthate complexes and analogous fragments were found in the mass spectrum of $PhHg(S_2CNEt_2)$. However, a careful examination of the high molecular mass region for the $PhHg(S_2COMe)$ compound established the presence of additional ions. These high mass fragments, present in low abundance, have been assigned to the $[Ph(HgS_2C)(HgS_2COMe)]^+$ and $[Ph(Hg)(HgS_2COMe)]^+$ ions and may be considered to be derived from the compound $Ph[Hg(S_2COMe)_2$. This observation may indicate that the $Ph[Hg(S_2COMe)_2$ compound, reported earlier [1], is formed as a minor product in the preparation of $Ph(HgS_2COMe)_2$ (described above) and that the crystal chosen for the original X-ray analysis [1] was not in fact representative of the bulk sample. No evidence for additional peaks was found in the mass spectra for the remaining compounds.

The crystal structure analysis of $PhHg(S_2COMe)$ confirms the stoichiometry of the compound however due to the low accuracy of the determination the crystal structure of a higher homologue, $PhHg(S_2CO^iPr)$ was undertaken. The Hg atom exists in the expected linear geometry in both of these compounds and also in the related dithiocarbamate derivative, $PhHg(S_2CNEt_2)$. The Hg–S distances lie in the narrow range 2.374(4)–2.394(4) Å which indicates that the primary Hg–S bonds thus formed are of similar strength regardless of the nature of the dithiolate ligand. This is not true however for the secondary Hg ··· S intramolecular interactions in these compounds. In the xanthate compounds the average Hg ··· S interaction is of the order 3.14 Å whereas in the dithiocarbamate compound the average distance is 2.95 Å. This difference reflects the different contributions of the $^{2-}S_2CO^+R$ and $^{2-}S_2CN^+R_2$ resonance structures to the overall bonding of xanthate and dithiocarbamate ligands [5,6]. It is the presence of these additional weak Hg ··· S interactions which account for the deviation from the ideal linear geometry about the Hg atoms; the greatest deviation (ca. 172°) being found in $PhHg(S_2CNEt_2)$ where the additional Hg ··· S interactions are more pronounced.

In addition to the intramolecular Hg ··· S interactions described above, the structures feature significant intermolecular association via weak Hg ··· S contacts; see Table 8. The three molecules comprising the asymmetric unit in $PhHg(S_2CO^iPr)$ would appear to arise, in part, as a result of subtle differences in these secondary Hg ··· S contacts and a similar situation is found in the structure of $PhHg(S_2CNEt_2)$ in which two molecules comprise the asymmetric unit. The sum of the Van der Waals radii for Hg and S is 3.3 Å [7] however a larger value, i.e. 3.5 Å, has been suggested by others to be a better estimate [8]. On this basis it would appear that the Hg ··· S contacts in $PhHg(S_2COMe)$, ≥ 3.4 Å, are, if present, only weak and only marginally stronger Hg ··· S contacts are found in the structure of $PhHg(S_2CO^iPr)$. In contrast the intermolecular contacts in $PhHg(S_2CONEt_2)$ of 3.1–3.2 Å (between

TABLE 8

INTERMOLECULAR Hg–S INTERACTIONS (Å) LESS THAN 3.6 Å

Compound	Atoms	Distance	Symmetry operation
$PhHg(S_2COMe)$	Hg ··· S(1′)	3.445(9)	$x, 1+y, z$
	Hg ··· S(2″)	3.537(9)	$x, -y, 1/2+z$
$PhHg(S_2CO^iPr)$	Hg(1) ··· S(4′)	3.367(3)	$1/2+x, 1/2-y, z$
	Hg(1) ··· S(5′)	3.439(3)	$1/2+x, 1/2-y, z$
	Hg(1) ··· S(5)	3.510(3)	x, y, z
	Hg(2) ··· S(3″)	3.306(3)	$1-x, 1-y, 1-z$
	Hg(2) ··· S(2)	3.330(3)	x, y, z
	Hg(2) ··· S(5)	3.457(3)	x, y, z
	Hg(3) ··· S(3)	3.331(3)	x, y, z
	Hg(3) ··· S(1)	3.411(3)	x, y, z
	HG(3) ··· S(1‴)	3.483(3)	$-1/2+x, 1/2-y, z$
$PhHg(S_2CNEt_2)$	Hg(1) ··· S(2′)	3.191(2)	$-x, 1-y, -z$
	Hg(1) ··· S(3)	3.398(2)	x, y, z
	Hg(2) ··· S(4″)	3.133(2)	$-x, -y, 1-z$

centrosymmetrically related pairs) are indicative of substantial intermolecular association as was reported for MeHg(S_2CNEt_2) [9].

The structures of the PhHg derivatives closely resemble the structures found for the related MeHg(S_2COMe) [10] and MeHg(S_2CNEt_2) [9] compounds. In the MeHg derivatives the mode of coordination of the dithiolate ligands has been ascribed to a dative resonance scheme [11] and it appears that a similar resonance occurs in the PhHg dithiolates.

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