Crystal and Molecular Structure of a Lattice Adduct, $HgPh_2{\cdot}2[Hg(SCN)_2(PPh_3)_2]$: An Unusual Case of Two-and Four-co-ordinate Mercury in the Same Unit Cell†

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Reaction of phenylmercury(II) thiocyanate with triphenylphosphine in ethanol formed a product of unusual stoicheiometry, $HgPh_2{\cdot}2[Hg(SCN)_2(PPh_3)_2]$ which has been characterised by *X*-ray crystallography. The complex crystallises in the triclinic space group $P\bar{1}$ with unit-cell parameters $a = 10.426(1)$, $b = 19.576(3)$, $c = 9.821(2)$ Å, $\alpha = 94.26(3)$, $\beta = 97.00(4)$, and $\gamma = 87.08(2)°$. Four-co-ordinate $Hg(SCN)_2(PPh_3)_2$ molecules represent a new crystalline modification of the previously reported monoclinic form. The adduct $HgPh_2{\cdot}2[Hg(SCN)_2(PPh_3)_2]$ represents an unusual case of the existence of two-co-ordinate linear Hg^{II} and distorted tetrahedral Hg^{II} in the same unit cell.

Recently, it has been found that the reaction of phenylmercury(II) nitrate with triphenylphosphine formed the adduct $[HgPh(PPh_3)(NO_3)]$[1] which did not undergo the symmetrisation reaction (1) as reported by Coates and Lauder.[2] This

$$2[HgPh(PPh_3)(NO_3)] \rightleftharpoons [Hg(PPh_3)_2(NO_3)_2] + HgPh_2 \quad (1)$$

adduct became the first structurally characterised complex of organomercury(II) with a phosphorus-containing ligand.[3] In the present investigation, it was intended to prepare $[HgPh(SCN)(PPh_3)]$ from the reaction of $[HgPh(SCN)]$ with PPh_3 in an organic solvent. However, an unusual lattice adduct containing one $HgPh_2$ sandwiched between two $Hg(SCN)_2(PPh_3)_2$ units was formed instead.

Experimental

Phenylmercury(II) thiocyanate was prepared by the reaction of phenylmercury(II) nitrate with potassium thiocyanate in dry ethanol.

To a solution of phenylmercury(II) thiocyanate (128 mg, 0.38 mmol) in ethanol (35 cm^3) was added a solution of PPh_3 (Sisco Chemicals, Bombay) (100 mg, 0.38 mmol) in ethanol (35 cm^3). The mixture was stirred on a magnetic stirrer for 1 h. The filtrate was allowed to evaporate slowly (20 °C) when colourless prismatic crystals were formed after 3—4 d.

X-Ray Structure Determination.—Crystal data. $C_{88}H_{70}Hg_3N_4P_4S_4$, $M = 2\,037.4$, triclinic, $a = 10.426(1)$, $b = 19.576(3)$, $c = 9.821(2)$ Å, $\alpha = 94.26(3)$, $\beta = 97.00(4)$, $\gamma = 87.08(2)°$, $U = 1\,982.2(1)$ Å^3 [by least-squares refinement of 25 automatically centred reflections ($13 \leqslant \theta \leqslant 15°$), $\lambda = 0.710\,69$ Å], space group $P\bar{1}$ (no. 2), $Z = 1$, $D_c = 1.707$ g cm^{-3}, D_m not measured, approximate dimensions 0.3 × 0.3 × 0.35 mm, $F(000) = 990$, $\mu(Mo\text{-}K_\alpha) = 60.2$ cm^{-1}.

Data collection and processing. Enraf-Nonius CAD4 diffractometer; ω—2θ mode with scan width $= 0.75 + 0.35 \tan\theta$, scan speed 3.33° min^{-1} to maximum of 90 s for weak reflections, graphite-monochromated Mo-K_α radiation. 7 385 Reflections ($h \pm k \pm l$, $1 \leqslant \theta \leqslant 25°$), 6 946 unique, with 6 468 (93%) having $I > 3\sigma(I)$. During the course of the data collection (144 h) a standard reflection indicated a decay in the crystal of 15%, a correction for which was applied.

Structure analysis and refinement. The structure was solved by the heavy-atom method with the co-ordinates of both mercury atoms being derived. Subsequent Fourier maps determined the positions of all the remaining non-hydrogen atoms. Full-matrix anisotropic refinement of the mercury atoms and isotropic refinement of the other atoms converged at $R = 0.095$ with hydrogen atoms in calculated positions. An absorption correction by DIFABS[4] reduced $R = 0.059$. Subsequent full-matrix anisotropic refinement of all non-hydrogen atoms, hydrogens fixed as before, converged at $R = 0.025$, $R' = 0.035$. The weighting scheme $w = 1/[\sigma(I)^2 + 0.075(I)^2]^{\frac{1}{2}}$ gave a satisfactory agreement analysis. All calculations were performed on a DEC Microvax II computer using scattering factor data from ref. 5.

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

Table 1 contains the atomic positional parameters and Table 2 selected bond lengths and angles.

The unit cell contains both two-co-ordinate, $HgPh_2$, and four-co-ordinate, $Hg(SCN)_2(PPh_3)_2$, molecules. In the $HgPh_2$ unit the geometry is essentially similar to that found in both the isolated $HgPh_2$ molecule[6] and the weak adduct $[HgPh_2\{Ph_2P(S)CH_2CH_2(S)PPh_2\}]$.[7] The $Hg(SCN)_2(PPh_3)_2$ molecules lie on either side of the centrosymmetric $HgPh_2$ moiety, Figure, and represent a new crystalline modification of the previously reported monoclinic form.[8]

There are no significant interactions between the phenyl ring of $HgPh_2$ and the $Hg(SCN)_2(PPh_3)_2$ molecule, the shortest non-bonded interaction being 3.5 Å. This is somewhat surprising although for the corresponding monoclinic form Makhija *et al.*[8] report that the immediate environment of the phosphorus atoms is not exceptionally overcrowded. Thus, it is possible that small variations in the geometry around the Hg(2) and P atoms

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Fractional atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses for $HgPh_2 \cdot 2[Hg(SCN)_2(PPh_3)_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Hg(1)	0.000	0.000	0.000	C(19)	0.682 3(5)	0.421 1(3)	0.929 2(5)
Hg(2)	0.211 76(1)	0.265 95(1)	0.686 50(1)	C(20)	0.610 0(5)	0.395 8(3)	0.809 8(5)
S(1)	0.006 6(1)	0.329 44(7)	0.759 8(1)	C(21)	0.488 6(4)	0.306 0(2)	0.542 0(4)
S(2)	0.317 5(2)	0.210 19(6)	0.903 1(1)	C(22)	0.590 6(4)	0.263 0(2)	0.592 1(5)
P(1)	0.381 85(9)	0.349 11(5)	0.657 64(9)	C(23)	0.664 1(5)	0.226 5(3)	0.503 1(6)
P(2)	0.138 21(9)	0.194 68(5)	0.472 21(9)	C(24)	0.638 4(5)	0.231 2(3)	0.364 2(5)
N(1)	0.104 5(6)	0.457 2(3)	0.851 4(7)	C(25)	0.536 9(5)	0.273 8(3)	0.312 2(5)
N(2)	0.263(1)	0.075 2(3)	0.858 4(8)	C(26)	0.462 9(4)	0.311 6(2)	0.401 5(4)
C(1)	0.067 2(5)	0.405 2(3)	0.813 1(5)	C(27)	0.267 3(4)	0.140 4(2)	0.408 9(4)
C(2)	0.284 0(6)	0.130 7(3)	0.874 7(6)	C(28)	0.378 9(4)	0.128 2(2)	0.497 1(5)
C(3)	−0.121 1(6)	0.087 7(3)	−0.003 4(5)	C(29)	0.476 4(5)	0.085 3(3)	0.453 2(6)
C(4)	−0.251 1(6)	0.085 2(3)	0.013 6(6)	C(30)	0.465 3(5)	0.055 3(3)	0.321 3(6)
C(5)	−0.333 4(7)	0.141 2(3)	0.006 7(7)	C(31)	0.354 9(6)	0.067 6(3)	0.232 6(6)
C(6)	−0.288 5(8)	0.203 8(3)	−0.016 9(6)	C(32)	0.255 2(5)	0.109 4(2)	0.276 1(5)
C(7)	−0.160 0(8)	0.208 8(3)	−0.031 6(6)	C(33)	0.080 4(4)	0.252 9(2)	0.341 0(4)
C(8)	−0.077 4(7)	0.151 7(3)	−0.024 1(5)	C(34)	0.154 2(4)	0.268 6(2)	0.239 9(4)
C(9)	0.314 1(4)	0.425 2(2)	0.578 3(4)	C(35)	0.111 8(5)	0.320 0(3)	0.154 5(5)
C(10)	0.374 2(4)	0.487 3(2)	0.602 7(4)	C(36)	−0.003 6(6)	0.355 2(3)	0.166 4(5)
C(11)	0.317 3(5)	0.544 9(2)	0.541 4(5)	C(37)	−0.077 5(5)	0.339 6(3)	0.264 7(5)
C(12)	0.203 7(5)	0.540 4(2)	0.455 9(5)	C(38)	−0.036 8(4)	0.288 9(2)	0.352 8(4)
C(13)	0.143 8(5)	0.479 5(2)	0.430 1(5)	C(39)	0.008 2(4)	0.138 5(2)	0.485 3(4)
C(14)	0.197 6(4)	0.421 7(2)	0.492 6(5)	C(40)	−0.013 3(4)	0.118 8(2)	0.612 6(4)
C(15)	0.482 7(4)	0.377 4(2)	0.812 1(4)	C(41)	−0.103 6(5)	0.070 0(3)	0.620 1(5)
C(16)	0.430 6(5)	0.384 4(2)	0.935 9(4)	C(42)	−0.172 1(4)	0.041 5(2)	0.503 4(5)
C(17)	0.505 1(6)	0.409 8(3)	1.054 3(5)	C(43)	−0.152 7(5)	0.062 0(2)	0.376 7(5)
C(18)	0.630 1(5)	0.428 1(3)	1.049 3(5)	C(44)	−0.063 7(4)	0.111 3(2)	0.367 5(4)

Table 2. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Hg(2)–P(1)	2.522(1)	Hg(1)–C(3)	2.078(7)
Hg(2)–P(2)	2.498(1)	P(1)–C(9)	1.804(4)
Hg(2)–S(1)	2.571(1)	P(1)–C(15)	1.805(4)
Hg(2)–S(2)	2.566(1)	P(1)–C(21)	1.820(4)
S(1)–C(1)	1.665(7)	P(2)–C(27)	1.813(4)
S(2)–C(2)	1.609(6)	P(2)–C(33)	1.811(4)
C(1)–N(1)	1.129(8)	P(2)–C(39)	1.811(4)
C(2)–N(2)	1.116(9)		
P(1)–Hg(2)–P(2)	114.11(3)	P(2)–Hg(2)–S(2)	120.98(4)
P(1)–Hg(2)–S(1)	111.04(4)	S(1)–Hg(2)–S(2)	104.73(5)
P(1)–Hg(2)–S(2)	100.11(4)	Hg(2)–S(1)–C(1)	99.4(2)
P(2)–Hg(2)–S(1)	105.49(4)	Hg(2)–S(2)–C(2)	104.2(2)

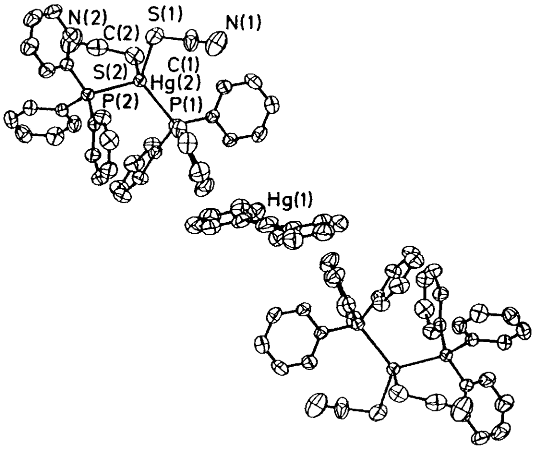

Figure. The molecular structure of $HgPh_2 \cdot 2[Hg(SCN)_2(PPh_3)_2]$ showing two centrosymmetrically related molecules. The phenyl groups bonded to P(1) are C(9)–C(14), C(15)–C(20), and C(21)–C(26)

are possible in order to avoid unduly close intermolecular contacts. In the monoclinic form the volume of the unit cell per molecule is 862 Å^3. The equivalent volume in our form (calculated by subtracting the contribution of the $HgPh_2$ molecules[6]) is 867 Å^3 indicating about the same packing efficiency.

Both Hg(2)–P distances are longer than in the triclinic form, and also in the structures of $[HgPh(PPh_3)(NO_3)]$[1] and $[Hg(PPh_3)_2(NO_3)_2]$[9] and are comparable to those in the orthorhombic modification of $[HgCl_2(PPh_3)_2]$[10] [Hg–P(1) 2.503(6); Hg–P(2) 2.532(4) Å].

Both Hg–S distances are longer than those expected for Hg^{II}. The SCN groups are linear and as commonly observed for mercury compounds bind to the metal through the sulphur atoms. The variations in the angles about Hg(2) between the two forms is reported in Table 2.

The C–P–C angles of the PPh_3 moiety are in agreement with those reported for $[Hg(PPh_3)_2I_2]$[11] and the monoclinic form, and the P–C and C–C bond lengths show no unusual variations from those found in free PPh_3.[12]

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