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Mixed Mercury(II) Complexes of Di-isopropylphosphorothioate and Di-isopropylphosphonate Containing Halide and Pseudohalide Ligands

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New mixed complexes $[(RO)_2POS]HgX$ *(*$R = Me_2CH$*;* X *= Cl, Br, I, CN, SCN, and* $OP(OR)_2$*) and* $[(RO)_2PO]HgX$ *(*$R = Me_2CH$*;* X *= Cl, Br, I, CN, NCO, SCN, and SeCN) are described. Phosphorus-31 chemical shifts show that* $[(RO)_2POS]HgX$ *contain Hg–S bonds, while the* ^{31}P *chemical shifts and the infrared spectra of* $[(RO)_2PO]HgX$ *support a constitution containing Hg–P bonds. The* ^{31}P *chemical shifts in* $[(RO)_2PO]HgX$ *correlate only rather poorly with the substituent constants* σ_R^0 *and* σ_I *of the group X, but correlate extremely well with the electronegativity of the atom in X directly bonded to Hg: as this electronegativity increases, the chemical shift moves to high field.*

Introduction

In a previous paper [1], the mercury(II) complex $[(RO)_2POS]_2Hg$ ($R = Me_2CH$ throughout this paper) was described, and shown by ^{31}P n.m.r. to adopt a constitution containing Hg–S bonds, thus $[(RO)_2P(O)S]_2Hg$. Fox and Venezky have reported the preparation of the related complexes $[(RO)_2PO]_2Hg$ [2], and $[(RO)_2PO]HgOCOCH_3$ and $[(RO)_2PO]HgCl$ [3]. In the present paper, a range of complexes of types $[(RO)_2POS]HgX$ and $[(RO)_2PO]HgX$ are described.

Experimental

Infra-red spectra were recorded in KBr discs using a Perkin–Elmer model 621. ^{31}P and ^{13}C n.m.r. spectra were recorded using Varian CFT-20 and XL-100 instruments. $[(RO)_2PO]_2Hg$ was prepared by reaction of $(RO)_2PHO$ with a two-fold molar excess of yellow mercury(II) oxide in diethyl ether [3]. $[(RO)_2PO]HgOCOCH_3$ was prepared by reaction of $(RO)_2PHO$ with 1.1 molar excess of mercury(II) acetate in toluene [2]. Fox and Venezky reported that mixing mercury(II) acetate with diethyl phosphite $(EtO)_2PHO$ in the absence of a solvent caused a marked and rapid rise in temperature [2]: no such temperature rise has been observed with di-isopropyl phosphite $(RO)_2PHO$.

Preparation of $[(RO)_2PO]HgX$

X = Cl, Br, I, CN, SCN

Equimolar mixtures of $[(RO)_2PO]_2Hg$ and HgX_2 were refluxed during 2 h in benzene solution: the

TABLE I. Microanalytical Data for New Compounds $[(Me_2CHO)_2PO]HgX$ and $[(Me_2CHO)_2POS]HgX$.

Compound	Found (/%)			Required (/%)		
	C	H	N	C	H	N
$[(Me_2CHO)_2PO]HgBr$	16.4	3.4	0.0	16.2	3.2	0.0
$[(Me_2CHO)_2PO]HgI$	14.7	3.0	0.0	14.6	2.9	0.0
$[(Me_2CHO)_2PO]HgCN$	21.3	3.7	3.6	21.5	3.6	3.6
$[(Me_2CHO)_2PO]HgNCO$	21.2	3.8	4.0	20.6	3.5	3.4
$[(Me_2CHO)_2PO]HgSCN$	19.6	3.4	3.7	19.8	3.3	3.3
$[(Me_2CHO)_2PO]HgSeCN$	17.5	2.9	3.1	17.9	3.0	3.0
$[(Me_2CHO)_2PO]Hg[SOP(OCHMe_2)_2]$	25.5	4.7	0.0	25.6	5.0	0.0
$[(Me_2CHO)_2POS]HgCl$	16.8	3.4	0.0	16.6	3.3	0.0
$[(Me_2CHO)_2POS]HgBr$	14.8	3.1	0.0	15.1	3.0	0.0
$[(Me_2CHO)_2POS]HgI$	13.7	2.9	0.0	13.7	2.7	0.0
$[(Me_2CHO)_2POS]HgCN$	19.7	3.7	3.5	19.8	3.3	3.3
$[(Me_2CHO)_2POS]HgSCN$	18.0	3.4	3.2	18.4	3.1	3.1

TABLE II. Phosphorus-31 Chemical Shifts in $[(Me_2CHO)_2POS]HgX$.

X	δ_P/p.p.m.[a]
$(Me_2CHO)_2PO$	+32.0
$(Me_2CHO)_2POS$	+28.4
Cl	+29.6
Br	+29.3
I	+27.9
CN	+28.1
SCN	+28.0

[a] $CDCl_3$ solution.

solution was filtered, and reduced to small volume, and then the product was filtered off and dried.

X = NCO, SeCN, OSP(OR)₂

Equimolar quantities of $[(RO)_2PO]HgOCOCH_3$ and NaX were mixed in aqueous solution: the mixture was evaporated to dryness and extracted with 4 X 25 ml of dry acetone. Evaporation of the extract gave the product. When X = F, NO_3 and PF_6, the acetate was recovered unchanged. Microanalytical data are in Table I.

Preparation of $[(RO)_2POS]HgX$

Equimolar quantities of $[(RO)_2POS]_2Hg$ and HgX_2 were mixed in solution in propan-2-ol (X = Cl, Br, I, SCN) or acetone (X = CN), and stirred at room temperature during 2 h. Filtration and reduction of the solvent volume precipitated the products. Microanalytical data are in Table I.

Preparation of $[(RO)_2PO]_2Cd$

Cadmium oxide (2.3 g) and $(RO)_2PHO$ (3.3 g) were stirred together, in the absence of solvent, during 1 week at room temperature. An essentially quantitative yield of product was obtained by repeated decantation with petroleum ether. Found: C, 32.3; H, 6.6%. $C_{12}H_{28}CdO_6P_2$ requires: C, 32.6; H, 6.4%. Attempts to prepare this compound by reaction of CdO with $(RO)_2PHO$ in the presence of solvents, whether at room temperature or on heating, were uniformly unsuccessful.

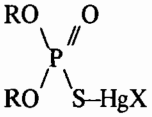
No reactions were observed between: (i) $CdCO_3$ and $(RO)_2PHO$ (Et_2O, reflux), (ii) HgS and $(RO)_2PHO$ (Et_2O, reflux), (iii) $Cd(OCOCH_3)_2$ and $(RO)_2PHO$ (toluene, room temperature, (iv) ZnO and $(RO)_2PHO$ (no solvent, room temperature).

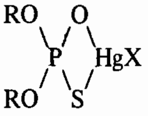
Results and Discussion

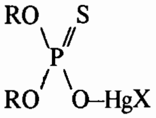
The symmetrical mercury(II) phosphorothiolate $[(RO)_2P(O)S]_2Hg$ reacts with mercury(II) halides and pseudohalides to yield complexes of composition $[(RO)_2POS]_2HgX$, equation (1).

$$[(RO)_2P(O)S]_2Hg + HgX_2 \longrightarrow 2[(RO)_2POS]HgX \qquad (1)$$

The ^{31}P chemical shifts (Table II) indicate that all these species contain unidentate $(RO)_2POS$ ligands and Hg–S bonds [1], structure (I), rather than structures (II) or (III):


(I)


(II)


(III)

Structures of types (II) and (III) would exhibit ^{31}P chemical shifts, δ_P(/p.p.m.) in the ranges $30 < \delta_P < 58$ and $58 < \delta_P$ respectively [1]. In these complexes, the ^{31}P chemical shift is almost independent of the group X.

By contrast the chemical shifts (Table III) in the complexes $[(RO)_2PO]HgX$, prepared according to equations (2) and (3),

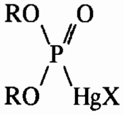
$$[(RO)_2PO]_2Hg + HgX_2 \longrightarrow 2[(RO)_2PO]HgX \qquad (2)$$

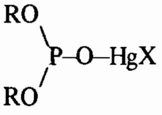
(X = Cl, Br, I, CN, SCN)

$$[(RO)_2PO]HgOCOCH_3 + NaX \longrightarrow NaOCOCH_3 + [(RO)_2PO]HgX \qquad (3)$$

(X = NCO, SeCN, $OSP(OR)_2$)

span a remarkably wide range from +105.5 p.p.m. in $[(RO)_2PO]_2Hg$ to +53.6 p.p.m. in $[(RO)_2PO]HgOCOCH_3$, with an increase in the electronegativity of the group X causing a shift in δ_P to ***high*** field: such a shift has been observed also [4] as a function of R′ in alkylphosphonates $R'P(O)(OR)_2$, which is suggestive of the existence of the phosphonate constitution (IV) for $[(RO)_2PO]HgX$, rather than the alternative phosphite constitution (V).


(IV)


(V)

Further support for constitution (IV) for $[(RO)_2PO]HgX$ is found in the following observations: (i) in $[(RO)_2POS]HgX$, which cannot contain Hg–P bonds, the range spanned by the ^{31}P chemical shifts is only a few p.p.m., around 10% of that in $[(RO)_2PO]HgX$ species; (ii) all $[(RO)_2PO]HgX$ compounds contain in their infra-red spectra a strong band in the

TABLE III. Spectroscopic Data for $[(Me_2CHO)_2PO]HgX$.

X	δ_P/p.p.m.[a]	ν(P=O)/cm^{-1}	Other
$(Me_2CHO)_2PO$	+105.5	1176	
$(Me_2CHO)_2POS$	+ 75.1	1172 1196	
Cl	+ 60.1	1164	
Br	+ 63.6	1179	
I	+ 70.3	1153	
CN	+ 76.8	1158	ν(CN), 2189 cm^{-1}
NCO	+ 58.8	1167	$\nu(NCO)_{as}$, 2191 cm^{-1}; $\nu(NCO)_s$, 1345 cm^{-1}
SCN	+ 67.5	1182	ν(CN), 2134 cm^{-1}; ν(CS), 712 cm^{-1}
SeCN	+ 72.9	1177	ν(CN), 2110 cm^{-1}
OCOMe	+ 53.6	1199	ν(CO), 1641, 1310 cm^{-1}

[a] $CDCl_3$ solution.

TABLE IV. Solvent Effects on Spectra of $[(Me_2CHO)_2PO]HgOCOMe$.

Solvent	Dielectric[a] Constant	Donor[a] Number	ν(CO)/cm^{-1}	ν(PO)/cm^{-1}	δ_{CO}/p.p.m.	δ_{PO}/p.p.m.
$CDCl_3$	5.0	*ca.* 0	1572, 1331	1178	177.8	53.58
THF	7.6	20	1559, 1330	1168	c	51.70
MeCOOH	8.5	?	b	b	179.8	52.64
Me_2CHOH	24	?	1568, 1340	1176	177.3	52.29
MeCN	38	14.1	1558, 1331	1168	c	49.58
H_2O	81	18	b	b	182.1	55.84
KBr Disc	–	–	1641, 1310	1199	–	–

[a] Ref. 19 [b] Not recorded. [c] Not observed, solubility and stability insufficient.

range 1150–1190 cm^{-1}, which is assigned [5] as ν(P=O), although this assignment cannot be regarded as wholly unambiguous [6]; (iii) the compound $[(RO)_2PO]_2Hg$ undergoes no reaction with either iodoethane or butane-2,3-dione (reactions with these reagents to yield phosphonates or pentaoxophosphoranes are generally regarded as diagnostic of phosphites); (iv) in the related compounds $[(MeO)_2PO]_2Hg$ [7] and $[(EtO)_2PO]HgCl$ [8], the presence of Hg–P has been demonstrated in the solid state. These observations taken together strongly point to (IV) as the constitution in solution.

The infra-red data (Table III) also suggest that the cyanate group is bound to mercury through nitrogen, and that the thiocyanate and selenocyanate are bonded *via* sulphur and selenium respectively. $[(RO)_2PO]HgOCOCH_3$ shows no reaction with NaX when X^- is a poorly coordinating anion such as NO_3^- or PF_6^-, showing that the cation $[\{(RO)_2PO\}Hg]^+$ is most reluctant to form. Similarly when X = F, no reaction occurs; this is unsurprising in view of the instability of HgF_2 towards water.

It has been demonstrated [9–11] in a number of series of compounds of general type Monitor–Cavity–Variable that the chemical shift of a monitor nucleus *e.g.* ^1H, ^{13}C, ^{19}F, is a linear function of a suitable substituent parameter of the variable group. In testing the application of this treatment to the present series of phosphonates $[(RO)_2P(O)]HgX$ the Monitor is taken as the ^{31}P atom, the Cavity as mercury and the Variable as the group X. The substituent parameter σ_R^0 has previously been found [10] to be satisfactory when the cavity is saturated: however, neither this parameter nor σ_I gave linear plots *versus* δ_P: of the six substituents of known σ_R^0, four (Cl, Br, SCN and CN) fell on a straight line, but I and $OCOCH_3$ were markedly deviant. A similar series of compounds in which the Cavity is mercury is [12] Me_3CCH_2HgX; taking the methylene carbon nucleus as the Monitor, plots of σ_R^0 and σ_I against δ_C were again markedly non-linear and non-monotonic. In contrast a plot of δ_P against the Pauling electronegativity of that atom in the group X which is directly bonded to mercury gave a smooth curve, from which the largest deviation, for SCN was *ca.* 4 p.p.m.; similarly in the Me_3CCH_2HgX series, the δ_{CH_2} values of all the species, save that for X = CN, lie on a smooth curve when plotted against electronegativity.

Fox and Venezky reported [3] that the acetates $[(RO)_2PO]Hg)OCOCH_3$ were tetrameric in benzene and monomeric in acetic acid. The only plausible modes of oligomerisation are coordination of either phosphoryl or carbonyl oxygen to mercury, and in an attempt to distinguish between these, the infrared and n.m.r. spectroscopic parameters of the P=O and C=O groups have been determined in a number of solvents (Table IV). The variations in δ_C are somewhat larger than the analogous changes found in ethyl acetate [13], but smaller than those found in acetone [14], and are probably therefore not indicative of any change in coordination. The values of δ_P cover a range of some 6.3 p.p.m., rather greater than generally found for phosphorus shifts: thus the variation of δ_P in $(MeO)_3PO$ in a wide variety of solvents covered a range of only 1.0 p.p.m. [15] and solvent effects are very small also in $Ph_3PCH_3^+$ [16] and $Ph_3PNSO_2C_7H_7$ [17]. The infra-red frequencies suggest that the constitution of the acetate differs in the solid state from that in solution, and it is possible that weak intermolecular P=O···Hg and C=O···Hg interactions occur in the solid state as in $[(Me_3CCO)_2CH]HgOCOCH_3$ [18]. Although oligomers persist in a non-polar, non-donor solvent, they are disrupted in a polar, donor solvent [3]: however there are no correlations between ν(C=O), ν(P=O), δ_C or δ_P and either the dielectric constant or the donor number [19] of the solvent (Table IV).

$(RO)_2PHO$ reacts with CdO, although not with ZnO, to yield $[(RO)_2PO]_2Cd$: this compound appears to have a phosphonate constitution analogous to (IV). Its ^{31}P shift is +4.02 p.p.m., typical of four-connected phosphorus, and the infra-spectrum contains ν(P=O) at 1192 cm^{-1}: a strong band at 410 cm^{-1} is tentatively identified as ν(Cd–P). Unlike mercury(II) acetate, cadmium acetate did not react with $(RO)_2PHO$.

For the two isomerisations described in equations (4) and (5)

(4)

(5)

The $\Delta H^{\ominus}$ terms may be written:

$$\Delta H^{\ominus}(4) = [B(P\text{–}O) - B(P{=}O)] + [B(Hg\text{–}O) - B(Hg\text{–}P)]$$

$$\Delta H^{\ominus}(5) = [B(P\text{–}O) - B(P{=}O)] - [B(P\text{–}S) - B(P{=}S)] + [B(Hg\text{–}O) - B(Hg\text{–}S)]$$

Now [B(P–O) − B(P=O)] is −272 kJ mol^{-1} [20], and [B(P–S) − B(P=S)] is [21] −162 kJ mol^{-1} [21]: the problem in the estimation of the $\Delta H^{\ominus}$ values arises from the terms involving mercury. An estimate of B(Hg–O) can be derived from the $\Delta H_f^{\ominus}$ value, −90.8 kJ mol^{-1} [22] of red HgO. Taking values of 498.4 kJ mol^{-1} for D(O=O) [22], and +61.3 kJ mol^{-1} for the enthalpy of vapourisation of mercury [23], B(Hg–O) may be evaluated:

$$2B(Hg\text{–}O)(/kJ\ mol^{-1}) = 61.3 + 249.2 - 90.8 - (\Delta H^{\ominus})_{vap}$$

where $(\Delta H^{\ominus})_{vap}$ is the enthalpy per mol HgO for $HgO_{(S)} \rightarrow HgO_{(g)}$, whence $B(Hg\text{–}O)(/kJ\ mol^{-1}) = 200.7 - \frac{1}{2}(\Delta H^{\ominus})_{vap}$.

Consequently:

$$\Delta H^{\ominus}(4)(/kJ\ mol^{-1}) = -272 + [200.7 - \tfrac{1}{2}(\Delta H^{\ominus})_{vap}] - B(Hg\text{–}P)$$

and irrespective of the value of B(Hg–P), $\Delta H^{\ominus}(4)$ must be negative, showing that the phosphonate isomers (IV) observed for the series $[(RO)_2PO]HgX$ are the thermodynamically more stable. Similarly:

$$\Delta H^{\ominus}(5)\ (/kJ\ mol^{-1}) = -272 + 162 + [B(Hg\text{–}O) - B(Hg\text{–}S)]$$

which will be negative unless [B(Hg–O) − B(Hg–S)] > 110 kJ mol^{-1}. The maximum value of B(Hg–O) is 200 kJ mol^{-1}, and a more probable value, based on $(\Delta H^{\ominus})_{vap}$ values for other heavy metal oxides [22], lies in the range 100–150 kJ mol^{-1}, in which case $\Delta H^{\ominus}(5)$ will be negative, unless B(Hg–S) is exceedingly small. In view of the generally high affinity of mercury for sulphur, it is possible even that B(Hg–S) > B(Hg–O): for the gaseous diatomic molecule HgS, D(HgS) is 287 kJ mol^{-1} [20]. Hence the isomers (I) observed for the series $[(RO)_2POS]HgX$ are thermodynamically the more stable.

References

1 C. Glidewell, *Inorg. Chim. Acta, 24,* 255 (1977).
2 D. L. Venezky and R. B. Fox, *J. Am. Chem. Soc., 78,* 1664 (1956).
3 R. B. Fox and D. L. Venezky, *J. Am. Chem. Soc., 75,* 3967 (1953).
4 J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc., 78,* 5715 (1956).
5 L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta, 20,* 467 (1964).
6 J. McKechnie, D. S. Payne, and W. Sim, *J. Chem. Soc.,* 3500 (1965).
7 G. G. Mather and A. Pidcock, *J. Chem. Soc. Dalton,* 560 (1973).
8 J. Bennett, A. Pidcock, C. T. Waterhouse, P. Coggan, and A. McPhail, *J. Chem. Soc. A,* 2094 (1970).
9 W. A. Sheppard and R. W. Taft, *J. Am. Chem. Soc., 94,* 1919 (1972).
10 S. K. Dayal, S. Ehrenson, and R. W. Taft, *J. Am. Chem. Soc., 94,* 9113 (1972).

11 S. Bradamante, F. Gianni, and G. A. Pagani, *Chem. Comm.*, 478 (1976).

12 G. Singh and G. S. Reddy, *J. Organometal. Chem.*, *42*, 267 (1972).

13 G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, *42*, 2752 (1965).

14 G. E. Maciel and G. C. Rubin, *J. Am. Chem. Soc.*, *85*, 3903 (1963).

15 R. A. Y. Jones, and A. R. Katritzky, *Angew. Chem.*, *74*, 60 (1962).

16 S. O. Grimm, W. McFarlane, E. F. Davidoff, and T. J. Marks, *J. Phys. Chem.*, *70*, 581 (1966).

17 C. Glidewell, unpublished observations.

18 R. Allmann, K. Flatau, and H. Musso, *Chem. Ber.*, *105*, 3067 (1972).

19 V. Gutmann, "Coordination Chemistry in Non-Aqueous Solvents", Springer-Verlag, Vienna (1968).

20 C. Glidewell, *Inorg. Chim. Acta*, *24*, 149 (1977).

21 I. A. Duncan and C. Glidewell, *J. Organometal. Chem.*, *97*, 51 (1975).

22 O. Kubaschewski, E. Ll. Evans, and C. B. Alcock, "Metallurgical Thermochemistry", Pergamon, Oxford (1967).

23 H. A. Skinner and L. Pilcher, *Quart. Revs.*, *17*, 264 (1963).