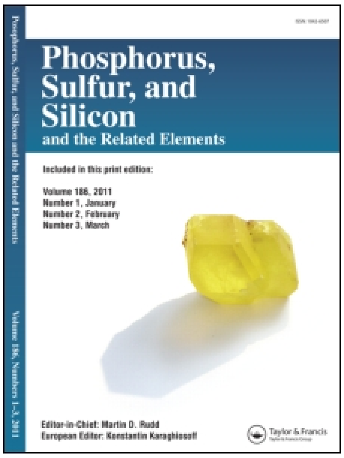

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J. S. Yadav[a]; R. K. Mehrotra[a]; G. Srivastava[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

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METAL AND ORGANOMETAL COMPLEXES OF OXY- AND THIOPHOSPHORUS ACIDS. PART II. REACTIONS OF O,O-ALKYLENE DITHIOPHOSPHORIC ACIDS WITH TITANIUM(IV) ISOPROPOXIDE

J. S. YADAV, R. K. MEHROTRA and G. SRIVASTAVA*
Department of Chemistry, University of Rajasthan, Jaipur-302004 India

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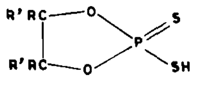
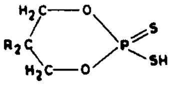
Replacement reactions of titanium(IV) isopropoxide with O,O-alkylene dithiophosphoric acids proceed in 1:1 and 1:2 molar ratios in refluxing benzene to yield tri- and diisopropoxytitanium alkylene dithiophosphates, $(\mathrm{OPr}^i)_{4-n}\mathrm{Ti}(\mathrm{S_2}\overline{\mathrm{POGO}})_n$ ($n = 1$ and 2; $G = $ —CMe$_2$CMe$_2$—, —CH$_2$CMe$_2$CH$_2$—, —CH$_2$CEt$_2$CH$_2$—, and —CHMeCHMe—) as hydrolysable, orange solids or viscous liquids, soluble in common organic solvents and monomeric in nature. Further replacement of isopropoxy groups to give tris and tetrakis dithiophosphates does not occur. The isopropoxy groups in the mixed derivatives, however, can be replaced by tert-butoxy groups. All these compounds have been characterized by elemental analyses, molecular weight determinations and IR and NMR (^{1}H, ^{13}C and ^{31}P) spectral data which are consistent with bidentate chelating behaviour of the dithiophosphate ligands.

INTRODUCTION

O,O-Dialkyl and alkylene dithiophosphoric acids behave as versatile bidentate dithio ligands and form a variety of stable complexes with transition[1,2] as well as nontransition[3–6] elements. A perusal of literature reveals that no systematic work has been carried out on titanium(IV) dithiophosphates although a marked tendency of titanium to form stable complexes with other bidentate sulphur donor ligands, such as N,N-dialkyl dithiocarbamic[7,8] and O-alkyl dithiocarbonic[9] acids is well documented. In continuation of our recent studies on reactions of titanium tetrachloride with O,O-dialkyl and alkylene dithiophosphate salts,[10] we report the reactions of titanium tetraisopropoxide with O,O-alkylene dithiophosphoric acids in this communication. The acids chosen for these studies are 5-membered tetramethyl- and 1,2-dimentyl-ethylene dithiophosphoric acids as well as 6-membered 2,2-dimethyl- and 2,2-diethyl-trimethylene dithiophosphoric acids, which, unlike their acyclic analogues, can be obtained in high purity.



R = R' = Me
R = H, R' = Me



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* Author to whom correspondence should be addressed.

RESULTS AND DISCUSSION

Mixed isopropoxide alkylene dithiophosphates of titanium(IV) have been synthesized in quantitative yield by the reactions of titanium tetraisopropoxide with alkylene dithiophosphoric acids in 1:1 and 1:2 molar ratio in refluxing benzene.

$$\mathrm{Ti(OPr^i)_4} + n\ \mathrm{HS_2\overline{POGO}} \rightarrow \mathrm{(Pr^iO)_{4-\mathit{n}}Ti(S_2\overline{POGO})_{\mathit{n}}} + \mathrm{Pr^iOH}$$

$$n = 1, 2$$

(G = —CMe_2CMe_2—, —$CH_2CMe_2CH_2$—, —$CH_2CEt_2CH_2$— and —CHMeCHMe—)

These replacement reactions are quite slow and have to be pushed to completion by continuously removing the liberated isopropanol azeotropically with the solvent. The colour of the reaction mixture changes from colourless to dark orange with the progress of the reaction. The disubstituted derivatives are the final products even under forcing conditions, e.g. excess of dithiophosphoric acid and refluxing toluene medium. In contrast to this, titanium tetrachloride, shows higher reactivity and, with alkali metal or ammonium salts of dithiophosphoric acids, all of its chlorines are replaced.[10]

The mixed isopropoxytitanium alkylene dithiophosphates are yellow orange solids or viscous liquids soluble in benzene, chloroform, carbon tetrachloride and dimethyl sulphoxide. In contrast to the mixed chloride alkylene dithiophosphates $\mathrm{Cl_{4-\mathit{n}}Ti(S_2\overline{POGO})_{\mathit{n}}}$, which slowly change into intractable solids,[10] these compounds are more stable and do not show any change in their spectroscopic (IR and NMR) properties even after keeping for long time. These derivatives are highly sensitive towards moisture. Cryoscopic molecular weight determination (Table I) in benzene of one representative example of both the series of isopropoxytitanium dithiophosphates indicates the monomeric nature of these complexes.

The derivatives, tri-*tert*-butoxytitanium tetramethylethylene dithiophosphate and di-*tert*-butoxytitanium bis (tetramethylethylene dithiophosphate) have also been obtained by the reactions of the corresponding isopropoxy derivatives with excess of tert-butanol in refluxing benzene with slow azeotropic fractionation of the liberated isopropanol.

$$\mathrm{(Pr^iO)_{4-\mathit{n}}Ti(S_2\overline{POCMe_2CMe_2O})_{\mathit{n}}} + 4 - n\ \mathrm{Bu^tOH}$$

$$\rightarrow \mathrm{(Bu^tO)_{4-\mathit{n}}Ti(S_2\overline{POCMe_2CMe_2O})_{\mathit{n}}} + 4 - n\ \mathrm{Pr^iOH}$$

$$n = 1, 2$$

These tert-butoxy derivatives show close resemblance with the isopropoxy derivatives in their properties.

IR Spectra:

The IR spectral assignments (Table II) are based on earlier reports on other metal dithiophosphates[2,11] and on titanium-sulphur bonded compounds.[12,13]

TABLE I

Synthesis and properties of mixed isopropoxytitanium(IV) alkylenedithiophosphates

	Reactants (g)					% Analyses Found (Calc.)		
Sl. No.	$Ti(OPr^i)_4$	$HS_2\overline{POGO}$ G	Molar ratio	Product*/Physical State	Pr^iOH Liberated Found (Calc.)	Ti	S	Molecular weight Found (Calcd.)
1.	1.60	—CMe_2CMe_2—	1:1	$(Pr^iO)_3TiS_2\overline{POCMe_2CMe_2O}$	0.32	11.10	14.74	453
		1.20		Orange semi-solid	(0.33)	(10.98)	(14.68)	(435)
2.	1.09	—CMe_2CMe_2—	1:2	$(Pr^iO)_2Ti(S_2\overline{POCMe_2CMe_2O})_2$	0.45	8.20	21.80	581
		1.63		Yellow semi solid†	(0.46)	(8.14)	(21.77)	(587)
3.	1.16	—$CH_2CMe_2CH_2$—	1:1	$(Pr^iO)_3TiS_2\overline{POCH_2CMe_2CH_2O}$	0.24	11.50	15.30	428
		0.81		Red semi-solid	(0.24)	(11.35)	(15.16)	(421)
4.	1.93	—$CH_2CMe_2CH_2$—	1:2	$(Pr^iO)_2Ti(S_2\overline{POCH_2CMe_2CH_2O})_2$	0.80	8.65	22.99	
		2.70		Orange viscous liquid	(0.81)	(8.55)	(22.86)	
5.	1.32	—$CH_2CEt_2CH_2$—	1:1	$(Pr^iO)_3TiS_2\overline{POCH_2CEt_2CH_2O}$	0.27	10.73	14.26	
		1.06		Yellow viscous liquid	(0.28)	(10.64)	(14.22)	
6.	1.15	—$CH_2CEt_2CH_2$—	1:2	$(Pr^iO)_2Ti(S_2\overline{POCH_2CEt_2CH_2O})_2$	0.47	7.85	20.82	
		1.85		Red sticky solid	(0.48)	(7.77)	(20.78)	
7.	1.68	—CHMeCHMe—	1:1	$(Pr^iO)_3TiS_2\overline{POCHMeCHMeO}$	0.35	11.60	15.75	
		1.09		Orange viscous liquid	(0.35)	(11.74)	(15.69)	
8.	1.39	—CHMeCHMe—	1:2	$(Pr^iO)_2Ti(S_2\overline{POCHMeCHMeO})_2$	0.55	9.15	24.12	
		1.75		Red viscous liquid	(0.55)	(9.00)	(24.06)	

* All the products are obtained in 97–99% yield.

† Solidified slowly on keeping for long periods.

TABLE II

Some relevant IR spectral data for mixed isopropoxy titanium(IV) alkylene dithiophosphates

Compound	ν (P)–O–C	ν P–O–(C)	Ring vibrations	ν P═S	ν P–S	ν Ti–S
$(Pr^iO)_3TiS_2\overline{POCMe_2CMe_2O}$	1140 s	860 m	960 s	680 m	630 s 590 w	350 w
$(Pr^iO)_2Ti(S_2\overline{POCMe_2CMe_2O})_2$	1140 s	860 m	955 s	670 m	630 s 600 m	350 w
$(Pr^iO)_3TiS_2\overline{POCH_2CMe_2CH_2O}$	1050 s	850 s	960 s	670 s	610 s	340 w
$(Pr^iO)_2Ti(S_2\overline{POCH_2CMe_2CH_2O})_2$	1045 s	850 s	955 s	975 s	635 m	345 w
$(Bu^tO)_3TiS_2\overline{POCMe_2CMe_2O}$	1140 s	865 s	960 s	680 m	640 s 615 w	350 w
$(Bu^tO)_2Ti(S_2\overline{POCMe_2CMe_2O})_2$	1140 s	860 m	960 s	680 m	635 s 600 b	340 w

s = strong, m = medium, b = broad and w = weak.

The bands present in the region 1140–1050 cm^{-1} and 870–850 cm^{-1} may be assigned to ν(P)–O–C and P–O–(C) stretching vibrations respectively. The bands of sharp to medium intensities in the region 960–950 cm^{-1} may be attributed to the ring vibrations of dioxaphospholanes and dioxaphosphorinanes which are probably coupled with C–C stretching vibrations[14,15] and remain unchanged on complexation. A sharp band present at 680–670 cm^{-1} is due to ν P=S vibrations. It has been observed that in all the titanium complexes, there is a small but consistent shift ($\Delta\nu = 20–10\ cm^{-1}$) to lower frequency in the ν (P=S) vibrations in comparison to the values in the corresponding free acids. This lowering is probably due to coordination of thiophosphoryl sulphur to titanium. The bands in the region ~630 cm^{-1} and 350–340 cm^{-1} have been assigned to ν (P–S) (symmetric and asymmetric)[2] and Ti–S[13] vibrations, respectively. Formation of (Ti–S) bond is also supported by complete disappearance of ν S–H band (at ~2500 cm^{-1}) in the complexes.

NMR Spectra:

The PMR spectra (Table III) of titanium(IV) alkylene dithiophosphates recorded in CCl_4 show the expected peak patterns. There is considerable overlapping of peaks due to glycoxy and isopropoxy protons. The peak due to S–H proton (present at δ 3.10–3.50 ppm in the spectra of dithiophosphoric acids)[16] is expectedly absent in the corresponding titanium(IV) complexes showing the formation of Ti–S bond by deprotonation. The methylene (OCH_2—) protons in the complexes derived from 2,2-dimethyl and -diethyltrimethylene dithiophosphoric acids appear as a doublet centred in the range δ 3.77–4.04 ppm with $^3J(^1H\text{-}^{31}P) = 15$ Hz.

The spectra of diisopropoxytitanium bis(alkylene dithiophosphates) show the presence of only one type of isopropoxy and dithiophosphate moieties and are consistent with a *trans*-octahedral structure, if the dithiophosphate moieties are bidentate as indicated by the IR data. In the spectrum of triisopropoxytitanium mono(tetramethylethylene dithiophosphosphate), the isopropoxymethyl protons are present as two doublets centered at δ 1.10 ppm and δ 1.20 ppm ($J = 7$ Hz) with peak area of 2:1; the smaller doublet being in the higher field. These results indicate a trigonal bipyramidal structure for the above complex. Other triisopropoxy derivatives of this series do not show splitting of the isopropoxy methyl doublet; however, the peaks are broadened.

The ^{13}C NMR spectra of tetramethylethylene dithiophosphate derivatives were measured in CCl_4 at ambient temperature (Table IV). A comparison of ^{13}C chemical shift values with those found in $Ti(OPr^i)_4$ and the parent dithiophosphoric acid does not indicate any appreciable change except in the position of the secondary carbon of the isopropoxy groups. The reason for the deshielding of this carbon in the dithiophosphate complexes is not clear.

The ^{31}P NMR chemical shifts of the 5- and 6-membered parent acids are 93.0–95.4 ppm and 77.8–78.6 ppm respectively, thus exhibiting the pronounced effect of ring size on ^{31}P chemical shifts.[16] All the alkoxy titanium(IV) alkylene dithiophosphates exhibit a low field shift of ~15 ppm of the ^{31}P signal with respect

TABLE III

^1H and ^{31}P NMR spectral data for titanium(IV) alkylene dithiophosphates

Compound	^1H chemical shift in δppm (in CCl_4)	^{31}P chemical shift in δppm (in CCl_4)
$(Pr^iO)_3TiS_2\overline{POCMe_2CMe_2O}$	$\left.\begin{array}{l}1.10, d(J=7\,Hz)\\1.20, d(J=7\,Hz)\end{array}\right\}18H(\underline{Me}_2CH)$ 1.32, s, 12H(Me_2C) 4.50–5.30, 3H(—CHO)	109.4
$(Pr^iO)_2Ti(S_2\overline{POCMe_2CMe_2O})_2$	1.03, d($J = 7$ Hz), 12H($\underline{Me}_2CH$) 1.18, s, 24H(Me_2O) 4.40–5.20, m, 2H(—CHO)	109.1
$(Pr^iO)_3TiS_2\overline{POCH_2CMe_2CH_2O}$	0.88, s, 6H(Me_2C) $\left.\begin{array}{l}1.02, d(J=7\,Hz)\\1.11, d(J=7\,Hz)\end{array}\right\}18H(\underline{Me}_2CH)$ 3.77, d($J = 15$ Hz), 4H(CH_2O—) 4.40–5.20, m, 3H(—CHO)	94.4
$(Pr^iO)_2Ti(S_2\overline{POCH_2CMe_2CH_2O})_2$	0.90, s, 12H(Me_2C) 1.13, d($J = 7$ Hz), 12H($\underline{Me}_2CH$) 3.82, d($J = 15$ Hz), 8H(—CH_2O) 4.50–5.30, m, 2H(—CHO)	94.6
$(Pr^iO)_3TiS_2\overline{POCH_2CEt_2CH_2O}$	0.96, t($J = 6$ Hz), 6H(Me) $\left.\begin{array}{l}1.23, d(J=7\,Hz)\\1.38, d(J=7\,Hz)\end{array}\right\}18H(\underline{Me}_2CH)$ 1.70–1.45, q, 4H(CH_2) 4.04, d($J = 15$ Hz), 4H(CH_2O) 4.65–5.40, m, 3H(CHO)	89.7
$(Pr^iO)_2Ti(S_2\overline{POCH_2CEt_2CH_2O})_2$	0.92, t($J = 6$ Hz), 12H(Me) 1.30, d($J = 7$ Hz), 12H($\underline{Me}_2CH$) 1.71–1.40, q, 8H(CH_2) 4.04, d($J = 15$ Hz) 8H(CH_2O) 4.65–5.40, m, 2H(CHO)	95.9
$(Pr^iO)_3TiS_2\overline{POCHMeCHMeO}$	—	113.0
$(Pr^iO)_2Ti(S_2\overline{POCHMeCHMeO})_2$	—	94.2, 113.4
$(Bu^tO)_3TiS_2\overline{POCMe_2CMe_2O}$	—	108.5
$(Bu^tO)_2Ti(S_2\overline{POCMe_2CMe_2O})_2$	—	109.3

s = singlet; d = doublet, t = triplet, q = quartet and m = multiplet.

to the parent acid suggesting the bidentate chelating nature of the ligand moiety. In case of the diisopropoxytitanium bis(1,2-dimethylethylene dithiophosphate), the appearance of two peaks (at 94.2 and 113.4 ppm) is probably due to the presence of diastereoisomers.

The IR, NMR (^1H, ^{13}C and ^{31}P) and molecular weight data are thus consistent with a trigonal bipyramidal structure for triisopropoxy derivatives and a trans-octahedral structure for the diisopropoxy derivatives.

With three unidentate and one bidentate substituents, the trigonal bipyramidal structure of triisopropoxy derivatives can adopt either *mer* or all-*cis* structure. In view of the small bite of the dithiophosphate ligands forming 4-membered rings with the metal atom, the latter structure in which the dithiophosphate moiety occupies the axial-equatorial positions should be preferred. This conclusion finds

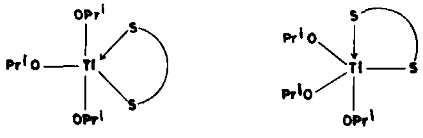
TABLE IV

^{13}C NMR spectral data for mixed alkoxytitanium(IV) alkylene dithiophosphates

Compound	^{13}C Chemical shift, in δppm			
	Isopropoxy or tert-butoxy		Alkylene dithiophosphates†	
	CH_3	OCH	OC	CH_3
$Ti[(OCH(CH_3)_2]_4$	24.65	74.33	—	—
$HS_2POC(CH_3)_2C(CH_3)_2O$	—	—	90.15 ($J = 2.44$ Hz)	24.21 ($J = 4.88$ Hz)
$[(CH_3)_2CHO]_3TiS_2POC(CH_3)_2C(CH_3)_2O$	25.19	83.37	88.73	24.26 ($J = 2.44$ Hz)
$[(CH_3)_2CHO]_2Ti(S_2POC(CH_3)_2C(CH_3)_2O]_2$	25.12	83.25	88.94	24.36 ($J = 2.44$ Hz)
$[(CH_3)_3CO]_3TiS_2POC(CH_3)_2C(CH_3)_2O$	31.15	*	88.30	24.05
$[(CH_3)_3CO]_2Ti[S_2POC(CH_3)_2C(CH_3)_2O]_2$	31.20	*	88.40 ($J = 2.44$ Hz)	24.27 ($J = 2.44$ Hz)

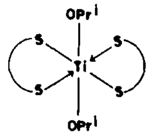
* The peak due to the tertiary carbon of the tert-butoxy group could not be observed.

† Coupling with phosphorus was observed in some cases; the J values are given.



mer all *cis*

Trigonal bipyramidal



Trans-octahedral

further support from the recently reported X-ray crystallographic structural determinations of triphenyltin tetramethylethylene dithiophosphate.[17] 5-Coordinate titanium complexes are rather rare and although their formation has been reported in several reactions,[18] detailed structural analyses do not appear to have been carried out.

Octahedral titanium complexes with two bidentate and two unidentate ligands generally adopt *cis*-arrangement.[19,20] In the present cases of diisopropoxytitanium bis(dithiophosphates), however, the *cis* structure may be sterically too crowded. It may, however, be pointed out that anisobidentate binding of dithiophosphate moieties with metal atoms is quite common as shown by X-ray crystallographic data[17,21] of various organotin complexes.

Titanium alkoxides tend to form adducts with amines,[22,23] probably with the breaking of oxy bridges. Adduct formation tendency appears to be reduced in diisopropoxytitanium bis(alkylene dithiophosphate); thus the addition of two moles of pyridine to $(Pr^iO)_2Ti(S_2\overline{POCMe_2CMe_2O})_2$ in benzene does not show any change in ^{31}P chemical shift (being observed at 108.4 ppm). However, when the complex is dissolved in excess of pyridine, the ^{31}P signal shifts to 123.8 ppm, a position reported earlier for tetramethyldithiophosphate anion.[10]

^{31}P NMR spectral data have also been used to study co-disproportionation reactions between $Ti(OPr^i)_4$ and $Ti(S_2\overline{POCMe_2CMe_2O})_4$ (obtained from $TiCl_4$).[10] The product obtained by heating an equimolar mixture in benzene shows a chemical shift of 109.1 ppm indicating the quantitative formation of the mixed derivative $(Pr^iO)_2Ti(S_2\overline{POCMe_2CMe_2O})_2$.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture during experimental manipulations. Titanium tetraisopropoxide[24] and alkylene dithiophosphoric acids[16] were prepared by the methods reported in literature. Sulphur and titanium were estimated gravimetrically as barium sulphate (Messenger's method) and titanium oxide (Cupferron method), respectively. Isopropanol was estimated by the potassium dichromate oxidation method.[25]

Molecular weights were determined cryoscopically in benzene. IR spectra were recorded as neat liquids or nujol mulls on a Perkin-Elmer 577 spectrometer in the range 4000–200 cm^{-1} using CsI cells. ^1H NMR spectra were recorded in carbon tetrachloride on a Perkin-Elmer R 12 B spectrometer using TMS as an external standard. ^{31}P and ^{13}C NMR spectra were recorded in carbon tetrachloride on Jeol FX 90Q spectrometer using H_3PO_4 and TMS as an external standard, respectively.

Methods of Preparation

(a) Reactions of titanium(IV) isopropoxide with alkylene dithiophosphoric acids in different molar ratios:

A mixture of titanium isopropoxide and alkylene dithiophosphoric acid in anhydrous benzene in different molar ratios (1:1 and 1:2) was refluxed on a fractionating column for ~3 hrs and isopropanol liberated during the course of the reaction was collected azeotropically with benzene and estimated. Removal of the excess solvent yielded the desired product.

Analytical and other relevant data for these experiments are given in Table I.

(b) Reaction of triisopropoxytitanium(IV) tetramethyl ethylenedithiophosphate with excess of tertiary butanol:

To a benzene solution (~40 ml) of $(Pr^iO)_3TiS_2\overline{POCMe_2CMe_2O}$ (1.38 g) was added Bu^tOH (1.86 g) and the reaction mixture was refluxed (~12 hrs) with continuous azeotropic removal of liberated isopropanol (Found: 0.53 g, Calcd.: 0.57 g), until the reaction was complete (as indicated by absence of isopropanol in azeotrope). Removal of the excess of solvent and drying the residue under reduced pressure left a yellow semi-solid product (1.50 g, 99%), which was purified by washing with *n*-hexane. Found: Ti, 10.13; S, 13.40; Calcd. for $C_{18}H_{39}O_5PS_2Ti$: Ti, 10.02; S, 13.39%.

(c) Reaction of diisopropoxytitanium(IV) bis(tetramethylethylene dithiophosphate) with excess of tertiary butanol:

The reaction of $(Pr^iO)_2Ti(S_2\overline{POCMe_2CMe_2O})_2$ (1.67 g) in ~50 ml benzene with Bu^tOH (1.82 g) carried out as above, gave isopropanol (Found: 0.33 g, Calcd: 0.34 g) in the azeotrope and the product (1.71 g, 97.7%) as a yellow semi-solid. Found: Ti, 7.81; S, 20.84; Calcd. for $C_{20}H_{42}O_6P_2S_4Ti$: Ti, 7.77; S, 20.78%.

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