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Crystal Structure
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(Dicyclohexyldithiophosphinato-*S*,*S*′)-[2-(2-pyridyl-*N*)phenyl]mercury(II)

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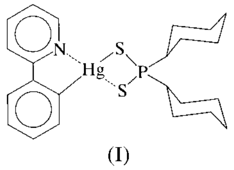
The crystal structure of the title compound, [Hg($C_{11}H_8N$)($C_{12}H_{22}PS_2$)], consists of molecules in which the Hg atom is coordinated strongly to the C atom in position 2 of the phenyl group and to one of the dithiophosphinate S atoms, and at longer distances to the pyridine N atom and the other S atom. The C—Hg—S fragment involving the S atom more strongly bound to Hg is almost linear [C—Hg—S = 178.9 (3)°].

Comment

In the reaction of [2-(2-pyridyl)phenyl]mercury(II) acetate, [Hg(PhPy)(OAc)], with diphenyldithiophosphinic acid, HS_2PPh_2, the C—Hg bond is broken to afford phenylpyridine and [$Hg_2(S_2PPh_2)_4$] (Casas *et al.*, 1997). The reaction of dicyclohexyldithiophosphinic acid, HS_2PCy_2, with an appropriate mole ratio of the $TlPh_2^+$ cation in chloroform likewise produces protodemetallation (*i.e.* the loss of one or more alkyl or aryl groups from the metal with formation of an alkane or arene), affording Tl^{3+} species and benzene (Casas *et al.*, 1995). To explore this type of process further, we reacted [Hg(PhPy)(OAc)] with HS_2PCy_2. At room temperature, the reaction afforded a black solid which probably contains HgS, but near 273 K, in an ice bath, it yielded a product from which colourless crystals of the title organomercury dithiophosphinate, [Hg(PhPy)(S_2PCy_2)], (I), were isolated, showing that no protodemetallation process had occurred.



(I)

Fig. 1 shows the molecular structure of (I) and the atom-numbering scheme used. Selected interatomic distances and angles are listed in Table 1. The Hg atom is strongly coordinated to C8, the carbon at position 2 of the phenyl group [Hg—C8 = 2.088 (11) Å], and to one of the dithiophosphinate S atoms (S1). The C8—Hg—S1 fragment is almost linear [178.9 (3)°], as is usual in monoorganomercuric thiolate derivatives (Casas *et al.*, 1999). The Hg—S1 distance [2.365 (3) Å] lies in the range observed for other organomercury(II) dithiophosphates and dithiophosphinates (Zukerman-Schpector *et al.*, 1991; Vázquez-López *et al.*, 1992; Casas *et al.*, 1994). The Hg—N distance of 2.694 (9) Å is also shorter than the sum of the van der Waals radii (3.55 Å; Casas *et al.*, 1999; Bondi, 1964); it is close to the values found in [Hg(PhPy)Cl] [2.63 (1) and 2.67 (1) Å; Constable *et al.*, 1989], but is clearly shorter than in [Hg(PhPy)(AcO)] [2.727 (9) Å; Casas *et al.*, 1996] and longer than in [Hg(PhPy)(Hstsc)] [2.576 (6) Å; H_2stsc = 2-formyl-(2-hydroxybenzene)thiosemicarbazone; Lobana *et al.*, 1998]. The phenyl and pyridinyl rings of the $[Hg(PhPy)]^+$ moiety in (I) are not coplanar but form a dihedral angle of 19.3 (6)°, and the interplanar angle is narrower than in the acetate derivative (Casas *et al.*, 1996).

The other dithiophosphinato sulfur, S2, lies 3.336 (3) Å from the Hg atom. This distance, too, is shorter than the sum of the corresponding van der Waals radii (3.8 Å; Casas *et al.*, 1999; Bondi, 1964), and though longer than that observed in [HgPh (S_2PEt_2)] [3.182 (3) Å; Casas *et al.*, 1994], is within the usual range for secondary Hg···S bonds in mono-organomercury dithiophosphates and dithiophosphinates. Taking this Hg···S interaction into account, the coordination geometry around the Hg atom can be described as distorted square planar [the largest displacement from the least-squares plane through Hg/N/C8/S1/S2 is for N, which is 0.35 (1) Å out of the plane].

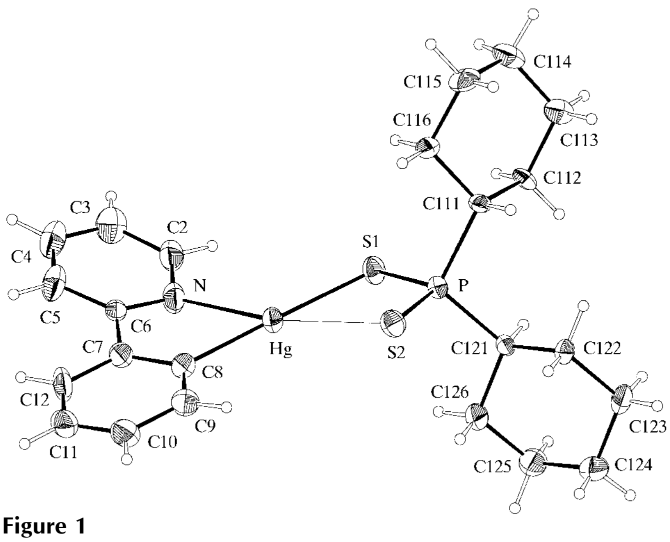


Figure 1
A view of the molecule of compound (I) (*ZORTEP*; Zsolnai & Huttner, 1994) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii.

Secondary Hg···S bonds in monoorganomercury dithiophosphates and dithiophosphinates are generally intermolecular, organizing the molecules into centrosymmetric dimers, as in [HgMe(S_2PPh_2)] (Zukerman-Schpector *et al.*, 1991) and [HgPh{$S_2P(OEt)_2$}] (Vázquez-López *et al.*, 1992), or into linear chains of identically oriented monomers, as in [HgPh(S_2PEt_2)]. In the case of (I), these possibilities are probably prevented by steric hindrance. The structure of (I) is probably most similar to that of 2-formyl-(2-hydroxybenzene)thiosemicarbazonate, [Hg(PhPy)(Hstsc)] (Lobana *et al.*, 1998). The lattices of these compounds consist of molecules which have no intermolecular interactions and in which the Hg atom has two primary bonds [Hg—C8, Hg—S1 and C8—Hg—S1 in the dithiophosphinate complex, (I) (Table 1); Hg—C = 2.083 (7) and Hg—S = 2.357 Å, and C—Hg—S = 177.7 (2)° in the thiosemicarbazonate] and two secondary bonds [Hg—N and Hg—S2 in (I) (Table 1); two Hg—N bonds with distances 2.576 (6) and 3.126 (6) Å in the thiosemicarbazonate]. Finally, the $S_2PCy_2^-$ ligand is more anisobidentate in (I) (see Table 1) than in [$TlPh_2(S_2PCy_2)$] [Tl—S1 = 2.789 (3) and Tl—S2 = 2.816 (3) Å; Casas *et al.*, 1995]. In keeping with this, the P—S1 bond, corresponding to S strongly coordinated to metal, is longer and the P—S2 bond shorter in (I) (Δ/σ = 18.2) than in the latter compound.

Experimental

[2-(2-Pyridyl)phenyl]mercury acetate (21.6 mg, 0.052 mmol) and dicyclohexyldithiophosphinic acid (13.7 mg, 0.052 mmol) were dissolved in chloroform at 273 K. Slow evaporation in the refrigerator gave colourless crystals suitable for X-ray analysis.

Crystal data

[$Hg(C_{11}H_8N)(C_{12}H_{22}PS_2)$]
M_r = 616.16
Monoclinic, $P2_1/n$
a = 14.923 (2) Å
b = 9.9557 (10) Å
c = 15.728 (2) Å
β = 95.088 (10)°
V = 2327.5 (5) Å^3
Z = 4
D_x = 1.758 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 8–15°
μ = 6.87 mm^{-1}
T = 293 (2) K
Block, colourless
0.25 × 0.25 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
κ-geometry diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: analytical (Alcock, 1970)
$T_{\min}$ = 0.428, $T_{\max}$ = 0.709
4252 measured reflections
4094 independent reflections
2272 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.060
$\theta_{\max}$ = 24.97°
h = −17 → 17
k = 0 → 11
l = 0 → 18
1 standard reflection
frequency: 30 min
intensity decay: −3%

Refinement

Refinement on F^2
$R(F)$ = 0.039
$wR(F^2)$ = 0.103
S = 0.961
4094 reflections
253 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.67 e Å^{-3}
$\Delta\rho_{\min}$ = −0.712 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Hg—C8	2.088 (11)	P—C111	1.839 (9)
Hg—S1	2.365 (3)	P—C121	1.843 (8)
Hg—N	2.694 (9)	P—S2	1.963 (4)
Hg—S2	3.336 (3)	P—S1	2.066 (4)
C8—Hg—S1	178.9 (3)	C111—P—S2	112.8 (3)
C8—Hg—N	72.7 (4)	C121—P—S2	113.0 (3)
S1—Hg—N	106.9 (2)	C111—P—S1	104.6 (3)
C8—Hg—S2	109.5 (3)	C121—P—S1	104.8 (3)
S1—Hg—S2	70.99 (8)	S2—P—S1	115.24 (17)
N—Hg—S2	171.8 (2)	P—S2—Hg	74.18 (11)
C111—P—C121	105.5 (4)	P—S1—Hg	99.12 (13)

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); data reduction: *XCAD*-4 (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELX*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELX*97; software used to prepare material for publication: *SHELX*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1445). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (2000). C**56**, 182–183 José S. Casas *et al.* • [$Hg(C_{11}H_8N)(C_{12}H_{22}PS_2)$] **183**