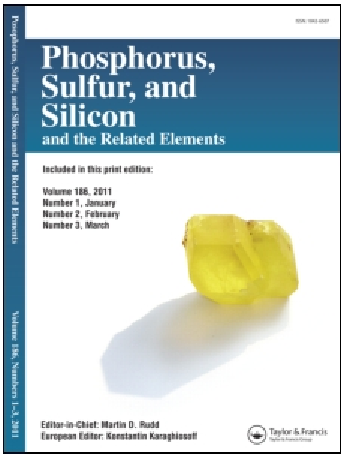

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METAL AND ORGANOMETAL COMPLEXES OF OXY- AND THIOPHOSPHORUS ACIDS. VIII. REACTIONS OF O,O-DIISOPROPYL AND O,O-ALKYLENE DITHIOPHOSPHORIC ACIDS WITH TITANIUM AND TIN TETRACHLORIDE

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METAL AND ORGANOMETAL COMPLEXES OF OXY- AND THIOPHOSPHORUS ACIDS.
VIII. REACTIONS OF O,O-DIISOPROPYL AND O,O-ALKYLENE DITHIOPHOSPHORIC ACIDS WITH TITANIUM AND TIN TETRACHLORIDE

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Reactions of O,O-diisopropyl dithiophosphoric acid with $TiCl_4$ and $SnCl_4$ proceed with ready elimination of HCl and formation of the substituted derivatives, $Cl_2M[S_2P(OR)_2]_2$ (M = Ti, Sn). Cyclic O,O-alkylene dithiophosphoric acids, $\overline{OGOP}(S)SH$ (G = $—CMe_2CMe_2—$, $—CH_2CMe_2CH_2—$, $—CH_2CEt_2CH_2—$), on the other hand, form stable 2:1 adducts with these metal halides which are insoluble in common organic solvents but sparingly soluble in CH_2Cl_2, DMSO and DMF. These have been characterised by IR and NMR (^1H and ^{31}P) spectral data which are consistent with cis-octahedral structures involving dative bonding only from the thiophosphoryl sulphur to the metal atom.

INTRODUCTION

Metal halides usually react with alcohols and carboxylic acids with the initial formation of adducts[1,2] which, depending on the nature of the metal atom, may be quite stable (e.g., $SnCl_4 \cdot 2ROH$ are sublimable)[3] or may undergo facile hydrogen halide elimination to form substituted derivatives. Such studies with thiols are still limited. In one publication, however, both $TiCl_4$ and $SnCl_4$ have been reported[4] to form 1:2 adducts with thiols and 1:1 adducts with dithiols which are hydrolytically and thermally unstable and decompose with elimination of HCl. The complexation chemistry of thiophosphoryl compounds with metallic species, on the other hand, has been widely studied.[5,6] Stable adducts of these with $TiCl_4$ and $SnCl_4$ (e.g., $MCl_4 \cdot 2Ph_3PS$, $MCl_4 \cdot R_2P(S)P(S)R_2$ etc.) have been isolated and their spectroscopic behaviours have been studied in detail.[7–9]

O,O Dialkyl and alkylene dithiophosphoric acids contain both —SH as well as P═S groups and thus, may behave either as a unidentate or a bidentate ligand in adduct formation with metal species. Although the formation of complexes of their anions with a large number of transition and nontransition metals has been extensively investigated,[10,11] there is no information concerning the donor properties of these acids as neutral ligands. In continuation to our studies on reactions of titanium[12,13] and tin[14] tetrachlorides with salts of dialkyl and alkylene dithiophosphoric acids, the present paper describes the reactions of these metal chlorides with the parent acids in absence of an HCl acceptor and reports the interesting difference in the behaviour of open chain and cyclic dithiophosphoric acids for the first time.

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RESULTS AND DISCUSSION

The reactions of titanium and tin tetrachlorides with alkylene dithiophosphoric acids in benzene at low temperature (~5°C) resulted in the formation of addition compounds of 1:2 stoichiometry:

G = $-CMe_2CMe_2-$; M= Ti (1) , Sn (2)

G = $-CH_2CMe_2CH_2-$, M = Ti (3) , Sn (4)

G = $-CH_2CEt_2CH_2-$, M = Ti (5), Sn(6)

These adducts (Table I) are precipitated out immediately on dropwise addition of the metal chloride in benzene to the benzene solution of alkylene dithiophosphoric acids (and also by the reverse mode of addition) with constant stirring (in case of compound 3, precipitation occurs after stirring the reaction mixture for 2 hours). No evolution of HCl is observed during the course of the reaction. The products are filtered, washed with benzene several times and finally dried under reduced pressure.

When the reactions of metal chlorides ($TiCl_4$, $SnCl_4$) with alkylene dithiophosphoric acids are carried out in 1:1 and 1:3 molar ratios, only 1:2 adducts are precipitated leaving the excess of metal chloride or the free ligand in the solution. Thus, these results indicate that 1:2 stoichiometry is preferred under all conditions.

The titanium and tin derivatives are respectively reddish orange and light yellow powdery solids. All of these are insoluble in benzene, carbon tetrachloride, hexane and diethylether but freshly prepared titanium derivatives are sparingly soluble in chloroform and dichloromethane. Tin derivatives are fairly soluble in DMSO and DMF and sparingly soluble in dichloromethane. All these compounds are hydrolysed by water as indicated by the ^{31}P NMR spectra of their aqueous solutions.

Reactions of $SnCl_4$ with $(Pr^iO)_2P(S)SH$ in 1:2 molar ratio, carried out under similar conditions for the sake of comparison, gave immediate evolution of HCl during mixing of the reactants and finally a soluble light yellow crystalline product, identified as $Cl_2Sn[S_2P(OPr^i)_2]_2$ on the basis of elemental analysis and spectroscopic data [IR, cm^{-1}, ν P=S 620s, ν Sn—Cl 320 broad; ^1H NMR δ ppm, 1.36 d (J = 7.0 Hz); 4.92–5.50m; ^{31}P NMR, 86.4s]. Reaction of $TiCl_4$ with $(Pr^iO)_2P(S)SH$ also takes a similar course and yields $Cl_2TiS_2P(OPr^i)_2$, identical with the compound described earlier.[12]

The above substitution reaction may probably be proceeding via initial formation of 1:2 adduct. Thus, it seems that the course of these reactions depends on the solubility of the adduct. It may be pointed out that all the previously reported stable adducts of $TiCl_4$ and $SnCl_4$ with sulphur donor ligands are insoluble solids.[5–9]

IR SPECTRA

The strong intensity bands present in the region 1140–1035 cm^{-1} and 820–800 cm^{-1} may be assigned to ν (P)—O—C and ν P—O—(C) vibrations respectively.[15] A strong band due to dioxaphospholane and dioxaphosphorinane ring vibrations is present in the region 990–930 cm^{-1} and these are probably coupled with C—C stretching vibrations.[16] A sharp band present in the region 660–635 cm^{-1} can be assigned to ν P═S vibrations.[15] This band shows a notable shifting (Δ = 45–20 cm^{-1}) towards lower frequency with respect to its position in the free ligands. This shifting is probably due to the coordination of sulphur of the P═S group to the metal atom. The bands of medium intensities in the region 610–535 cm^{-1} may be attributed to ν P—S asymmetric and symmetric vibrations.

A number of new bands are observed in the region 400–300 cm^{-1} due to metal-chlorine and metal-sulphur stretching vibrations. In the titanium derivatives, two strong bands are present at 380 cm^{-1} and 340 cm^{-1} assigned to ν Ti—Cl and ν Ti—S vibrations, respectively.[4,17] Other bands due to ν Ti—Cl (e.g. at 325, 310 and 290 cm^{-1} in case of complex 2) are of weak intensity. In tin tetrachloride complexes, the ν Sn—S and ν Sn—Cl vibrations are present in the region 375–360 cm^{-1} and 325–310 cm^{-1}, respectively.[4,18] In the latter region, broad bands with shoulders are observed in the case of $SnCl_4 \cdot 2HS(S)POCH_2C(Me)_2CH_2O$. The S—H vibration, expected in the region 2500–2400 cm^{-1}, could not be observed in the spectra of solid compounds. The solution spectra unfortunately could not be obtained due to the insoluble nature of these adducts. Details regarding the individual peaks have been included in Table II.

PMR SPECTRA

The PMR spectra (Table III) of alkylene dithiophosphoric acid adducts of $TiCl_4$ and $SnCl_4$ have been recorded in $CDCl_3$ and DMSO-d_6, respectively. In both the cases, the S—H protons have been observed in the range 3.30–2.68 ppm, the titanium derivatives showing in some cases a minor shift (of ~ 0.40 ppm) towards higher field in comparison to its position in the parent acids.[19] In other respects, there is a close similarity between the spectra of the adducts and the parent acids. The three bond coupling constants between the protons on α-carbons of P—O—C chain and ^{31}P remains unaffected. Interestingly, $TiCl_4 \cdot 2HS_2\overline{POC(Me)_2C(Me)_2O}$ shows two closely separated singlets (at 1.5 ppm) of equal intensity. This is in contrast to the parent acid, which shows only one singlet (at 1.49 ppm) without any noticeable 4-bond coupling with phosphorus. It seems that the adduct formation enhances the difference in the environments of the *cis* and *trans* methyls in the dioxaphospholane ring (with respect to the thiophosphoryl group). The corresponding tin compound, however, shows only one singlet.

^{31}P NMR SPECTRA

The ^{31}P NMR spectra (Table III) for titanium and tin derivatives have been recorded in $CHCl_3$ and CH_2Cl_2, respectively, and show only one signal for each compound,

TABLE I

Reactions of $TiCl_4$ and $SnCl_4$ with O,O-alkylene dithiophosphoric acids in 1:2 molar ratio

Compound No.	Reactants (g)/(mmoles)		Adduct Physical State Yield (%)	Decomp. Temp. (°C)	Analyses % Found (Calcd)		
	MCl_4 M =	HS(S)POGO G =			M	S	Cl
1	Ti 0.57 (3.0)	$—C(Me)_2C(Me)_2—$ 1.28 (6.0)	Reddish orange powdery solid 1.78 (96)	178	7.88 (7.80)	20.98 (20.86)	22.87 (23.10)
2	Ti 1.18 (6.2)	$—CH_2C(Me)_2CH_2—$ 2.47 (12.5)	Reddish orange sticky solid 3.50 (96)	—	8.25 (8.18)	21.90 (21.84)	24.15 (24.21)
3	Ti 0.40 (2.1)	$—CH_2C(Et)_2CH_2—$ 0.97 (4.3)	Reddish orange powdery solid 1.31 (95)	135	7.51 (7.46)	19.99 (19.95)	22.02 (22.10)
4	Sn 0.58 (2.2)	$—C(Me)_2C(Me)_2—$ 0.95 (4.5)	Light yellow powdery solid 1.38 (91)	201	17.43 (17.34)	18.62 (18.70)	20.52 (20.71)
5	Sn 1.60 (6.1)	$—CH_2C(Me)_2CH_2—$ 2.44 (12.3)	Light yellow powdery solid 3.39 (84)	247	18.26 (18.08)	19.52 (19.50)	20.82 (20.68)
6	Sn 1.23 (4.7)	$—CH_2C(Et)_2CH_2—$ 2.14 (9.5)	Light yellow powdery solid 2.86 (85)	173	16.82 (16.66)	18.03 (17.96)	19.20 (19.35)

TABLE II

Some relevant IR spectral data (cm^{-1}) for titanium and tin tetrachloride bis(alkylene dithiophosphoric acid) adducts

Sl. No.	Compound	ν (P)—O—C	ν P—O—(C)	Ring Vibration	ν P=S	ν P—S	ν M—S	ν M—Cl
1.	$\mathrm{TiCl_4 \cdot 2HS(S)\overline{POC(Me)_2C(Me)_2O}}$	1130, s	810, s	930, s	650, s	600, s	—	360, m, br
2.	$\mathrm{TiCl_4 \cdot 2HS(S)\overline{POCH_2C(Me)_2CH_2O}}$	1035, s	800, s	980, s	655, s	600, m 545, m	340 s, br	380, s, br 325, m 310, w 290, m
3.	$\mathrm{TiCl_4 \cdot 2HS(S)\overline{POCH_2C(Et)_2CH_2O}}$	1050, s	810, s	970, s	660, m	600, w 550, m	340, m	380, m, br 320, w 300, w
4.	$\mathrm{SnCl_4 \cdot 2HS(S)\overline{POC(Me)_2C(Me)_2O}}$	1140, s	810, m	930, s	635, s	610, s	375, w	330, s 320, s 290
5.	$\mathrm{SnCl_4 \cdot 2HS(S)\overline{POCH_2C(Me)_2CH_2O}}$	1040, s	810, m	990, s	650, s	535, s	370, w	340, w, 320, w 300, m 280, w
6.	$\mathrm{SnCl_4 \cdot 2HS(S)\overline{POCH_2C(Et)_2CH_2O}}$	1060, s	820, m	980, s	660, s	545, s	360, w	325, br

TABLE III

^1H and ^{31}P NMR spectral data (δ ppm) for titanium and tin tetrachloride bis(alkylene dithiophosphoric acid) adducts

Sl. No.	Compound	^1H	^{31}P (down field shift from parent acid)
1.	$\mathrm{TiCl_4 \cdot 2HS(S)\overline{POC(Me)_2C(Me)_2O}}$	1.45, d (J = 4Hz), 24H(Me) 3.25, s, 2H(SH)	103.1 (11.6)
2.	$\mathrm{TiCl_4 \cdot 2HS(S)\overline{POCH_2C(Me)_2CH_2O}}$	1.10, s, 12H(Me) 2.90, s, 2H(—SH) 4.04, d (J = 16 Hz), 8H(—CH_2O)	86.7 (8.1)
3.	$\mathrm{TiCl_4 \cdot 2HS(S)\overline{POCH_2C(Et)_2CH_2O}}$	0.88, t (J = 6 Hz), 12H(Me) 1.27–1.62, q, 8H(—CH_2O) 2.68, s, 2H(—SH) 4.09 (J = 16 Hz), 8H(—CH_2O)	88.8 (10.7)
4.	$\mathrm{SnCl_4 \cdot 2HS(S)\overline{POC(Me)_2C(Me)_2O}}$	1.49, s, 24H(Me) 3.30, s, 2H(SH)	109.6 (18.1)
5.	$\mathrm{SnCl_4 \cdot 2HS(S)\overline{POCH_2C(Me)_2CH_2O}}$	1.32, s, 12H(Me) 2.94, s, 2H(SH) 4.18, d (J = 16 Hz), 8H(CH_2O)	95.6 (17.0)
6.	$\mathrm{SnCl_4 \cdot 2HS(S)\overline{POCH_2C(Et)_2CH_2O}}$	0.88, t (J = 6 Hz), 12H(Me) 1.22–1.89, q, 8H(—CH_2) 3.08, s, 2H(SH) 4.19, d (J = 16 Hz), 8H(CH_2O)	96.6 (18.5)

thus indicating equivalence of the dithiophosphate ligands. There is a marked shifting of the signal towards lower field by 8 to 18 ppm from its position in the corresponding acid[19] and this is probably due to the dative $P{=}S \rightarrow M$ bonding. Interestingly, this shift is more pronounced in the tin derivative which is probably indicative of stronger metal-sulphur bond formation in these cases.

In alkylene dithiophosphoric acids, both thiolato and thiono sulphur atoms are potential donors. However, the stoichiometry of the adducts formed indicates that these acids are behaving as monodentate ligands towards $TiCl_4$ and $SnCl_4$. The molecular weight data could have given supporting evidence but these, unfortunately, could not be obtained due to the poor solubility of the adducts. The shift in the position of the peak due to P=S in the IR spectra show that donor centre in the acid molecule is the phosphorothionyl sulphur. Based on the above and ^{31}P NMR spectroscopic data, an octahedral structure may be assigned to these adducts.

The *cis* and *trans* complexes of the type $MCl_4 \cdot 2L$ may be easily differentiated on the basis of IR data in the ν M—Cl region.[4,7,18] The *trans* isomers are expected to show only two peaks in this region while six peaks should be observed for the *cis* isomers. In the case of new complexes of $TiCl_4$, there are five distinct peaks (one of strong and four of weak intensity) in the region 340–290 cm^{-1} which can be assigned to ν Ti—Cl. The missing sixth peak is probably present in combination with strong intensity peak, thus giving it a broad shape. Similar peak pattern has also been observed in the tin adducts. Broad bands with shoulders are observed in the case of complexes 1 and 6. The IR data are thus indicative of *cis*-geometry for these addition complexes.

It may be pointed out that addition compounds of titanium and tin tetrachlorides with other sulphur donors like thiols, tertiary phosphine sulphides and bis(dialkyl phosphorothionyl) disulphides have also been discussed on the lines of hexacoordinated *cis*-geometry.[4-7]

EXPERIMENTAL

Owing to the extremely hydrolysable nature of starting materials as well as newly synthesised titanium and tin adducts, stringent precautions were taken to exclude the moisture. Solvents (benzene, chloroform and dichloromethane) were dried by standard methods. Titanium tetrachloride and tin tetrachloride were distilled before use. O,O-Diisopropyl and O,O-alkylene dithiophosphoric acids were prepared by the methods reported in the literature.[19,20]

IR spectra were recorded as nujol mulls using CsI pellets on a Perkin-Elmer 577 spectrophotometer in the range 4000–200 cm^{-1}. The ^1H NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 using TMS as external reference on a Jeol FX 90Q at 89.55 MHz. ^{31}P NMR spectra were recorded in $CHCl_3$ and CH_2Cl_2 using H_3PO_4 as external reference on the same instrument at 36.23 MHz.

Reactions of tin and titanium tetrachlorides with alkylene dithiophosphoric acids in 1:2 molar ratio: The solution of metal tetrachloride in benzene was added dropwise with constant stirring to the ice cooled solution of O,O-alkylene dithiophosphoric acid in benzene resulting into immediate precipitation of orange or light yellow compound. Stirring was continued for ~2 hrs to ensure complete precipitation. The solid product was filtered out, washed with benzene and finally dried under reduced pressure.

The relevant data for the above reactions have been given in Table I.

Reaction of tin tetrachloride with O,O-diisopropyl dithiophosphoric acid in 1:2 molar ratio: A benzene solution of tin tetrachloride (1.88 g, 7.2 mmol) was added to diisopropyl dithiophosphoric acid (3.09 g, 14.4 mmol) in benzene under similar conditions as above. Hydrogen chloride was evolved immediately. Stirring was continued until evolution of HCl ceased. On removal of the solvent under reduced pressure, a greenish yellow crystalline solid (4.28 g, 96%; m.p. 84–86°C) was obtained. Found: Sn, 19.39; S, 20.68; Cl, 11.43.

Calc. for $C_{12}H_{28}Cl_2O_4P_2S_4Sn$: Sn, 19.28; S, 20.80; Cl, 11.51.

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