

Dicyclohexyldithiophosphinates and diethyldithiophosphinates of methylmercury(II) and phenylmercury(II): crystal and molecular structure of $[\text{HgPh}(\text{S}_2\text{PEt}_2)]$

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Abstract

Methylmercury(II) and phenylmercury(II) dithiophosphinates $[\text{HgR}(\text{S}_2\text{PR}'_2)]$ ($\text{R} = \text{Me}$ or Ph ; $\text{R}' = \text{Et}$ or Cy) were synthesized. In $[\text{HgPh}(\text{S}_2\text{PEt}_2)]$ the mercury atom is coordinated to a phenyl carbon atom and to one S atom of the dithiophosphinate ($\text{Hg}-\text{C}$, 2.07(2) Å, $\text{Hg}-\text{S}$, 2.375(3) Å). The other sulphur atom of the dithiophosphinate forms two weak $\text{Hg}\cdots\text{S}$ interactions, one intramolecular and other intermolecular ($\text{Hg}-\text{S}$, 3.182(3) Å and 3.183(3) Å respectively). The mass, IR, Raman and ^1H , ^{13}C , ^{31}P and ^{199}Hg nuclear magnetic resonance spectra of the compounds are discussed.

Key words: Mercury; Methyl; Phenyl; Dithiophosphinate; Dithiolate; X-ray diffraction

1. Introduction

Structural studies of monoorganomercury(II) dithiocarbamates and xanthates [1,2] show that these two types of dithiolate complex have primary $\text{Hg}-\text{S}$ bonds of similar strength but differ significantly as regards intermolecular and intramolecular secondary $\text{Hg}\cdots\text{S}$ bonds. These characteristics seem also to hold for monoorganomercury dithiophosphinates and dithiophosphates although, in these compounds, only intermolecular secondary bonds have been observed [3,4]. We have now prepared some new methylmercury(II) and phenylmercury(II) dithiophosphinates and solved the structure of $[\text{HgPh}(\text{S}_2\text{PEt}_2)]$ by X-ray diffraction.

2. Experimental details

Methylmercury and phenylmercury acetates (Alfa), tetraethylphosphine disulphide (Alfa) and dicyclohexyldithiophosphinic acid (Strem) were used as re-

ceived. Sodium diethyldithiophosphinate dihydrate and tetraethylammonium dicyclohexyldithiophosphinate were prepared by a published method [5,6]. Elemental analysis was performed with a Carlo Erba 1108 microanalyser or by Galbraith Laboratories Inc. (Knoxville, TN, USA). Mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS90 data system and operating under electron impact (EI) conditions (direct insertion probe; 70 eV; 250°C). All the ions included in Table 4 were identified using DS90 software. IR spectra were recorded in KBr pellets on Perkin-Elmer 1130 and Mattson FT-IR Cygnus 100 spectrometers, and Raman spectra were obtained with a Dilor Omars 89 spectrometer (argon ion laser; 5145 Å) using powdered samples in capillary tubes. Fluorescence problems prevented the Raman spectrum of $[\text{HgR}(\text{S}_2\text{PEt}_2)]$ from being recorded. ^1H (250.13 MHz), proton-decoupled ^{13}C (62.83 MHz), ^{31}P (101.26 MHz) and ^{199}Hg (44.80 MHz) nuclear magnetic resonance (NMR) spectra were recorded in CDCl_3 (in tubes of 5 mm outside diameter at room temperature) on a Bruker WM-250 spectrometer and referred to the solvent signal (^1H , 7.27 ppm; ^{13}C , 77.00 ppm), 85% H_3PO_4 and

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95% HgMe₂ in Et₂O respectively. X-ray crystallographic data were obtained on an Enraf–Nonius CAD-4 diffractometer. Calculations were performed on a DEC MicroVAXII computer.

2.1. Synthesis of (diethyldithiophosphinato)methylmercury(II)

To a suspension of methylmercury acetate (1.03 g, 3.75 mmol) in ethanol (20 ml) at 0°C was added the stoichiometric quantity of NaS₂PEt₂·2H₂O (0.79 g) dissolved in the same solvent (20 ml). The mixture was stirred for 3 h at 0°C, and the solution obtained was vacuum concentrated and stored for several days at 4°C. The white crystals formed were filtered off and vacuum dried (melting point (m.p.), 40°C). Anal. Found: C, 16.4; H, 3.7. C₅H₁₃HgPS₂ calc.: C, 16.3; H, 3.6%.

2.2. Synthesis of (dicyclohexyldithiophosphinato)methylmercury(II)

To a suspension of methylmercury acetate (1.00 g, 3.64 mmol) in chloroform (25 ml) at 0°C was added the stoichiometric quantity of HS₂PCy₂ (0.96 g) dissolved in the same solvent (25 ml). The solution obtained was stirred for 3 h at 0°C and vacuum concentrated. The white precipitate obtained by addition of cold methanol was filtered off and vacuum dried (m.p., 145–148°C). Anal. Found: C, 32.6; H, 5.3%. C₁₃H₂₅HgPS₂ calc.: C, 32.7; H, 5.3%.

2.3. Synthesis of (diethyldithiophosphinato)phenylmercury(II)

To a suspension of phenylmercury acetate (1.00 g, 2.97 mmol) in ethanol (25 ml) at 0°C was added the stoichiometric quantity of NaS₂PEt₂·2H₂O (0.63 g) dissolved in the same solvent (20 ml). After stirring for 3 h at 0°C the solution was filtered and stored at 4°C for several days until crystals suitable for X-ray diffraction measurements formed (m.p., 92–93°C). Anal. Found: C, 28.3; H, 3.7. C₁₀H₁₅HgPS₂ calc.: C, 27.9; H, 3.5%.

2.4. Synthesis of (dicyclohexyldithiophosphinato)phenylmercury(II)

To a suspension of phenylmercury acetate (1.01 g, 3.00 mmol) in chloroform (25 ml) at 0°C was added the stoichiometric quantity of HS₂PCy₂ (0.79 g) dissolved in the same solvent (25 ml). The solution was stirred for 3 h at 0°C and the solvent removed under vacuum. 0.64 g of the solid obtained were dissolved in dichloromethane and the solution cooled to –30°C for several days. The white precipitate formed was filtered off and vacuum dried (m.p., 177°C). Found: C, 39.9; H, 5.0. C₁₈H₂₇HgPS₂ calc.: C, 40.1; H, 5.1%.

2.5. X-ray data collection, structure analysis and refinement

A colourless prismatic crystal of [HgPh(S₂PEt₂)] was mounted on a glass fibre and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range 8° < θ < 12°. Data were collected at 293 K using Mo Kα radiation (λ = 0.71073 Å) and the ω–2θ scan technique. The data were corrected for Lorentz and polarization effects and empirical absorption [7], and secondary extinction corrections were applied [8].

The structure was solved by direct methods that revealed the position of all non-hydrogen atoms and refined on *F* by a full-matrix least-squares procedure

TABLE 1. Crystal data, data collection and structure refinement parameters of [HgPh(S₂PEt₂)]

Formula	C ₁₀ H ₁₅ PS ₂ Hg
Molecular weight	430.93
Crystal class	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit-cell dimensions	
<i>a</i> (Å)	6.238(1)
<i>b</i> (Å)	20.162(2)
<i>c</i> (Å)	11.281(1)
β (°)	104.63(1)
Volume	1372.9(3) Å ³
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	2.085
μ(Mo Kα) (cm ⁻¹)	115.83
F(000)	808
Crystal shape	Prismatic,
Dimensions (mm × mm × mm)	0.08 × 0.16 × 0.32
Minimum/maximum absorption correction	0.557/1.244
Maximum value of (sin θ)/λ reached in intensity measurement	0.930
Ranges of <i>h</i> , <i>k</i> and <i>l</i>	0 < <i>h</i> < 8, 0 < <i>k</i> < 26, –14 < <i>l</i> < 14
Interval of standard reflections measured (s)	3600
Total number of reflections measured;	
θ range (°)	3702; 3–28
Number of unique reflections; <i>R</i> _{int}	3114; 0.023
Number of observed reflections	1841
Criterion for observed reflections	<i>I</i> > 3σ(<i>I</i>)
Weighting scheme	1/σ ² (<i>F</i>)
Number of parameters refined	128
Value of <i>R</i>	0.032
Value of <i>R</i> _w	0.036
Ratio Δ/σ of maximum least-squares shift to estimated deviation	0.001
Maximum height in final Δ <i>F</i> map; (electrons Å ⁻³)/minimum height in final Δ <i>F</i> map (electrons Å ⁻³)	0.634; –0.583
Error in an observation of unit weight	2.389
Secondary extinction coefficient	1.4860 × 10 ⁻⁷

TABLE 2. Positional and equivalent isotropic thermal parameters

Atom	x	y	z	U_{eq}^a (Å ²)
Hg	-0.02198(7)	0.36167(2)	0.41998(4)	0.0550(2)
S(1)	-0.0428(4)	0.2973(2)	0.2411(3)	0.071(2)
S(2)	0.4730(5)	0.3310(1)	0.4090(1)	0.060(1)
P	0.2917(4)	0.2815(1)	0.2680(2)	0.051(1)
C(1)	0.013(2)	0.4191(5)	0.575(1)	0.061(5)
C(2)	-0.163(2)	0.4530(6)	0.598(1)	0.071(6)
C(3)	-0.133(2)	0.4930(6)	0.702(1)	0.080(7)
C(4)	0.073(2)	0.4996(7)	0.782(1)	0.082(7)
C(5)	0.249(2)	0.4648(6)	0.760(1)	0.072(8)
C(6)	0.218(2)	0.4246(6)	0.660(1)	0.063(6)
C(11)	0.356(2)	0.3002(6)	0.124(1)	0.065(6)
C(12)	0.356(2)	0.3756(7)	0.095(1)	0.09(1)
C(21)	0.335(2)	0.1939(6)	0.283(1)	0.071(7)
C(22)	0.258(3)	0.1615(7)	0.386(1)	0.09(1)

^a U_{eq} is defined as one third of the trace of the orthogonalized tensor U_{ij} .

using anisotropic displacement factors. The positions of H atoms were calculated geometrically and included in structure factor calculation with $B_{iso} = 5.0 \text{ \AA}^2$ fixed but not refined. The programs used were SHELXS86 [9] and VAX/SDP [10]. Experimental details and refinement results are listed in Table 1. Positional and equivalent thermal parameters are given in Table 2. The data have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. X-ray structure of [HgPh(S₂PEt₂)]

Figure 1 shows the molecule of this compound with the numbering scheme used. The main bond lengths and angles are given in Table 3. The mercury atom is coordinated to the C(1) atom of the phenyl group and to the S(1) atom of the dithiophosphate; the C(1)–Hg–S(1) fragment is almost linear (C(1)–Hg–S(1), 177.0(3)°). The Hg–S(1) distance (2.375(3) Å) lies in

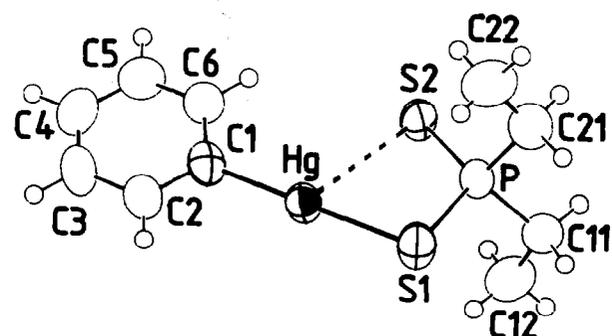


Fig. 1. ORTEP drawing showing the molecular structure of [HgPh(S₂PEt₂)], with the atom numbering scheme.

TABLE 3. Selected interatomic distances and angles for [HgPh(S₂PEt₂)]

Distance (Å)		Distance (Å)	
Hg–S(1)	2.375(3)	C(11)–C(12)	1.55(2)
Hg–C(1)	2.07(2)	C(21)–C(22)	1.51(2)
Hg–S(2)	3.182(3)	C(1)–C(2)	1.37(2)
Hg–S(2) ⁱ	3.183(3)	C(2)–C(3)	1.39(1)
S(1)–P	2.057(4)	C(3)–C(4)	1.38(2)
S(2)–P	1.975(4)	C(4)–C(5)	1.38(3)
P–C(11)	1.81(1)	C(5)–C(6)	1.36(2)
P–C(21)	1.79(1)	C(1)–C(6)	1.39(1)
Angle (°)		Angle (°)	
S(1)–Hg–S(2)	72.92(8)	S(1)–P–C(11)	106.3(4)
S(1)–Hg–S(2) ⁱ	91.13(9)	S(1)–P–C(21)	106.9(4)
S(2)–Hg–S(2) ⁱ	157.18(8)	S(2)–P–C(11)	114.1(4)
S(1)–Hg–C(1)	177.0(3)	S(2)–P–C(21)	112.2(4)
S(2)–Hg–C(1)	104.3(3)	P–C(11)–C(12)	113.9(9)
S(2) ⁱ –Hg–C(1)	91.8(3)	P–C(21)–C(22)	116(1)
S(1)–P–S(2)	113.2(2)	C(11)–P–C(21)	103.3(7)

Symmetry code: $i = x - 1, y, z$.

the range observed for other dithiolate complexes [1–4]. The S(2) atom is at equal distances from the mercury atom to which S(1) is bonded and the metal atom of a neighbouring molecule; these distances (Table 3) are shorter than the sum of the van der Waals radii [11], showing that S(2) bridges the two molecules via secondary bonds. The Hg...S(2)ⁱ interactions form chains throughout the crystal (Fig. 2). The coordination mode of the diethyldithiophosphate can thus be described as bimetal triconnective [12]. The diethyldithiophosphate has the usual antiplanar, antiplanar (ap, ap) conformation. A similar bonding arrangement for mercury has been observed in one of the two molecules constituting the asymmetric unit in [HgPh(S₂CNEt₂)] [2], although in this case the intramolecular and inter-

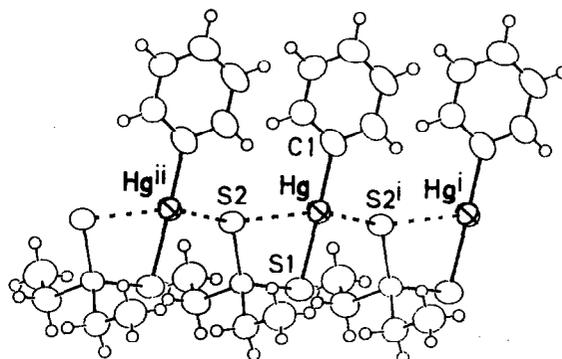


Fig. 2. ORTEP drawing of [HgPh(S₂PEt₂)], showing the intermolecular and intramolecular secondary Hg...S bonds.

molecular distances are unequal and both shorter than in [HgPh(S₂PEt₂)].

Certain differences between the structures of [HgPh(S₂PEt₂)] and [HgPh(S₂P(OEt)₂)] [4] are worth noting. First, the fact that the Hg–S(1) distance is slightly but significantly shorter in the dithiophosphinate is in keeping with the expected inductive influence of R' or R'O substituents on the donor capacity of the PS₂ group. Secondly, the dithiophosphate has no intramolecular Hg ··· S(2) interaction (and the intermolecular Hg ··· S(2) distance is longer). The inability of (EtO)₂PS₂⁻ to form a PS₂Hg ring cannot be ascribed to the differences from Et₂PS₂⁻ concerning the internal geometry of the PS₂ group because, the P–S distances are longer in the dithiophosphinate although the S(1)–P–S(2) angle is narrower in the dithiophosphinate (113.2(2)° as against 116.1(2)° in the dithiophosphate [4]). Rather, in [HgPh(S₂P(OEt)₂)] the S(2) atom is too far from the metal atom to form a pseudochelate ring because the torsion angle S(2)–P–S(1)–Hg is 53.3(4)°, whereas in [HgPh(S₂PEt₂)] the Hg, P, S(1) and S(2) atoms are almost coplanar (S(2)–P–S(1)–Hg, –6.1(2)°).

Finally, the P–S(1) and P–S(2) distances are longer and shorter, and the S(1)–P–S(2) and C(11)–P–C(21) angles smaller than the analogues in NaS₂PEt₂ · 2H₂O [13].

3.2. Mass spectra

The most significant peaks in the EI mass spectra of the compounds, and the fragments to which they are attributed are listed in Table 4. All the spectra feature

TABLE 4. Mass spectroscopy (MS) of compounds [HgR(S₂PR'₂)]

	MS <i>m/e</i> ^a (relative intensity (%))			
	HgMe(S ₂ PR' ₂)		HgPh(S ₂ PR' ₂)	
	R' ≡ Et	R' ≡ Cy ^b	R' = Et ^c	R' ≡ Cy ^c
HgR(S ₂ PR' ₂)	370 (22.0)	478 (36.7)	432 (6.6)	540 (1.7)
HgR(S ₂ PR') + H	342 (37.0)	369 (92.6)	404 (6.5)	458 (12.1)
HgR(S ₂ P) + 2H	—	314 (80.7)	—	376 (6.4)
HgR(S ₂ P) + H	313 (11.8)	—	375 (4.1)	—
HgRSP	—	280 (14.8)	—	342 (1.7)
HgRS	—	264 (1.3)	—	311 (0.9)
HgR ₂ S	—	264 (1.3)	—	—
HgR ₂	—	232 (1.7)	356 (16.9)	356 (16.3)
HgR	217 (26.3)	217 (22.8)	279 (12.3)	279 (10.7)
Hg	202 (100.0)	202 (6.2)	202 (< 0.5)	202 (1.9)
S ₂ PR' ₂	153 (22.4)	261 (16.1)	153 (6.8)	261 (1.3)
SPR' ₂	121 (30.5)	229 (23.7)	121 (4.0)	229 (3.8)

^a *m/e* values were computed for following: H, 1; C, 13; P, 31; S, 32; and Hg, 202.

^b Base peak |C₆H₁₁|.

^c Base peak |C₆H₅|.

TABLE 5. IR and Raman^a data for compounds [HgR(S₂PR'₂)]^b

Compound	$\nu_{\text{asym}}(\text{PS})$ (cm ⁻¹)	$\nu_{\text{sym}}(\text{PS})$ (cm ⁻¹)	$\Delta\nu$ (cm ⁻¹)	$\delta_{\text{sym}}(\text{CH}_3)$ (cm ⁻¹)	$\nu(\text{Hg-C})$ (cm ⁻¹)
NaS ₂ PEt ₂ · 2H ₂ O	619vs —	511m (512vs)	108	—	—
[HgMe(S ₂ PEt ₂)]	590vs	465s	125	1170w	530m
[HgPh(S ₂ PEt ₂)]	575vs	470s	105	—	—
HS ₂ PCy ₂	632vs —	522s (525s)	110	—	—
[Et ₄ N][S ₂ PCy ₂]	620vs (615w)	555s (551s)	65	—	—
[HgMe(S ₂ PCy ₂)]	620vs —	535s (532m)	85	1180w (1181s)	535s (542s)
[HgPh(S ₂ PCy ₂)]	618vs —	535s (536s)	83	—	—

^a Raman data in parentheses.

^b m, medium; vs, very strong; s, strong; w, weak.

the molecular ion but no polymetal species, showing the ease with which the weak intermolecular links are broken under electron impact. As in other organomercury(II) dithiophosphinates [3], at least two fragmentation pathways seem to be followed under the experimental conditions used: the breaking of the Hg–S bond followed by subsequent fragmentation of [S₂PR'₂] and [HgR] ions; the progressive breakdown of the dithiophosphinate moiety while the sulphur–mercury bond persists. The spectral intensities suggest the stability sequence [HgMe(S₂PR'₂)] > [HgPh(S₂PR'₂)].

3.3. Vibrational spectra

Table 5 lists the most significant IR and Raman data of the [HgR(S₂PR'₂)] compounds. For compounds of this type the difference $\Delta\nu$, between $\nu_{\text{asym}}(\text{PS})$ and $\nu_{\text{sym}}(\text{PS})$ has been used as an indication of coordination behaviour [14–16]; values of $\Delta\nu$ greater than 95 cm⁻¹ are taken to indicate monodentate coordination, values of 50–70 cm⁻¹ isobidentate coordination, and values of 70–90 cm⁻¹ anisobidentate coordination. According to this scheme, the $\Delta\nu$ values for the dialkyldithiophosphinate compounds studied in this work (Table 5) suggest anisobidentate coordination in the cyclohexyl derivatives and monodentate coordination in the ethyl derivatives, consistent with the X-ray results for [HgPh(S₂PEt₂)]. It should be borne in mind, however, that previous findings [6] suggest that, for S₂PEt₂, $\Delta\nu$ is not a sufficiently sensitive indicator of the coordination mode.

The values of $\delta_{\text{sym}}(\text{CH}_3)$ and $\nu(\text{Hg-C})$ in methylmercury complexes are close to those found in other compounds with sulphur-coordinated mercury [3,17].

3.4. Nuclear magnetic resonance studies

Table 6 shows the most significant NMR data of the dithiophosphinates and complexes. ³¹P and ¹⁹⁹Hg NMR data for diphenyldithiophosphinates [3] are included for comparison. Coordination shifts the signals of both the phosphorus atom and the α -carbon of the dithiophosphinates to higher frequency than in the acids, probably owing to the inductive effect of the metal. The shift is larger for the phosphorus nuclide due to its closer proximity to the donor atom.

The coupling constant ²J(¹H–¹⁹⁹Hg) is related to the stability constant β of methylmercury(II) compounds [18]. For structurally similar ligands possessing the same donor group as those included in this study, ²J decreases linearly as log β increases. The usual qualitative explanation for this relationship assumes that a strongly bound ligand *trans* to the R group in [HgRL] compounds weakens the Hg–C bond and decreases its s character. Since ²J is dominated by the Fermi contact term, this decrease reduces the value of the coupling constant [19]. Not surprisingly, ¹J(¹³C–¹⁹⁹Hg) is also sensitive to the *trans* influence of L, showing good linear correlation with ²J in some cases [19], although discrepancies have been observed when very different ligands are compared [20]. On these

grounds, the values of ¹J(¹³C–¹⁹⁹Hg) and ²J(¹H–¹⁹⁹Hg) in Table 6 suggest the following stability sequence for the methylmercury derivatives: [HgMe(S₂PCy₂)] \approx [HgMe(S₂PEt₂)] > [HgMe(S₂PPh₂)]. The same sequence may hold for the phenylmercury(II) derivatives, to judge by the ²J(¹H–¹⁹⁹Hg) values of these compounds (Table 6) and the similar thermodynamic stabilities of methylmercury(II)-thiolato and phenylmercury(II)-thiolato complexes [21].

Although the diamagnetic term can not be overlooked, the chemical shift of the ¹⁹⁹Hg nuclide is determined largely by the paramagnetic contribution σ_p [22]. According to the average energy approximation, this term is given by [23] the following equation:

$$\sigma_p = -A \Delta E^{-1} \langle r^{-3} \rangle P_u$$

Here A is a constant, ΔE is the average electronic excitation energy, r is the average distance between the 6p electrons and the nucleus and P_u is the “p-electron imbalance”, which depends largely upon the coordination number of the atom, the hybridization of its bonding orbitals and the ionicity of its bonds. An increase in the electron density on the mercury nucleus expands the 6p orbitals, reduces $\langle r^{-3} \rangle$ and σ_p and increases the shielding. However, the charge density on

TABLE 6. Selected nuclear magnetic resonance data in CDCl₃ solution

Compound	$\delta(^{13}\text{C}(\text{C}-\text{P}))^a$ (ppm)	¹ J(¹³ C– ³¹ P) (Hz)	$\delta(^{31}\text{P})^b$ (ppm)	$\delta(^1\text{H}(\text{R}-\text{Hg}))$ (ppm)	² J(¹ H– ¹⁹⁹ Hg) (Hz)	$\delta(^{13}\text{C}(\text{C}-\text{Hg}))$ (ppm)	ⁿ J(¹³ C– ¹⁹⁹ Hg) (Hz)	$\delta(^{199}\text{Hg})^b$ (ppm)
DS ₂ PEt ₂	31.65d	52.2	73.43s	—	—	—	—	—
HS ₂ PCy ₂	41.82d	46.7	85.84s	—	—	—	—	—
HS ₂ PPh ₂	135.63d	85.6	54.01s ^c	—	—	—	—	—
[HgMe(S ₂ PEt ₂)]	35.55d	50.2	82.46s	0.97	190.0	10.46	1392.2	–591.7s
[HgMe(S ₂ PCy ₂)]	42.41d	44.9	94.21s	0.92	189.4	10.53	1393.3	–566.7s
[HgMe(S ₂ PPh ₂)] ^c	139.65d	81.5	62.46s	1.00	192.1	10.85	1531.0	–607.6s
[HgPh(S ₂ PEt ₂)]	33.21d	49.3	84.88s	H _o , 7.37	181.9	C _i , 155.87 C _o , 136.19 C _m , 128.97 C _p , 128.73	113.5 185.8 34.9	–898.4s
[HgPh(S ₂ PCy ₂)]	42.22d	44.7	95.40s	H _o , 7.37	180.9	C _i , 156.31 C _o , 136.21 C _m , 128.88 C _p , 128.57	113.5 185.1 33.8	–871.3s
[HgPh(S ₂ PPh ₂)] ^c	138.79d	82.0	62.29s	H _o , 7.32	187.0	C _i , 155.78 ^c C _o , 136.14 C _m , 128.94 C _p , 128.73	111.9 ^d ^d	–926.2s

^a d, doublet.

^b s, singlet.

^c Data (some unpublished) obtained in the work reported in ref. 3.

^d Satellites of Hg–C coupling overlapped by the ligand phenyl signals.

Hg cannot be the dominant contribution to σ_P in dithiophosphinate compounds, because it is the least strong donor (Ph₂PS₂⁻ according to the J values; see Table 6) that gives the most shielded signal (a similar inverse relationship between the chemical shift and electronic charge of ¹⁹⁹Hg has been observed in silylmercury derivatives [22]). Hence it is ΔE and/or P_0 that must dominate the paramagnetic factor in dithiophosphinates.

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