Inorganica Chimica Acta, *88* (1984) 201–207

Cyclic O,O-alkylenedithiophosphates of Phenyl-arsenic and -antimony

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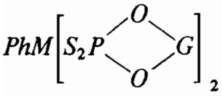
Received January 20, 1984

O,O-alkylenedithiophosphate derivatives of the general formula,



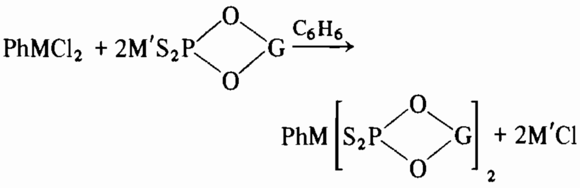
(where M = As, Sb; G = $-CH_2-C(Me_2)-CH_2-$, $-C(Me_2)-C(Me_2)-$, $-C(Me_2)-CH_2-CH(Me)-$ and $-CH(Me)-CH(Me)-$) were synthesized and characterized by elemental analyses and molecular weight determinations. These new complexes are soluble in common organic solvents, and their IR and NMR (^1H, ^{31}P) spectral data have been used to investigate a plausible geometry. On the basis of mass spectral data the fragmentation pattern of these derivatives has also been discussed.

Introduction

Cyclic O,O-alkylenedithiophosphoric acids have not attracted much attention [1–3] as a ligand in comparison to the open chain dialkyldithiophosphoric acids [4, 5]. Our continuing interest in organoarsenic and -antimony complexes [6, 7] led us to investigate the synthesis and characteristics of phenylarsenic and -antimony bis-O,O-alkylenedithiophosphates. The structural features of these derivatives have been discussed with the help of IR, NMR (^{1}H, ^{31}P) and mass spectral data.

Results and Discussion

Phenyl dichloro-arsine or -stibine react with O,O-alkylenedithiophosphoric acids or their ammonium salts (M'L) in 1:2 molar ratio to afford complexes of the type $PhML_2$ in benzene solutions (see Table I):



Where M = As, Sb; M' = H, NH_4; G = $-CH_2-C(Me_2)-CH_2-$, $-C(Me_2)-C(Me_2)-$, $-C(Me_2)-CH_2-CH(Me)-$ and $-CH(Me)-CH(Me)-$

The reactions employing the ammonium salts of the ligands are facile and can be completed at room temperature by stirring the reactants for 3–4 hours. The free acid has been used in the case of G = $-CH(Me)-CH(Me)-$ (ammonium salt of this acid could not be isolated) and reactions are complete after 6–8 hours of refluxing in benzene solutions. All these complexes are soluble in common organic solvents, monomeric in refluxing benzene and nonvolatile, even under reduced pressure.

IR Spectra

The IR spectra of these complexes (Table II) show the bands in the regions 950–1050 and 810–890 cm^{-1} which have been attributed to $\nu_{(P)O-C}$ and $\nu_{P-O(C)}$ stretching modes [4, 8], while the strong bands in the region 920–990 cm^{-1} are due to dioxaphospholane and dioxaphosphorinane ring vibrations [9, 10]. A strong band in the region 660–680 cm^{-1} can be ascribed to $\nu_{P=S}$ stretching vibrations [11] and the bands present in the region 490–600 cm^{-1} are due to ν_{P-S} symmetric and asymmetric vibrations [1, 12]. The ν_{M-C} [13, 14] and ν_{M-S} [15] vibrations appear in the region 455–490 and 310–370 cm^{-1} respectively.

NMR Spectra

The characteristic resonances of the corresponding alkylene and aryl protons present in the ^{1}H NMR spectra of these complexes are given in Table II. A sharp singlet (δ 3.1–3.7) due to S–H protons in O,O-alkylenedithiophosphoric acids is absent in the

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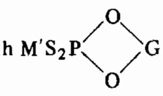
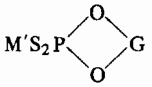
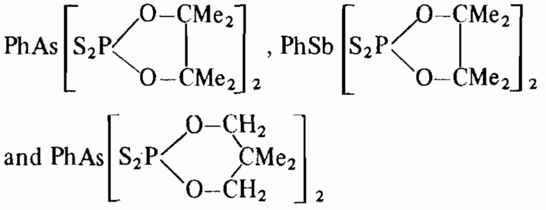
TABLE I. Reactions of $PhMCl_2$ with  in 1:2 Molar Ratios.

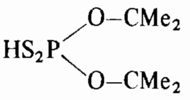
Sl No.	Reactants					Ammonium chloride (g) Found (Calcd.)	Physical state (m.p.) °C	Analysis (%) Found (Calcd.)		Mol. Wt. Found (Calcd.)
	$PhMCl_2$									
	M	(g)	M′	G	(g)			M	S	
1	As	1.17	NH_4	$-CMe_2$ CH_2 $-CHMe$	2.46	0.51 (0.56)	White solid (43–47)	13.15 (13.05)	22.15 (22.30)	586 (574)
2	As	1.13	NH_4	$-CMe_2$ $-CMe_2$	2.33	0.50 (0.54)	White solid (158–61)	13.28 (13.05)	22.16 (22.30)	580 (574)
3	As	1.40	NH_4	$-CH_2$ CMe_2 $-CH_2$	2.78	0.62 (0.67)	White solid (51–55)	13.80 (13.72)	23.30 (23.45)	–
4	Sb	0.68	NH_4	$-CMe_2$ $-CMe_2$	1.17	0.23 (0.27)	White solid (166, decomp.)	19.69 (19.61)	20.47 (20.62)	627 (621)
5	Sb	0.80	NH_4	$-CH_2$ CMe_2 $-CH_2$	1.30	0.30 (0.32)	White solid (133–37)	20.63 (20.54)	21.46 (21.59)	–
6	Sb	0.94	NH_4	$-CMe_2$ CH_2 $-CHMe$	1.62	0.34 (0.37)	White solid (122–25)	19.73 (19.61)	20.39 (20.62)	631 (621)
7	As	1.20	H	$-CHMe$ $-CHMe$	2.03	HCl ↑	Colourless pasty mass	14.74 (14.47)	25.07 (24.71)	–
8	Sb	0.78	H	$-CHMe$ $-CHMe$	1.11	HCl ↑	Yellowish solid (105, decomp.)	21.96 (21.56)	22.47 (22.66)	–

^1H NMR spectra of the corresponding complexes, indicating the formation of an M–S bond. Aromatic protons appear in the region δ 7.20–8.40 in two sets of multiplets having the integration in 2:3 ratio; thus, the downfield set can be ascribed to ortho-protons while meta- and para-protons appear upfield.

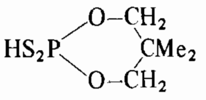
The ^{31}P NMR spectra of a few representative compounds were recorded in $CDCl_3$ solutions. Only a single peak was observed at δ 100.22, δ 105.85 and δ 83.03 for the complexes



respectively, while their free acids *viz.*,

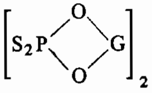


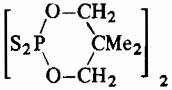
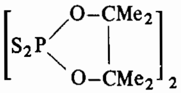
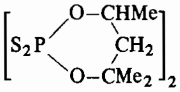
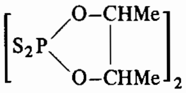
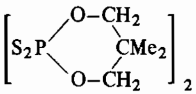
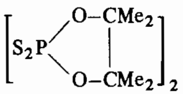
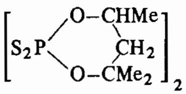
and

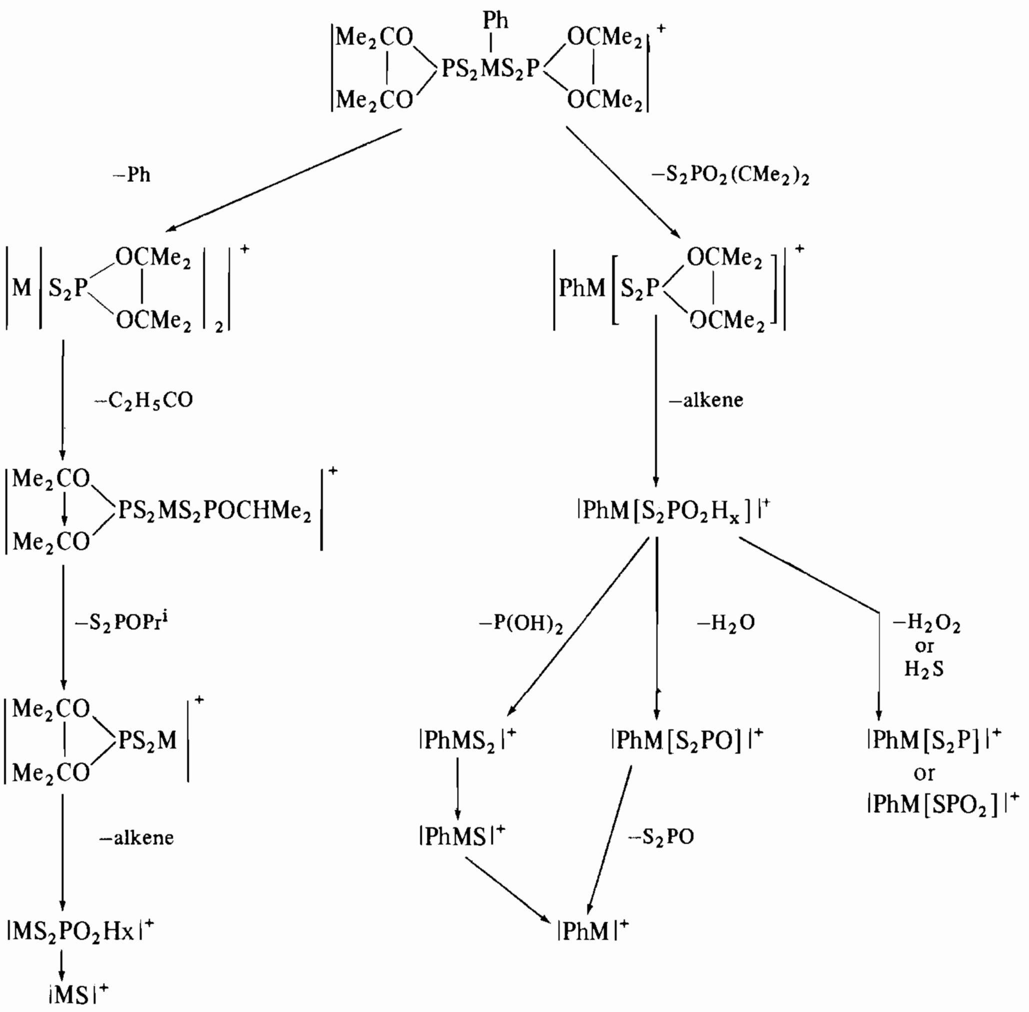


absorb at δ 93.07 and 78.55 respectively. This downfield shift of the ^{31}P signals in metal complexes indicates the bidentate nature of the ligands.

The monomeric nature and the IR and NMR spectral evidences indicate a penta-coordination for the central metal atom in these complexes. Although the actual geometry can only be established by further structural studies, the corresponding $PhAs(S_2CNEt_2)_2$ complex has been found to possess a square-pyramidal geometry with a phenyl group occupying an apical position [16].

TABLE II. IR and ^{1}H NMR Spectral Data of PhM  Complexes

Sl No.	Complex	IR Frequencies (cm^{-1})							PMR Chemical shifts (δ, ppm)	
		$\nu_{(P)O-C}$	$\nu_{P-O(C)}$	Ring vib.	$\nu_{P=S}$	ν_{P-S}	ν_{M-C}	ν_{M-S}	Alkylene	Aromatic
1	PhAs 	1042m	825w	985m,b	670b	604m	480m	292w	1.08(s), 12H(CH_3) 4.08(d), 8H(CH_2)	7.28–8.00(m)
2	PhAs 	1010s	864s	920s,b	661s	584s	490m	343s	1.46(s), 24H(CH_3)	7.38–8.00(m)
3	PhAs 	1000– 950s,b	890s	920m	660m	585s 500s	470m	370m	1.46–2.24(m) 22H(CH_3, CH_2) 4.80(m), 2H(CH)	7.30–7.96(m)
4	PhAs 	1035s	860m	940– 30s,b	660sb	590s 525m	455m	365w	1.68(d), 12H(CH_3) 4.90–4.27(m), 4H(CH)	7.40–8.20(m)
5	PhSb 	1050s	812s	990s,b	670s	605s 516w	470w	330w	1.06(s), 12H(CH_3) 4.07(d), 8H(CH_2)	7.20–8.10(m)
6	PhSb 	1010m	865s	920s	662s	600s, 490m,b	480s	310s,b	1.44(s), 22H(CH_3)	7.20–8.16(m)
7	PhSb 	1035s	875w	955s,b	680m	600m, 520m	450s	365w	1.28–2.37(m) 22H(CH_3, CH_2) 4.70– 5.20(m) 2H(CH)	7.40–8.40(m)



Scheme I

M = As, Sb

X = 0, 1, 2

Mass Spectra

Mass spectra of the two representative derivatives were recorded at ~200 °C and some important peaks are given in Table III. At lower temperatures, the intensities of peaks of higher m/e values decrease.

The spectra depict no detectable molecular ion peaks, which may indicate the pyrolytic decomposition of these derivatives. The mass spectral peaks indicate the formation of a variety of sulphides and fragments of the ligand moiety in the course of decomposition. The fragmentation of the complexes (Scheme I) appears to start with the loss of a phenyl group or one of the ligand moieties; subsequent losses are mainly due to alkenes or alkoxy groups.

Experimental

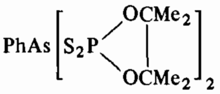
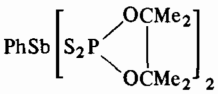
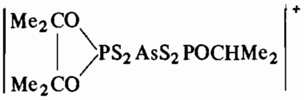
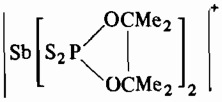
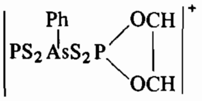
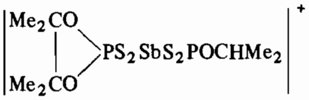
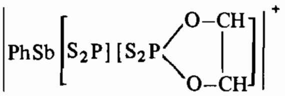
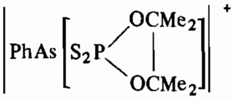
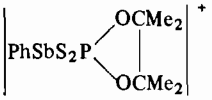
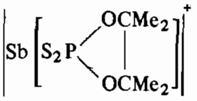
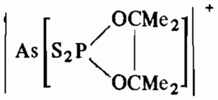
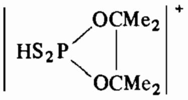
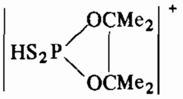
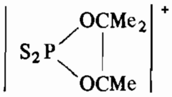
Phenyldichloroarsine [17], phenyldichlorostibine [18] and ligands [1] were prepared by the reported methods.

Arsenic and antimony were estimated iodometrically and sulphur was estimated gravimetrically as barium sulphate. Molecular weights were determined ebullioscopically using a Gallenkamp Ebulliometer equipped with a thermistor sensor. IR spectra were recorded (4000–200 cm^{-1}) as nujol mulls and ^{1}H and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions using TMS and 85% H_3PO_4 as internal standard. Mass spectra were recorded at ~200 °C with the ionization source operating at ~70 eV.

Reaction of Phenyldichloroarsine with the Ammonium O,O-hexylenedithiophosphate in 1:2 Molar Ratio

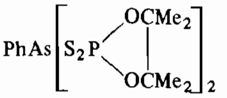
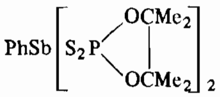
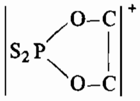
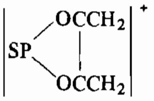
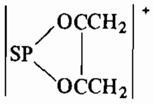
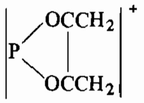
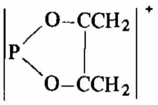
A benzene solution of phenyldichloroarsine (1.17 g) was added dropwise to the suspension of ammonium O,O-hexylenedithiophosphate (2.46 g) in benzene. After ~4 hours of stirring, the reaction mixture was filtered and solvent was stripped off under vacuum, giving a white solid which was

TABLE III. Mass[a] Spectral Data of O,O-alkylenedithiophosphate Complexes.

			
m/e	assignments	m/e	assignments
440		543	
400		486	
374	$\vert PhAs[S_2P][S_2PO_2]\vert^+$	446	
363		409	
357	$\vert As[S_2PO_2CH_2]_2\vert^+$	403	$\vert Sb[S_2PO_2CH_2]_2\vert^+$
291	$\vert PhAs[S_2PO_2C]\vert^+$	332	
286		327	$\vert PhSb[S_2P(OH)_2]\vert^+$
281	$\vert PhAs[S_2P(OH)_2]\vert^+$	309	$\vert PhSbS_2PO\vert^+$
263	$\vert PhAs[S_2PO]\vert^+$	294	$\vert PhSbS_2PH\vert^+$ or $\vert PhSbSPO_2H\vert^+$
248	$\vert PhAs[S_2PH]\vert^+$ or $PhAsSPO_2H^+$	262	$\vert PhSbS_2\vert^+$
216	$\vert PhAsS_2\vert^+$	249	$\vert Sb[S_2PO_2H]\vert^+$
212		230	$\vert PhSbS\vert^+$
203	$\vert As[S_2PO_2H]\vert^+$	212	
196		198	$\vert PhSb\vert^+$

(continued overleaf)

TABLE III. *(continued)*

			
m/e	assignments	m/e	assignments
184	$\vert PhAsS\vert^+$	186	$\vert SbSPH_2\vert^+$ or $\vert SbS_2H\vert^+$
154	$\vert S_2POPr^i\vert^+$	154	$\vert S_2POPr^i\vert^+$
152	$\vert PhAs\vert^+$	153	$\vert SbS\vert^+$
151		147	
147		123, 121	Sb^+
115		115	
107	$\vert AsS\vert^+$		

[a]Mass based upon ^{1}H, ^{12}C, ^{16}O, ^{31}P, ^{32}S, ^{75}As and ^{121}Sb.

recrystallized from petroleum ether (40–60 °C) and benzene mixture.

The other reactions employing ammonium salts of the ligands were carried out similarly, and details are summarized in Table I.

Reaction of Phenyldichloroarsine with the O,O-butane 2,3-dithiophosphoric Acid in 1:2 Molar Ratio

A benzene solution of phenyl dichloroarsine (1.20 g) was added to the benzene solution of O,O-butane 2,3-dithiophosphoric acid (2.03 g). The reaction mixture was refluxed for ~8 hours (or the evolution of HCl gas ended). The solvent was removed under reduced pressure and the resultant product was washed with petroleum ether (40–60 °C).

The results of these reactions are also summarised in Table I.

Acknowledgements

One of the authors (R.K.G.) thanks U.G.C., New Delhi for the financial assistance under Special Assistance Programme.

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