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Synthesis and structural characterization of diphenyldithiophosphinates of methyl- and phenylmercury(II). Crystal structure of $MeHgS_2PPh_2$

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Abstract

Methyl- and phenyl-mercury(II) derivatives of diphenyldithiophosphinic acid (HS_2PPh_2) have been prepared. The structure of crystalline $MeHgS_2PPh_2$ has been determined by X-ray diffraction and shown to consists of $MeHgS_2PPh_2$ molecules in which the mercury atom is bound to the methyl group and to one sulphur atom of the ligand, with a further weak intermolecular interaction (secondary bond) with the other sulphur atom of a neighbouring ligand holding the molecules in pairs in the lattice. The spectroscopic properties of $RHgS_2PPh_2$ (IR, Raman and ^1H, ^{13}C, ^{31}P and ^{119}Hg NMR) are discussed in the light of the X-ray results.

Introduction

Coordination studies of the compounds formed by monoorganomercury(II) cations and 1,1-dithio ligands are rather scarce. The structures of a few N,N-dithiocarbamates have been fully studied by X-ray diffraction methods [1,2], and those of the known methyl- and phenyl-mercury(II) derivatives of dithiophosphorus ligands have only been investigated spectroscopically [3,4]. In view of the coordination possibilities of ligands of this type [5] it seemed of interest to explore their bonding behaviour in complexes with organometallic cations that are stable under environmental conditions. We describe here the synthesis and spectroscopic properties of the diphenyldithiophosphinates of methyl- and phenylmercury(II), and the crystal structure of the methyl derivative.

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Experimental

Methyl- and phenylmercury acetates were purchased from Alfa and Ventron, respectively. Ammonium diphenyldithiophosphinate was prepared by the reaction of diphenylphosphine and sulphur in aqueous ammonia solution [6]. Some of the ammonium diphenyldithiophosphinate was treated with an excess of HCl in D_2O. $CDCl_3$ was then added and the two phases stirred for 1 day. The aqueous phase was removed to leave a solution of diphenyldithiophosphinic acid that was used directly in NMR studies.

Elemental analyses were performed by Galbraith Lab., Inc. (Knoxville, TN, USA).

Mass spectra. Mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS90 data system and operating under EI conditions (direct insertion probe, 70 eV, 250 ° C). All the ions included in Table 3 were identified by use of DS90 software.

Vibrational spectra. Infrared spectra were recorded in KBr pellets on a Perkin Elmer 180 spectrometer, and Raman spectra were obtained with a Dilor Omars 89 spectrometer (argon ion laser, 5145 Å).

NMR spectra. ^1H, and proton decoupled ^{13}C, ^{31}P and ^{199}Hg NMR spectra were recorded at room temperature on a Bruker WM-250 spectrometer.

Synthesis of $MeHgS_2PPh_2$

To a methanolic suspension of MeHgAcO in an ice-water bath was added one equivalent of ammonium diphenyldithiophosphinate in the same solvent. The mixture was stirred for 3 h and the white precipitate of $MeHgS_2PPh_2$ was then filtered off. (M.p.: 85 ° C. Anal. Found: C, 33.6; H, 2.8. $C_{13}H_{13}HgPS_2$ calc.: C, 33.58; H, 2.82%. Molar conductivity: 1.8 ohm^{-1} cm^2 mol^{-1} (10^{-3} *M* in DMSO).) Storage of the filtrate for several days in a refrigerator yielded crystals suitable for the X-ray structural determination.

Synthesis of $PhHgS_2PPh_2$

This was made as described for the methylmercury compound but starting from PhHgAcO. (M.p.: 170 ° C. Anal. Found: C, 40.8; H, 2.8. $C_{18}H_{15}HgPS_2$ calc.: C, 41.02; H, 2.87%. Molar conductivity: 0.9 ohm^{-1} cm^2 mol^{-1} (10^{-3} *M* in DMSO).)

Determination of the crystal structure of $MeHgS_2PPh_2$. A colourless prismatic crystal of $C_{13}H_{13}HgPS_2$ of approximately 0.12 × 0.20 × 0.28 mm was used.

Crystal data. $C_{13}H_{13}HgPS_2$, $M = 464.94$, triclinic, space group $P\bar{1}$, $a = 9.189(1)$, $b = 11.945(3)$, $c = 6.9930(9)$ Å, $\alpha = 105.79(1)$, $\beta = 96.03(1)$, $\gamma = 78.92(2)°$, $U = 723.7(3)$ Å^3, $Z = 2$, $D = 2.133$ g cm^{-3}, $F(000) = 436$, $\mu(\text{Mo-}K_\alpha) = 10.63$ mm^{-1}.

Data collection. Data for the structure determination were obtained at room temperature with a CAD-4 Enraf-Nonius four-circle diffractometer using graphite-monochromated Mo-K_α radiation. Cell constants were determined from the setting angles of 25 reflections. The ω/θ scan technique was used. 2986 reflections were collected for θ in the range 3–22°. Of 1707 symmetry-independent reflections ($R_{int} = 0.017$), 1411 with $|F_o| > 3\sigma(|F_o|)$ were used for refinement. Absorption corrections were applied at a later stage in the refinement [7].

Structure solution and refinement. The structure was solved by Patterson and difference Fourier techniques [8]. In the final cycles of full-matrix least-squares

Table 1

Final atomic coordinates and equivalent isotropic temperature factors (Å^2) for $MeHgS_2PPh_2$, with esd's in parentheses

Atom	x	y	z	B_{eq} [a]
Hg	0.4531(1)	0.4169(0)	0.2116(1)	3.20(1)
P	0.6910(3)	0.2726(2)	−0.1582(3)	2.49(9)
S(1)	0.5292(3)	0.3117(2)	−0.3485(4)	3.50(9)
S(2)	0.6988(3)	0.3944(2)	0.1114(4)	3.8(1)
C(1)	0.689(1)	0.1299(7)	−0.117(1)	2.6(3)
C(2)	0.594(1)	0.0576(8)	−0.231(1)	3.4(4)
C(3)	0.601(1)	−0.0547(8)	−0.203(1)	3.7(4)
C(4)	0.701(1)	−0.0925(8)	−0.061(2)	3.9(4)
C(5)	0.795(1)	−0.019(1)	0.052(2)	4.6(5)
C(6)	0.789(1)	0.0929(8)	0.026(1)	3.3(4)
C(7)	0.873(1)	0.2565(7)	−0.250(1)	2.4(3)
C(8)	0.979(1)	0.3222(8)	−0.149(1)	3.5(4)
C(9)	1.118(1)	0.3035(9)	−0.233(2)	3.9(4)
C(10)	1.145(1)	0.2250(9)	−0.407(2)	3.4(4)
C(11)	1.042(1)	0.157(1)	−0.508(1)	4.3(4)
C(12)	0.905(1)	0.1741(9)	−0.432(1)	3.8(4)
C(13)	0.246(1)	0.4296(9)	0.319(2)	4.2(4)

[a] $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j B_{ij}\mathbf{a}_i\mathbf{a}_j$.

refinement all non-H atoms were treated as anisotropic. H atoms were included at positions found from difference synthesis and not refined, all the phenyl H atoms with one common isotropic temperature factor, and the methyl hydrogens with another, which refined to $U = 0.07$ and 0.24 Å^2 respectively. R and R′ values were 0.030 and 0.025, respectively, for 156 refined parameters, maximum shift/esd was 0.002. Scattering factors and anomalous dispersion corrections were taken from [9]. Calculations were performed on a MICROVAX II computer. Positional and equivalent thermal parameters are given in Table 1. Thermal parameters and structure factors are available from the authors.

Results and discussion

The compounds obtained by treating methyl- and phenylmercury acetate with the ammonium salt of diphenyldithiophosphinic acid

$$RHgAc + NH_4S_2PPh_2 \rightarrow RHgS_2PPh_2 + NH_4Ac$$

are white solids soluble in non-polar organic solvents.

1. Structure of $MeHgS_2PPh_2$

The $MeHgS_2PPh_2$ molecule is represented in Fig. 1 [10] with the atomic numbering scheme. The mercury atom forms bonds with the methyl group (C(13)) and S(2) of the ligand. The fragment S(2)–Hg–C(13) is almost linear (175.0(3)°). The distances Hg–S(2) and Hg–C(13), 2.379(3) and 2.08(1) Å respectively, lie within the usual range for methylmercury compounds [1,11].

Since the sum of the Van der Waals radii for mercury and sulphur is 3.5 Å [12,13], the Hg···S(1) distance of 3.869(3) Å, rules out significant interaction

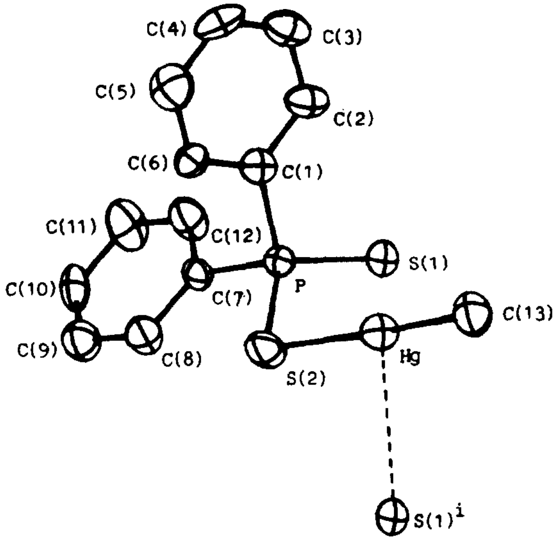

Fig. 1. ORTEP drawing of the molecular structure of $MeHgS_2PPh_2$, with the atom numbering scheme.

between Hg and S(1) but the Hg···S(1)^i distance of 3.152(3) Å implies the existence of effective secondary interaction between these atoms [14] (symmetry code *i*: $1-x$, $1-y$, $-z$). The Hg···S(1)^i interactions give rise to a unit cell in which two molecules are paired (Fig. 2, [10]) as centrosymmetric dimers, giving the mercury atom a T-shaped coordination environment. The Hg···S(1)^i bonds are too weak to modify appreciably the linearity of S(2)–Hg–C(13), or the distance Hg–C(13) [14], but do affect the ligand molecule: P–S(1) is slightly longer and

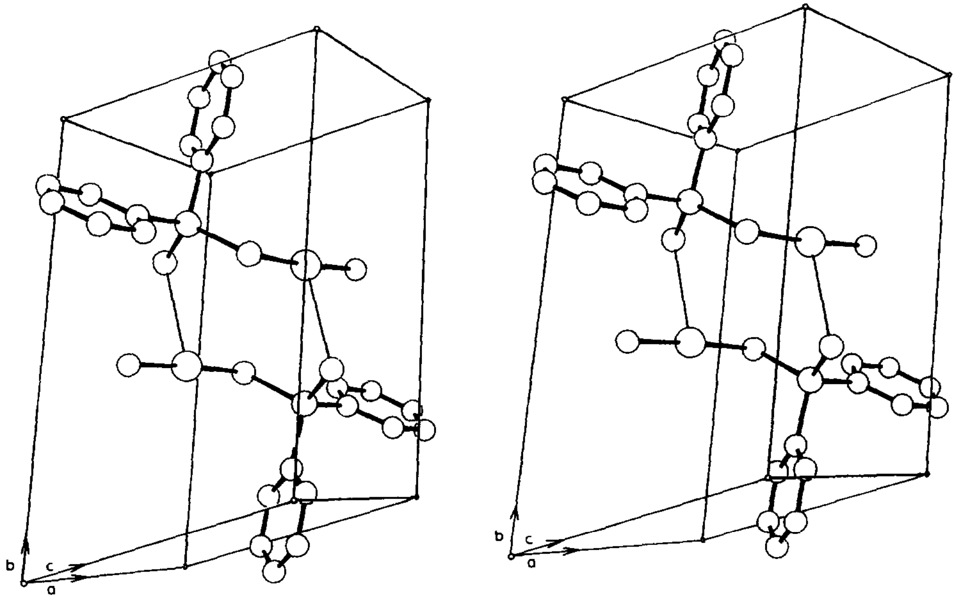

Fig. 2. ORTEP stereoview of the unit cell.

Table 2

Chief interatomic distances (Å) and angles (°) for $MeHgS_2PPh_2$ [a]

Interatomic distances			
Hg–S(2)	2.379(3)	P–S(1)	1.963(4)
Hg–C(13)	2.08(1)	P–S(2)	2.048(3)
Hg–S(1)	3.869(3)	P–C(1)	1.808(9)
Hg–S(1)^i	3.152(3)	P–C(7)	1.81(1)
Interatomic angles			
S(2)–Hg–C(13)	175.0(3)	S(1)–P–C(7)	112.7(3)
S(2)–Hg–S(1)^i	83.54(8)	S(2)–P–C(1)	109.0(3)
S(1)^i–Hg–C(13)	98.2(3)	S(2)–P–C(7)	103.7(3)
S(1)–P–S(2)	115.9(2)	C(1)–P–C(7)	103.6(4)
S(1)–P–C(1)	111.1(3)	Hg–S(2)–P	101.2(1)

[a] S(1)^i obtained from S(1) by $1-x$, $1-y$, $-z$.

P–S(2) slightly shorter than in HS_2PPh_2 [15], despite the fact that S(1) is also involved in a weak hydrogen bond in the dithiophosphinic acid [15]; protonation of S(2) thus seems to reduce the multiplicity of the P–S(2) bond slightly more effectively than metallation.

The angles S(1)–P–X (X = S(2), C(1), C(7)) are wider in the methylmercury complex than in the free acid, whereas the angle C(1)–P–C(7) is only slightly changed. This distortion may arise from the steric requirements necessary to place S(1)^i close to Hg, with which it weakly interacts. The coordination mode of the dithiophosphinate ligand can be classified as asymmetrical bimetallic biconnective [5]. The planes of the phenyl groups are nearly at right-angles (87.7(3)°).

The structure of the methylmercury compound has a certain similarity to that of methyl *N*,*N*-diethyldithiocarbamato mercury(II) [1], in which the individual molecules are likewise linked in centrosymmetric pairs by an intermolecular Hg···S bond, the length of which (3.147(7) Å) is similar, within the esd's, to that shown in Table 2 for Hg···S(1)^i. The weak intramolecular Hg···S bond observed in the dithiocarbamato is absent, however, possibly because, although the angle S–X–S (X = C or P) is similar in both compounds, the greater X–S distance and slightly

Table 3

70 eV monoisotopic mass spectra of $RHgS_2PPh_2$ (*m*/*e*, (%)) [a]

	R = Me	R = Ph
$[RHgS_2PPh_2]$	466(22.6)	528(1.6)
$[RHgSPPh_2]$	–	496(< 1.0)
[RHgSPPh]	357(7.8)	419(1.5)
[SHgPhR]	326(7.9)	388(1.7)
$[HgR_2]$	232(36.4)	356(9.4)
[HgR]	217(100.0)	279(7.2)
$[S_2PPh_2]$ [b]	249(15.5)	249(0.4)
[Hg]	202(29.8)	202(3.0)

[a] *m*/*e* values were computed for H = 1, C = 12, P = 31, S = 32, Hg = 202. [b] Signals for species $[SPPh_2]$, $[(C_6H_{11})_2P]$, $[(C_6H_4)_2]$ and $[C_6H_5]$ (this last is the base peak of $PhHgS_2PPh_2$) were also detected.

Table 4

Infrared and Raman data for diphenyldithiophosphinate compounds (in cm^{-1}) [a]

Compound	ν_{asym}(PS)	ν_{sym}(PS)	$\Delta\nu$	$\delta_{sym}(CH_3)$	ν(Hg-C)
$NH_4S_2PPh_2$	638s	565s	78		
	(-)	(565s)			
$MeHgS_2PPh_2$	645s	540s	105	1180m	529s
	(-)	(546m)		(1184m)	(529s)
$PhHgS_2PPh_2$	635s	550s	85		
	(-)	(551m)			

[a] IR (Raman) data; the spectra were recorded in KBr pellets. s = strong; m = medium.

greater X-S(2)-Hg angle in the dithiophosphinate may place S(1) too far from the Hg atom to allow significant interaction between them.

2. *Mass spectra*

The most significant peaks in the mass spectra are indicated in Table 3. In both cases the corresponding molecular ions were detected, though for R = Ph the signal was rather weak. Indeed, the mass spectra signals of $PhHgS_2PPh_2$ were in general weaker than those of $MeHgS_2PPh_2$, suggesting that the latter is the more stable compound [16].

There seem to be at least two fragmentation pathways; one involving breaking of the Hg-S bond and the other the progressive breakdown of the ligand. The abundance of $[HgR_2]$ ions is striking.

3. *IR and Raman spectra*

Table 4 lists the positions of the most significant bands in the IR and Raman spectra of the ammonium salt of the ligand and its complexes.

The two complexes and the ammonium salt all have a strong IR band around 646 cm^{-1} assigned [17] to ν_{asym} (P = S) and another, strong in IR and medium-strong in Raman, located around 540 cm^{-1} and assigned to ν_{sym} (P-S). The relative positions of these modes are indicative [17-19] of the coordination behaviour of the ligand: bidentate coordination is suggested by values of $\Delta\nu = \nu_{asym} - \nu_{sym}$ of 50-70 cm^{-1}, monodentate coordination by values greater than 95 cm^{-1}, and anisobidentate coordination by values between 70 and 90 cm^{-1}. The value observed for $MeHgS_2PPh_2$ is in keeping with the essentially monodentate behaviour of the ligand as discussed above. The secondary interaction $Hg \cdots S(1)$ may be the cause of $\Delta\nu$ being considerably smaller than in other diphenyldithiophosphinates in which the ligand is monodentate [19]. The value of $\Delta\nu$ for $PhHgS_2PPh_2$ clearly suggests that the ligand is anisobidentate in this compound.

The values of $\delta_{sym}(CH_3)$ (1184 cm^{-1}, IR and Raman) and ν(Hg-C) (529 cm^{-1}, IR and Raman) lie for $MeHgS_2PPh_2$ close to those found in other systems with Hg-S bonds [20].

4. *Studies in solution*

According to the conductivity values (see the experimental part), neither compound is ionized in DMSO.

Table 5

Significant NMR parameters

Compound	Solvent	${}^{n}J({}^{199}Hg-{}^{1}H)$	${}^{3}J({}^{31}P-{}^{1}H)$	$\delta({}^{13}C(Hg-C))$ [a,b]	$\delta({}^{31}P)$ [a,c]	$\delta({}^{199}Hg)$ [a,d]
DS_2PPh_2	$CDCl_3$		15.0		54.01s	
$NH_4S_2PPh_2$	DMSO		13.0		63.00s	
$MeHgS_2PPh_2$	$CDCl_3$	192.1	15.0	10.85s	62.46s	−607.6s
	DMSO	200.2	14.4	9.69s	64.61s	−685.6s
$PhHgS_2PPh_2$	$CDCl_3$	187.0	14.9	155.78s	62.67s	−926.2s
	DMSO	189.3	14.5	156.93s	65.61s	−1007.5s

[a] s = singlet. [b] TMS as external standard. [c] H_3PO_4 85% as external standard. [d] Me_2Hg as external standard.

Significant parameters of the ${}^{1}H$, ${}^{13}C$, ${}^{31}P$ and ${}^{199}Hg$ NMR spectra are shown in Table 5. The ${}^{2}J({}^{199}Hg-{}^{1}H)$ coupling constant and the chemical shift of the methyl group in $MeHgS_2PPh_2$ indicate a Hg–S bond [21]. Though the influence of the nature of the donor atom *trans* to the phenyl group in phenylmercury(II) complexes on the parameters ${}^{3}J({}^{199}Hg-{}^{1}H\mathit{o})$ and $\delta(C_i)$ has not been explored, the dependence of these parameters on the identity of the donor atom cannot be ruled out. The signal of the carbon C_i in fact seems to be at lower field when phenylmercury is bound to S, as here, than when it is bound to N [16].

The values of $\delta({}^{199}Hg)$ in these compounds are close to but less negative than those observed in other organomercury compounds with Hg–S bonds [16].

When data in the same solvent are compared, ${}^{3}J({}^{31}P-{}^{1}H)$ for the $RHgS_2PPh_2$ compounds is similar to the value for the acid. On the other hand, the signal in the ${}^{31}P$ NMR spectrum is at lower field for the complexes than for the acid, or at slightly higher field than for the ammonium salt. Although this parameter has been directly related to the denticity of dithiophosphates [22], it really depends on a complex set of related factors [23]; until more information on these systems is available, no firm conclusions can be drawn about coordination behavior.

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