Synthesis and *X*-Ray Crystal Structure of a Weak Molecular Adduct of Diphenylmercury(II) with 1,2-Bis(diphenylphosphinothioyl)ethane†

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Reaction of diphenylmercury(II) with 1,2-bis(diphenylphosphinothioyl)ethane in chloroform–n-hexane gives the molecular adduct $HgPh_2{\cdot}Ph_2P(S)(CH_2)_2(S)PPh_2$ which has been characterized by elemental analysis, i.r., u.v., ^1H n.m.r. spectroscopy and *X*-ray crystallography. The crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions a = 9.532(3), b = 10.065(2), c = 10.113(3) Å, α = 118.07(4), β = 96.29(3), and γ = 94.41(2)°. The angle C(1)–Hg–C(1′) is 180(–)°, while C(1)–Hg–S(1) and C(1′)–Hg–S(1) are 92.0(2) and 88.0(2)° respectively. The Hg ··· S(1) and Hg ··· S(1′) distances of 3.913(4) Å indicate very weak interaction.

The co-ordination chemistry of arylmercury(II) systems of the type $HgPh_2$ or HgPhX (X = Cl, NO_3, *etc.*) has been little studied unlike that of halogeno-substituted alkyl- or aryl-mercury(II) substrates.[1] Most of the studies deal with nitrogen-containing ligands. Canty and co-workers[2–4] have reported three molecular adducts of $HgPh_2$ with phenanthroline ligands having weak Hg ··· N interaction. In order to compare the donor property of nitrogen with that of the soft Lewis base sulphur, the reaction of $HgPh_2$ with $Ph_2P(S)(CH_2)_2(S)PPh_2$ has been studied.

Experimental

Materials and Methods.—Diphenylmercury(II) was prepared by reducing phenylmercury(II) chloride with hydrazine hydrate in ethanol as reported,[5] m.p. 119—120 (lit. 124—125 °C). The ligand 1,2-bis(diphenylphosphinothioyl)ethane was prepared by the oxidation of 1,2-bis(diphenylphosphino)ethane with powdered sulphur in dry benzene,[6] m.p. 219—221 (lit. 229—231 °C). Phenylmercury(II) chloride (Fluka) was recrystallised from chloroform before use. 1,2-Bis(diphenylphosphino)ethane was prepared by lithiation of triphenylphosphine in dry tetrahydrofuran followed by reaction with 1,2-dichloroethane.[7] Various solvents were of reagent grade and dried before use.

Preparation of $HgPh_2{\cdot}Ph_2P(S)CH_2CH_2(S)PPh_2$.—A solution of the ligand (0.28 mmol) in chloroform (10 cm^3) was added to a solution of diphenylmercury(II) (0.28 mmol) in chloroform (20 cm^3). The mixture was refluxed for 4 h and the volume reduced by two thirds. Addition of a few cm^3 of diethyl ether led to the separation of the complex. It was filtered off and dried *in vacuo* (Found: C, 55.25; H, 4.05; Hg, 24.95. Calc. for $C_{38}H_{34}HgP_2S_2$: C, 55.85; H, 4.15; Hg, 24.55%), m.p. 197—198 °C. Crystals for *X*-ray crystallography were grown by slow evaporation of a chloroform–n-hexane (1:3, v/v) solution (60 cm^3) of the complex (0.100 g) over a period of 7 d.

Spectroscopy.—I.r. spectra were recorded as KBr pellets on a Pye-Unicam P321 spectrophotometer (4 000—200 cm^{-1}), u.v. spectra in ethanol solution in the range 190—350 nm on a Shimadzu u.v.-visible recording spectrophotometer UV-240, and ^1H n.m.r. spectra in $CDCl_3$ on a JEOL (JNM-PMX) 60-MHz spectrometer with $SiMe_4$ as the internal standard.

Table 1. Fractional atomic co-ordinates (× 10^5 for Hg, × 10^4 for others) for $HgPh_2{\cdot}Ph_2P(S)CH_2CH_2(S)PPh_2$

Atom	*x*	*y*	*z*
Hg	50 000(–)	50 000(–)	50 000(–)
C(1)	3 061(8)	3 673(8)	3 796(9)
C(2)	2 881(9)	2 631(9)	2 263(10)
C(3)	1 571(11)	1 823(9)	1 467(10)
C(4)	407(9)	2 017(9)	2 173(10)
C(5)	535(8)	2 997(10)	3 684(10)
C(6)	1 874(8)	3 825(10)	4 506(9)
P(1)	3 667(2)	–3 169(2)	593(2)
S(1)	3 406(2)	–2 971(3)	–1 250(2)
C(7)	4 286(6)	–4 949(6)	268(8)
C(8)	5 013(6)	–1 709(6)	2 105(7)
C(9)	5 576(8)	–450(7)	1 996(8)
C(10)	6 642(9)	620(9)	3 140(10)
C(11)	7 133(8)	457(8)	4 348(9)
C(12)	6 608(8)	–787(8)	4 475(8)
C(13)	5 516(7)	–1 866(7)	3 363(8)
C(14)	2 046(6)	–3 094(6)	1 381(7)
C(15)	1 487(7)	–4 222(7)	1 686(8)
C(16)	209(8)	–4 119(8)	2 245(9)
C(17)	–495(7)	–2 879(9)	2 541(9)
C(18)	83(8)	–1 741(9)	2 254(9)
C(19)	1 326(7)	–1 869(8)	1 640(9)

Crystallography.—*Crystal data.* $C_{38}H_{34}HgP_2S_2$, M = 817.3, triclinic, a = 9.532(3), b = 10.065(2), c = 10.113(3) Å, α = 118.07(4), β = 96.29(3), γ = 94.41(2)°, U = 841.8 Å^3, space group $P\bar{1}$, D_m = 1.61, Z = 1, D_c = 1.612 g cm^{-3}, $F(000)$ = 404, Mo-K_α radiation, λ = 0.710 73 Å, μ = 47.73 cm^{-1}.

The intensity data for a well defined colourless crystal were measured at room temperature on an Enraf–Nonius CAD4F diffractometer using the ω—2θ scan technique in the range θ 1—27.5°. Of the total 5 686 reflections, 3 120 were considered observed with $I \geqslant 2.5\sigma(I)$. The intensities were corrected for Lorentz polarization and absorption effects (max., min. transmission factors 0.2715 and 0.1407).[8]

Solution and refinement of the structure. The interpretation of the Patterson synthesis enabled the location of the Hg atom and the remaining non-hydrogen atoms were located from sub-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 2. Selected bond distances (Å) and angles (°) for $HgPh_2 \cdot Ph_2P(S)CH_2CH_2(S)PPh_2$

C(1)–Hg	2.069(7)	C(2)–C(1)	1.385(12)
C(6)–C(1)	1.385(11)	C(3)–C(2)	1.369(13)
C(4)–C(3)	1.362(14)	C(5)–C(4)	1.358(13)
C(6)–C(5)	1.403(10)	S(1)–P(1)	1.956(2)
C(7)–P(1)	1.822(5)	C(8)–P(1)	1.819(6)
C(14)–P(1)	1.806(6)	C(7)–C(7)	1.513(11)
C(9)–C(8)	1.395(8)	C(13)–C(8)	1.394(9)
C(10)–C(9)	1.390(11)	C(11)–C(10)	1.347(13)
C(12)–C(11)	1.379(12)	C(13)–C(12)	1.395(9)
C(15)–C(14)	1.393(8)	C(19)–C(14)	1.387(8)
C(16)–C(15)	1.389(9)	C(17)–C(16)	1.384(11)
C(18)–C(17)	1.396(12)	C(19)–C(18)	1.384(10)
C(6)–C(1)–Hg	120.4(6)	C(19)–C(14)–P(1)	117.2(5)
C(2)–C(1)–Hg	122.2(6)	C(16)–C(15)–C(14)	119.9(6)
C(3)–C(2)–C(1)	121.3(8)	C(18)–C(17)–C(16)	119.4(6)
C(5)–C(4)–C(3)	120.4(8)	C(18)–C(19)–C(14)	119.9(7)
C(5)–C(6)–C(1)	121.0(7)	C(7)–P(1)–S(1)	112.5(2)
C(6)–C(1)–C(2)	117.4(7)	C(8)–P(1)–C(7)	104.1(3)
C(4)–C(3)–C(2)	120.5(8)	C(14)–P(1)–C(7)	106.7(3)
C(6)–C(5)–C(4)	119.3(8)	C(9)–C(8)–P(1)	120.5(5)
C(8)–P(1)–S(1)	113.5(2)	C(13)–C(8)–C(9)	119.6(6)
C(14)–P(1)–S(1)	112.7(2)	C(11)–C(10)–C(9)	120.9(7)
C(14)–P(1)–C(8)	106.7(3)	C(13)–C(12)–C(11)	119.5(7)
C(13)–C(8)–P(1)	120.0(4)	C(15)–C(14)–P(1)	122.9(4)
C(10)–C(9)–C(8)	119.3(7)	C(19)–C(14)–C(15)	119.9(6)
C(12)–C(11)–C(10)	121.0(7)	C(17)–C(16)–C(15)	120.4(6)
C(12)–C(13)–C(18)	119.6(6)	C(19)–C(18)–C(17)	120.4(6)

sequent difference maps. The structure was refined by a full-matrix least-squares 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. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were not included in the model. A weighting scheme, $w = [\sigma^2(F) + gF^2]^{-1}$, was introduced and the refinement continued until convergence: $R = 0.068$, $R' = 0.072$, and $g = 0.008$. The relatively high value of the final residual prompted an examination of the $P\bar{1}$ model; however, no improvement was evident. Fractional atomic co-ordinates and bond distances and angles are given in Tables 1 and 2 respectively. The scattering factors for C, H, P, and S were those incorporated in SHELX 76 (ref. 8) and those for neutral Hg (corrected for anomalous dispersion) were from ref. 9.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond distances and angles.

Results and Discussion

The i.r. spectrum of the adduct does not show any change in the vibrational frequency of the diagnostic (PS) group. The u.v.–visible [$\lambda_{max.}$, 215s, 220s, 245w, 255w, 260w, 267m, and 273 nm (sh)] and ^1H n.m.r. spectra [complex, δ 7.66 (m, 12, Ph), 7.17 (m, 18, Ph), 2.7 (d, 4, CH_2); ligand, 7.72 (m, 8, Ph), 7.20 (m, 12, Ph), 2.7 (d, 4, CH_2)] indicated some interaction in solution.

In order to establish the interaction of the ligand with mercury(II), the *X*-ray crystal structure of the adduct was undertaken (Figures 1 and 2). This shows that the Hg atom is situated on a crystallographic site of symmetry $\bar{1}$ at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Similarly, the ligand is situated about a crystallographic site of symmetry $\bar{1}$ at $(\frac{1}{2}, -\frac{1}{2}, 0)$. The P=S distance [P(1)–S(1) 1.956(2) Å] did not show any apparent lengthening (*cf.*[10] P=S 1.89—1.97 Å). All other bond lengths of the ligand are normal. The interatomic parameters of $HgPh_2$ in the adduct are equal, within experimental error, to those reported for the isolated $HgPh_2$ molecule.[11] The closest intermolecular contact involving $HgPh_2$ is between C(2) and S(1^I) of 3.825 Å (symmetry operation, $1 - x, -y, -z$), *cf.* sum of van der Waals radii 3.5 Å.

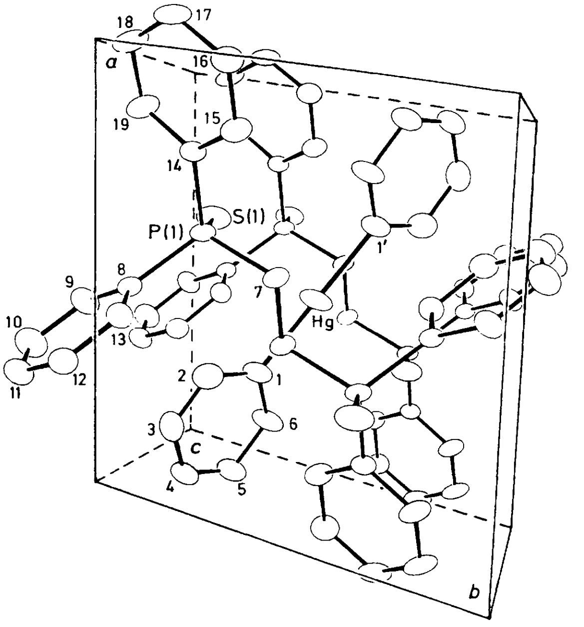

Figure 1. ORTEP 50% thermal ellipsoid depicting the packing in the unit cell

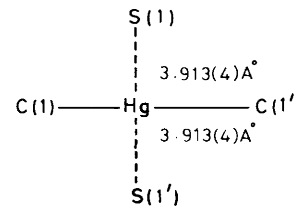

Figure 2. The geometry about Hg in the adduct

The angles C(1)–Hg–S(1) and C(1′)–Hg–S(1) are 92.0(2) and 88.0(2)° respectively. Since Hg is situated at a centre of inversion, the C(1)–Hg–C(1′) angle is crystallographically constrained to linearity and thus is taken as 180(–)°. The Hg–S(1) and Hg–S(1′) distances of 3.913(4) Å are higher than the sum of the van der Waals radii (Hg 1.73, S 1.85 Å).[12,13] Thus the compound may be described as a weak molecular adduct with weak Hg • • • S interactions.

This study demonstrates the extremely poor Lewis acidity of $HgPh_2$ which could be due to the interaction of π electrons of the Ph groups with empty *p* orbitals of Hg, thus reducing the formal positive charge on Hg. The donor properties of phenanthroline and $Ph_2P(S)CH_2CH_2(S)PPh_2$ towards $HgPh_2$ appear similar.

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