Notes

X-Ray Crystal and Molecular Structures of [(Diphenylphosphinomethyl)-diphenylphosphine sulphide]di-iodomercury(II) and [1,2-Bis(diphenylphosphinothioyl)ethane]dichloromercury(II)†

Tarlok S. Lobana* and (Miss) Maninderjeet K. Sandhu
Department of Chemistry, Guru Nanak Dev University, Amritsar-143005, India
Michael J. Liddell and Edward R. T. Tiekink*
Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001, Australia

Reaction of mercury(II) iodide with the unsymmetrical diphosphine ligand $Ph_2P(S)CH_2PPh_2$ resulted in the formation of a solid compound $[HgI_2\{Ph_2P(S)CH_2PPh_2\}]$ (**1**), which has been shown by *X*-ray crystallography to be monomeric with a flattened tetrahedral geometry about the mercury atom. The diphosphine co-ordinates *via* the sulphur and trivalent phosphorus atoms [Hg–S(1) 2.760(4), Hg–P(2) 2.503(5) Å] forming a five-membered ring; the two remaining tetrahedral sites are occupied by the iodide atoms [Hg–I 2.727(2) and 2.693(2) Å]. Crystals of (**1**) are monoclinic, space group $P2_1/c$, with unit-cell dimensions $a = 11.426(2)$, $b = 15.491(4)$, $c = 16.324(3)$ Å, $\beta = 109.79(1)$, and $Z = 4$. The structure was refined to final $R = 0.059$ for 2 632 reflections with $I \geqslant 3.0\sigma(I)$. The reaction of mercury(II) chloride with the symmetrical diphosphine $Ph_2P(S)CH_2CH_2(S)PPh_2$ led to the isolation of the adduct $[HgCl_2\{Ph_2P(S)CH_2CH_2(S)PPh_2\}]$ (**2**). Crystallographic studies revealed a distorted tetrahedral mercury centre defined by two chloride atoms [Hg–Cl 2.447(3) and 2.442(3) Å] and a chelating diphosphine ligand which co-ordinates *via* the sulphur atoms [Hg–S(1) 2.559(3) and Hg–S(2) 2.546(3) Å]. The mode of co-ordination of the diphosphine ligand results in the formation of a seven-membered ring, a result which is unprecedented in phosphine/arsine chalcogenide chemistry. Crystals of (**2**) are monoclinic, space group $P2_1/n$, with unit-cell dimensions $a = 8.404(4)$, $b = 16.829(3)$, $c = 19.354(3)$ Å, $\beta = 91.02(3)$, and $Z = 4$. The structure was refined to final $R = 0.056$ for 3 406 reflections with $I \geqslant 2.5\sigma(I)$.

There is growing interest in the co-ordination chemistry of tertiary phosphine chalcogenides and their study has been greatly facilitated by access to modern crystallographic techniques and multinuclear magnetic resonance measurements.[1] This paper reports the isolation and crystallographic characterization of two adducts of mercury(II) halides with sulphur-substituted diphosphines for which there is limited information available in the literature, a little surprising perhaps when one considers the large number of reports of mercury(II) adducts of tertiary phosphines.[2,3]

The reaction of mercury(II) chloride with $Ph_2P(S)CH_2CH_2(S)PPh_2$ in benzene was reported to yield a polymeric species of stoicheiometry $Hg_4Cl_8[Ph_2P(S)CH_2CH_2(S)PPh_2]_3$ for which it was suggested that the diphosphine ligand was bridging owing to the general belief that the seven-membered ring that would be formed if it chelated the mercury atom would lead to a less stable compound.[4] Moreover, an *X*-ray crystal structure for $[Cu_2Cl_2\{Ph_2P(S)CH_2CH_2(S)PPh_2\}_2]$ showed the diphosphine ligand to be bridging.[5] By contrast only weak interactions between the mercury atom and the sulphur atoms were found in the weak molecular adduct $[HgPh_2{\cdot}Ph_2P(S)CH_2CH_2(S)PPh_2]$.[6] There are also few reports in the literature of mercury(II) adducts with unsymmetrical diphosphines of the type $R_2P(S)(CH_2)_nPR_2$ ($n = 1,2$, *etc.*; R = alkyl or aryl). There are several reports, however, of substitution reactions involving $R_2P(E)CH_2PR_2$ (E = O, S, or Se) and Group 6 metal carbonyls[7,8] and more recently a series of platinum[9] and gold[10] compounds were characterized with ligands of this type. Reaction of mercury(II) iodide with $Ph_2P(S)CH_2PPh_2$ has been shown to result in the formation of a stable adduct in which the diphosphine ligand was suggested to be chelating.[11]

This paper reports mass and ^{31}P n.m.r. spectroscopic and *X*-ray crystallographic studies of the latter compound, $[HgI_2\{Ph_2P(S)CH_2PPh_2\}]$[11] (**1**) and of $[HgCl_2\{Ph_2P(S)CH_2CH_2(S)PPh_2\}]$ (**2**) in order to determine the mercury atom geometries and the mode of co-ordination of the diphosphine chalcogenide ligands.

Experimental

Starting Materials.—The compound $Ph_2P(CH_2)_2PPh_2$ was prepared by lithiation of PPh_3 in dry tetrahydrofuran.[12] Treatment of it with elemental sulphur (1:2 mole ratio) in benzene formed $Ph_2P(S)CH_2CH_2(S)PPh_2$.[13] The compound $Ph_2PCH_2PPh_2$ (Pressure Chem., Pittsburg) was treated with elemental sulphur (1:1 molar ratio) forming $Ph_2P(S)CH_2PPh_2$.[11] Mercury(II) salts (B.D.H.) were of A.R. grade and were used without further purification. Solvents were of A.R. grade and, unless otherwise stated, were used as supplied.

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Fractional atomic co-ordinates for complex (**1**)

Atom	*x*	*y*	*z*
Hg	0.175 95(8)	0.193 42(5)	0.218 17(5)
I(1)	0.379 1(2)	0.137 6(1)	0.351 2(1)
I(2)	−0.037 5(2)	0.176 0(1)	0.252 2(1)
S	0.204 8(5)	0.370 3(3)	0.217 1(3)
P(1)	0.258 4(4)	0.381 1(3)	0.114 9(3)
P(2)	0.207 1(5)	0.186 9(3)	0.073 7(3)
C(1)	0.192 2(17)	0.297 7(9)	0.030 1(10)
C(2)	0.423 0(10)	0.372 7(6)	0.142 3(6)
C(3)	0.480 1(10)	0.407 1(6)	0.086 3(6)
C(4)	0.606 1(10)	0.392 0(6)	0.101 8(6)
C(5)	0.675 0(10)	0.342 4(6)	0.173 2(6)
C(6)	0.617 9(10)	0.308 0(6)	0.229 1(6)
C(7)	0.491 9(10)	0.323 2(6)	0.213 6(6)
C(8)	0.209 0(9)	0.482 3(5)	0.058 6(6)
C(9)	0.142 2(9)	0.484 8(5)	−0.030 4(6)
C(10)	0.105 9(9)	0.565 4(5)	−0.071 1(6)
C(11)	0.136 5(9)	0.641 4(5)	−0.022 7(6)
C(12)	0.203 3(9)	0.637 9(5)	0.066 3(6)
C(13)	0.239 6(9)	0.558 3(5)	0.107 0(6)
C(14)	0.089 4(9)	0.129 9(7)	−0.012 1(7)
C(15)	0.113 2(9)	0.097 3(7)	−0.084 6(7)
C(16)	0.017 7(9)	0.058 9(7)	−0.152 1(7)
C(17)	−0.101 6(9)	0.053 2(7)	−0.147 3(7)
C(18)	−0.125 4(9)	0.085 9(7)	−0.074 8(7)
C(19)	−0.029 9(9)	0.124 3(7)	−0.007 3(7)
C(20)	0.356 3(11)	0.146 2(7)	0.077 6(7)
C(21)	0.403 0(11)	0.075 9(7)	0.132 3(7)
C(22)	0.517 2(11)	0.039 8(7)	0.137 6(7)
C(23)	0.584 7(11)	0.074 0(7)	0.088 2(7)
C(24)	0.537 9(11)	0.144 3(7)	0.033 5(7)
C(25)	0.423 8(11)	0.180 4(7)	0.028 2(7)

Table 2. Fractional atomic co-ordinates for complex (**2**)*

Atom	*x*	*y*	*z*
Hg	0.026 71(4)	0.223 39(2)	0.120 17(2)
Cl(1)	0.182 2(3)	0.340 3(2)	0.088 3(2)
Cl(2)	0.198 5(4)	0.110 4(2)	0.147 9(2)
S(1)	−0.114 8(3)	0.260 0(2)	0.231 8(1)
S(2)	−0.124 4(3)	0.178 8(3)	0.011 8(2)
P(1)	−0.337 4(3)	0.218 4(1)	0.229 8(1)
P(2)	−0.337 1(3)	0.230 7(2)	0.008 4(1)
C(1)	−0.403 9(11)	0.186 5(6)	0.143 2(4)
C(2)	−0.395 7(12)	0.259 2(6)	0.094 1(4)
C(3)	−0.474 7(7)	0.295 9(4)	0.255 8(3)
C(4)	−0.422 7(7)	0.374 5(4)	0.260 3(3)
C(5)	−0.528 1(7)	0.434 2(4)	0.279 6(3)
C(6)	−0.685 5(7)	0.415 4(4)	0.294 4(3)
C(7)	−0.737 5(7)	0.336 8(4)	0.289 9(3)
C(8)	−0.632 2(7)	0.277 1(4)	0.270 6(3)
C(9)	−0.363 0(9)	0.136 2(5)	0.286 4(4)
C(10)	−0.339 9(9)	0.149 8(5)	0.356 9(4)
C(11)	−0.359 4(9)	0.088 0(5)	0.404 0(4)
C(12)	−0.402 0(9)	0.012 4(5)	0.380 5(4)
C(13)	−0.425 1(9)	−0.001 3(5)	0.310 0(4)
C(14)	−0.405 7(9)	0.060 6(5)	0.262 9(4)
C(15)	−0.344 2(11)	0.326 9(7)	−0.037 5(5)
C(16)	−0.331 5(11)	0.399 4(7)	−0.002 9(5)
C(17)	−0.328 4(11)	0.470 2(7)	−0.040 3(5)
C(18)	−0.338 0(11)	0.468 5(7)	−0.112 3(5)
C(19)	−0.350 7(11)	0.396 0(7)	−0.146 9(5)
C(20)	−0.353 8(11)	0.325 2(7)	−0.109 5(5)
C(15′)	−0.337 9(13)	0.314 7(8)	−0.043 4(6)
C(16′)	−0.215 2(13)	0.369 0(8)	−0.031 0(6)
C(17′)	−0.213 0(13)	0.441 0(8)	−0.066 7(6)
C(18′)	−0.333 5(13)	0.458 8(8)	−0.114 7(6)
C(19′)	−0.456 2(13)	0.404 5(8)	−0.127 1(6)
C(20′)	−0.458 4(13)	0.332 5(8)	−0.091 5(6)
C(21)	−0.477 9(7)	0.162 0(4)	−0.028 7(3)
C(22)	−0.423 7(7)	0.090 6(4)	−0.056 2(3)
C(23)	−0.532 0(7)	0.036 2(4)	−0.084 3(3)
C(24)	−0.694 5(7)	0.053 2(4)	−0.085 0(3)
C(25)	−0.748 7(7)	0.124 7(4)	−0.057 5(3)
C(26)	−0.640 4(7)	0.179 1(4)	−0.029 3(3)

* Primed atoms have site occupancy factors of 0.28(1).

Synthesis and Crystal Growth of Complexes.—Complex (**1**) was prepared by the literature method[11] by treating mercury(II) iodide and $Ph_2P(S)CH_2PPh_2$ in 1:1 mole ratio in ethanol solution. Crystals thus obtained (m.p. > 250 °C) were analysed by *X*-ray crystallography. Complex (**2**) was prepared from the reaction of mercury(II) chloride with $Ph_2P(S)CH_2CH_2(S)PPh_2$ in acetone in 1:1 mole ratio. The mixture was refluxed for 0.5 h and then filtered. The filtrate was allowed to stand overnight when crystals suitable for *X*-ray studies were formed, m.p. 210 °C. Both compounds were colourless, air-stable solids.

Spectroscopy.—Phosphorus-31 n.m.r. spectra were run on a Bruker CXP-300 n.m.r. spectrometer at 121.49 MHz at room temperature. Chemical shifts to low field are denoted positive. The external reference was 0.1 mol dm^{-3} HCl–0.01 mol dm^{-3} H_3PO_4 in D_2O (δ +0.8 p.p.m.) and the shifts quoted are relative to 85% H_3PO_4. As the spectra were measured in dichloromethane solution a sample of D_2O in a concentric tube was used for the field lock. For complex (**1**) the ^{31}P n.m.r. spectrum showed two resonances: a doublet at δ 42.3 p.p.m. [^2J(P–P) 35 Hz] which is assigned to the sulphur-bound phosphorus atom and an high-field doublet (δ −4.1 p.p.m.) with poorly resolved ^{199}Hg satellites indicating co-ordination of this atom to mercury [$J(^{199}Hg–^{31}P)$ 1 548 Hz]. The ^{31}P n.m.r. spectrum of (**2**) showed a singlet at δ 47.8 p.p.m. consistent with the presence of two equivalent phosphorus atoms in solution.

Fast atom bombardment (f.a.b.) mass spectra were obtained on a VG ZAB 2HF instrument equipped with a f.a.b. source. Argon was used as the exciting gas, with the source pressure typically 10^{-6} mbar (10^{-4} Pa); the f.a.b. gun voltage was 7.5 kV, current 1 mA. The ion acceleration potential was 8 kV and the matrix was 3-nitrobenzyl alcohol. The complexes were made up as *ca.* 0.5 mol dm^{-3} solutions in dichloromethane; a drop was added to a drop of matrix and the mixture applied to the f.a.b. probe tip. The f.a.b. mass spectrum of complex (**1**) did not show the expected molecular ion with the highest ion corresponding to $[HgI\{Ph_2P(S)CH_2PPh_2\}]^+$; similarly for (**2**) the highest observed ion was $[HgCl\{Ph_2P(S)CH_2CH_2(S)PPh_2\}]^+$.

Crystallography.—Intensity data were measured (295 K) on an Enraf-Nonius CAD4 diffractometer with the use of graphite-monochromatized Mo-K_α radiation, λ = 0.7107 Å, and the ω—2θ scan technique to $\theta_{max.}$ of 25° in each case. The data sets were corrected for Lorentz and polarization effects and for absorption with the use of an analytical procedure.[14]

Table 3. Selected bond distances (Å) and angles (°) for complex (**1**)

Hg–I(1)	2.727(2)	Hg–I(2)	2.693(2)
Hg–S	2.760(4)	Hg–P(2)	2.503(5)
S–P(1)	1.968(6)	P(1)–C(1)	1.86(2)
P(1)–C(2)	1.79(1)	P(1)–C(8)	1.81(1)
P(2)–C(1)	1.84(1)	P(2)–C(14)	1.81(1)
P(2)–C(20)	1.80(1)		
I(1)–Hg–I(2)	113.0(1)	I(1)–Hg–S	104.4(1)
I(1)–Hg–P(2)	112.5(1)	I(2)–Hg–S	102.7(1)
I(2)–Hg–P(2)	128.2(1)	S–Hg–P(2)	88.8(1)
Hg–S–P(1)	99.3(2)	Hg–P(2)–C(1)	107.6(5)
Hg–P(2)–C(14)	116.4(4)	Hg–P(2)–C(20)	114.6(4)
S–P(1)–C(1)	114.1(6)	S–P(1)–C(2)	112.7(4)
S–P(1)–C(8)	111.8(4)	C(1)–P(1)–C(2)	105.3(6)
C(1)–P(1)–C(8)	104.2(5)	C(2)–P(1)–C(8)	108.1(5)
C(1)–P(2)–C(14)	102.0(7)	C(1)–P(2)–C(20)	107.6(7)
C(14)–P(2)–C(20)	107.6(5)	P(1)–C(1)–P(2)	113.5(8)
P(1)–C(2)–C(3)	119.7(3)	P(1)–C(2)–C(7)	119.9(3)
P(1)–C(8)–C(9)	122.0(3)	P(1)–C(8)–C(13)	118.0(3)
P(2)–C(14)–C(15)	121.8(3)	P(2)–C(14)–C(19)	118.1(3)
P(2)–C(20)–C(21)	116.7(3)	P(2)–C(20)–C(25)	123.3(3)

Table 4. Selected bond distances (Å) and angles (°) for complex (**2**)

Hg–Cl(1)	2.447(3)	Hg–Cl(2)	2.442(3)
Hg–S(1)	2.559(3)	Hg–S(2)	2.546(3)
S(1)–P(1)	1.998(3)	S(2)–P(2)	1.990(4)
P(1)–C(1)	1.837(8)	P(2)–C(2)	1.803(9)
P(1)–C(3)	1.819(7)	P(2)–C(15)	1.85(1)
P(1)–C(9)	1.780(8)	P(2)–C(21)	1.73(1)
Cl(1)–Hg–Cl(2)	111.4(1)	Cl(1)–Hg–S(1)	106.1(1)
Cl(1)–Hg–S(2)	106.9(1)	Cl(2)–Hg–S(1)	106.5(1)
Cl(2)–Hg–S(2)	103.6(1)	S(1)–Hg–S(2)	122.3(1)
Hg–S(1)–P(1)	110.4(1)	Hg–S(2)–P(2)	109.4(1)
S(1)–P(1)–C(1)	112.9(3)	S(1)–P(1)–C(3)	110.0(2)
S(1)–P(1)–C(9)	112.6(3)	C(1)–P(1)–C(3)	106.1(4)
C(1)–P(1)–C(9)	107.2(4)	C(3)–P(1)–C(9)	107.7(3)
S(2)–P(2)–C(2)	110.3(3)	S(2)–P(2)–C(15)	114.9(3)
S(2)–P(2)–C(21)	108.4(2)	C(2)–P(2)–C(15)	101.7(5)
C(2)–P(2)–C(21)	110.5(4)	C(15)–P(2)–C(21)	110.9(4)

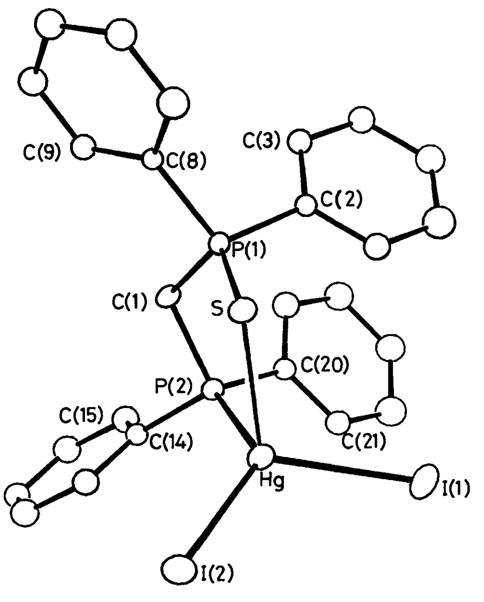

Figure 1. Crystallographic numbering scheme for complex (**1**)

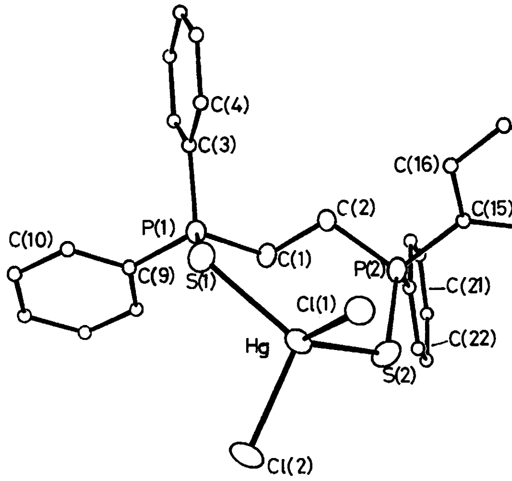

Figure 2. Crystallographic numbering scheme for complex (**2**)

Crystal data. (**1**), $C_{25}H_{22}HgI_2P_2S$, M = 870.8, monoclinic, space group $P2_1/c$, a = 11.426(2), b = 15.491(4), c = 16.324(3) Å, β = 109.79(1)°, U = 2 718.7 Å^3, D_m = 2.11 g cm^{-3} (flotation), Z = 4, D_c = 2.128 g cm^{-3}, $F(000)$ = 1 616, μ = 80.79 cm^{-1}, maximum and minimum transmission factors = 0.334 and 0.104. 5 922 Reflections measured, 4 790 unique, and 2 632 with $I \geqslant 3.0\sigma(I)$, R = 0.059, R' = 0.062.

(**2**), $C_{26}H_{24}Cl_2HgP_2S_2$, M = 734.0, monoclinic, $P2_1/n$, a = 8.404(4), b = 16.829(3), c = 19.354(3) Å, β = 91.02(3)°, U = 2 736.8 Å^3, D_m = 1.76 g cm^{-3} (flotation), Z = 4, D_c = 1.781 g cm^{-3}, $F(000)$ = 1 424, μ = 60.48 cm^{-1}, maximum and minimum transmission factors = 0.206 and 0.042. 5 602 Reflections measured, 4 804 unique, and 3 406 with $I \geqslant 2.5\sigma(I)$, R = 0.056, R' = 0.068.

Solution and refinement of the structures. Both structures were solved by interpretation of the Patterson function and refined by a full-matrix least-squares procedure based on F.[14] Phenyl groups were refined as hexagonal rigid groups with individual isotropic thermal parameters for the C atoms. The remaining non-H atoms were refined with anisotropic thermal parameters and H atoms were included in the models at their calculated positions. In the refinement of complex (**2**) the phenyl ring C(15)—C(20) was found to be disordered over two positions with the minor orientation (primed atoms in Table 2) having a site occupancy factor of 0.28(1). A weighting scheme of the form $k/[\sigma^2(F) + g|F|^2]$ was introduced and each refinement continued until convergence: (**1**), k = 12.11 and g = 0.0002; (**2**), k = 0.302 and g = 0.0300. Fractional atomic co-ordinates for complexes (**1**) and (**2**) are listed in Tables 1 and 2 respectively and selected interatomic parameters in Tables 3 and 4. The numbering schemes used are shown in Figures 1 and 2. The scattering factors for C, H, Cl, P, and S were those incorporated in SHELX 76 (ref. 14) and those for neutral Hg and I (corrected for anomalous dispersion) were from ref. 15.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

The molecular structure of complex (**1**) is shown in Figure 1 from which it can be seen that the mercury atom is co-ordinated by two iodide atoms and by the sulphur atom and trivalent phosphorus atom of the chelating diphosphine ligand in a distorted tetrahedral geometry (see below). The Hg–I distances of 2.727(2) and 2.693(2) Å are comparable to those of 2.733(1) and 2.763(1) Å found in $[HgI_2(PPh_3)_2]$[16] and the terminal

Hg–I distances of 2.671(2) and 2.684(2) Å in dimeric $[\{HgI_2(PPh_3)\}_2]$.[17] The diphosphine ligand chelates the mercury atom and thereby forms a puckered HgPCPS five-membered ring; similar five-membered rings have been observed previously in the structures of *trans*-$[PtCl(PEt_3)\{Ph_2PCH_2(S)PBu^t{}_2\}][ClO_4]$[9] and $[Au(C_6F_5)_2\{Ph_2PCH(S)PPh_2\}]$.[10] The Hg–P bond distance of 2.503(5) Å lies midway between those in dimeric $[\{HgI_2(PPh_3)\}_2]_2$ [2.461(8) Å[17]] and monomeric $[HgI_2(PPh_3)_2]$ [2.557(3) and 2.574(3) Å[16]]. Although the Hg–S bond distance is only slightly longer than those of 2.670(7) and 2.737(7) Å found in tetrahedral di-iodo(tetraethylthiuramdisulphide) mercury[18] [Hg–I 2 × 2.668(2) Å] all of these Hg–S distances are greater than the sum of the covalent radii for mercury and sulphur of 2.37 Å.[19] Further support for the weak co-ordination of the sulphur atom to mercury is found in the P=S bond distance of 1.968(6) Å which would be expected to be lengthened somewhat if the sulphur atom was involved in a strong interaction to the mercury atom. The P=S bond distance in complex (**1**) is close to the 1.956(2) Å found in the weak molecular adduct $[HgPh_2 \cdot Ph_2P(S)CH_2CH_2(S)PPh_2]$[6] [in which the mercury to sulphur interaction was 3.913(4) Å] and lies in the range expected for P=S bonds of 1.89—1.97 Å.[20] The mercury atom geometry is grossly distorted from ideal tetrahedral as a result of several factors including the restricted bite distance of the chelating ligand [S(1)–Hg–P(2) 88.8(1)°]. With the foregoing discussion in mind, in particular the relatively weak co-ordination of the sulphur atom, an alternative description of the co-ordination polyhedron based on a flattened tetrahedral geometry may be valid. The mercury atom lies 0.382 3(8) Å out of the least-squares plane defined by the I(1), I(2), and P(2) atoms in the direction of the capping S(1) atom. The angles subtended at the mercury atom by the three trigonal donor atoms are 112.5(1), 113.0(1), and 128.2(1)° and total 353.7°. In the extreme case, *i.e.* in the absence of Hg–S bond, the co-ordination geometry about the mercury atom would be best described as trigonal planar. This may be the situation in solution in which the diphosphine functions as a monodentate ligand *via* the phosphorus atom with the pendant sulphur atom not involved in co-ordination to the mercury atom.

The molecular structure of complex (**2**) is shown in Figure 2 and selected interatomic parameters are given in Table 4. The mercury atom is co-ordinated by two chloride atoms and two sulphur atoms derived from a chelating diphosphine ligand. The Hg–Cl bond distances of 2.447(3) and 2.442(3) Å are significantly less than those determined for a series of dichlorobis(tertiary phosphine)mercury structures[21–23] indicating relatively strong Hg–Cl bonds in (**2**) and thus, concomitantly, weaker Hg–S bonds. The Hg–S bond distances of 2.559(3) and 2.546(3) Å are less than that found for (**1**) but still longer than 2.52 Å (being the sum of the covalent radii of mercury and sulphur atoms[19]). Support for the presence of significant Hg–S interactions in (**2**) is found in the lengthening of the associated P=S bonds to 1.998(3) and 1.990(4) Å compared to 1.956(2) Å found for the P=S bonds to 1.998(3) and 1.990(4) Å compared to 1.956(2) Å found for the P=S bond in the adduct $[HgPh_2 \cdot Ph_2P(S)CH_2CH_2(S)PPh_2]$[6] as described above. The presence of a chelating diphosphine ligand in (**2**) has the result that a seven-membered ring, HgSPCCPS, is formed as shown in Figure 2. As a consequence of the flexibility in the ligand, the tetrahedral angles around the mercury atom range from 103.6(1) to 122.3(1)°, the larger angle being subtended by the two sulphur atoms. The only other crystal structure of a complex containing this ligand not already mentioned is that of $[Cu_2Cl_2\{Ph_2P(S)CH_2CH_2(S)PPh_2\}]$.[5] In this dimeric compound the two diphosphine ligands bridge the copper atoms which, in turn, are bridged by two chloride atoms.[5] The present study demonstrates that this diphosphine ligand can in fact function as a bidentate chelating ligand.

Acknowledgements

The Australian Research Council is thanked for support. Laboratory and other facilities from Guru Nanak Dev University are gratefully acknowledged.

References

1 T. S. Lobana, *Prog. Inorg. Chem.*, 1989, in the press.
2 N. A. Bell, L. A. March, and I. W. Nowell, *Inorg. Chim. Acta*, 1989, **156**, 195 and refs. therein.
3 A. M. Bond, R. Colton, D. Dakternieks, and K. W. Hanck, *Inorg. Chem.*, 1982, **21**, 117 and refs. therein.
4 S. S. Sandhu and T. Singh, *Indian J. Chem., Sect. A*, 1977, **15**, 829.
5 K. L. Brown, *Acta Crystallogr., Sect. B*, 1979, **35**, 462.
6 T. S. Lobana, M. K. Sandhu, and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 1988, 1401.
7 I. J. Colquhoun, S. O. Grim, W. McFarlane, J. D. Mitchell, and P. H. Smith, *Inorg. Chem.*, 1981, **20**, 2516.
8 A. M. Bond, R. Colton, and P. Panagiotidou, *Organometallics*, 1988, **7**, 1767.
9 D. E. Berry, J. Browning, K. R. Dixon, and R. W. Hilts, *Can. J. Chem.*, 1988, **66**, 1272.
10 R. Usón, A. Laguna, M. Laguna, M. N. Fraile, P. G. Jones, and C. F. Erdbrügger, *J. Chem. Soc., Dalton Trans.*, 1989, 73.
11 T. S. Lobana and P. K. Sharma, *Indian J. Chem., Sect. A*, 1988, **27**, 784.
12 L. Maier, in 'Organic Phosphorus Compounds,' eds. G. M. Kosolapoff and L. Maier, Wiley-Interscience, New York, 1972, vol. 4, ch. 1.
13 S. S. Sandhu and T. Singh, *Transition Met. Chem. (Weinheim, Ger.)*, 1976, **1**, 155; L. Maier, in 'Organic Phosphorus Compounds,' eds. G. M. Kosolapoff and L. Maier, Wiley-Interscience, New York, 1972, vol. 4, ch. 7.
14 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
15 W. C. Hamilton and J. A. Ibers, 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 149.
16 L. Fälth, *Chem. Scr.*, 1976, **9**, 71.
17 N. A. Bell, L. A. March, and I. W. Nowell, *Inorg. Chim. Acta*, 1989, **156**, 201.
18 C. Chieh, *Can. J. Chem.*, 1977, **55**, 1115.
19 D. Grdenic, *Q. Rev. Chem. Soc.*, 1965, **19**, 303.
20 C. D. Garner, N. C. Howlader, F. E. Mabbs, P. M. Boorman, and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1978, 1350.
21 N. A. Bell, L. A. March, and I. W. Nowell, *Inorg. Chim. Acta*, 1989, **156**, 195.
22 S. W. Cowan, D. Dakternieks, R. W. Gable, B. F. Hoskins, C. L. Rolls, and E. R. T. Tiekink, *Aust. J. Chem.*, 1986, **39**, 547.
23 T. S. Lobana, M. K. Sandhu, M. R. Snow, and E. R. T. Tiekink, *Acta Crystallogr., Sect. C*, 1988, **44**, 179.

Received 20*th June* 1989; *Paper* 9/02597I