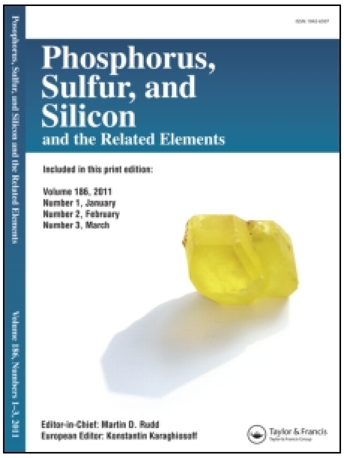

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DIALKYL DITHIOPHOSPHATES OF TANTALUM(V)

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Reactions of tantalum(V) isopropoxide with O,O′-dialkyldithiophosphoric acids in equimolar ratio yield tetraisopropoxy tantalum(V) dialkyl dithiophosphates, $(Pr^iO)_4Ta[S_2P(OR)_2]$ (where R = Et, Pr^n, Pr^i, Bu^i and C_6H_5) as hydrolysable, yellow viscous liquids, soluble in common organic solvents and monomeric in freezing benzene. These have been characterized by molecular weight determinations and spectral studies like IR and NMR (^1H, ^{13}C and ^{31}P). Octahedral structures with chelating bidentate dithiophosphate moieties are suggested for these complexes.

Key words: Dialkyl dithiophosphates; phosphoric acids; tantalum(V) isopropoxide; tetraisopropoxytantalum(V) dialkyl dithiophosphates

INTRODUCTION

O,O′-Dialkyl dithiophosphoric acids behave as versatile dithio ligands[1–2] and form a number of complexes with transition[3–7] and non-transition elements.[8–11] The anions are usually attached to a metal in a bidentate manner.[2,12] Some less common modes of bonding (e.g., monodentate) have also been reported.[13] In addition to their interesting structural features, these complexes find a variety of applications.[14–16]

A careful scanning of the literature reveals a lack of information on dialkyl dithiophosphates of tantalum. Only one reaction has been reported[17] in which mixed halide-methoxy derivatives have been synthesized but there is no information about pure alkoxy dialkyl dithiophosphates of tantalum(V).

The present paper deals with the reactions of tantalum(V) isopropoxide with dialkyl dithiophosphoric acids.

RESULTS AND DISCUSSION

Tetraisopropoxytantalum(V) dialkyl dithiophosphates have been synthesized in quantitative yields by replacement reactions of tantalum(V) isopropoxide with dialkyl dithiophosphoric acids in a 1:1 molar ratio in refluxing benzene:

$$Ta(OPr^i)_5 + HS_2P(OR)_2 \rightarrow (Pr^iO)_4Ta[S_2P(OR)_2] + Pr^iOH$$

(where R = Et, Pr^n, Pr^i, Bu^i and C_6H_5).

All these complexes are yellow viscous liquids, soluble in common organic solvents but insoluble in *n*-hexane and carbon tetrachloride. Molecular weight measurements in freezing benzene depict their monomeric nature. The derivatives are non-volatile even under reduced pressure and tend to decompose on heating. These

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TABLE I

Synthetic and other relevant data for tetraisopropoxytantalum(V) dialkyl dithiophosphates

Reactants (gm)		Product	% Yield Found	Pr^iOH Liberated Found (Calcd) (gm)	Analysis % Found (Calcd)				Mole. weight Found (Calcd)
$Ta(OPr^i)_5$ (gm)	$HS_2P(OR)_2$ (gm)				C	H	Ta	S	
0.644	Et 0.251	$(Pr^iO)_4Ta[S_2P(OEt)_2]$ (1)	98	0.0805 (0.0815)	31.02 (31.89)	6.29 (6.31)	30.33 (30.65)	10.85 (10.65)	610 (601.95)
0.677	Pr^n 0.304	$(Pr^iO)_4Ta[S_2P(OPr^n)_2]$ (2)	97	0.0861 (0.0853)	-	-	28.73 (28.72)	10.23 (10.15)	- (629.95)
0.585	Pr^i 0.263	$(Pr^iO)_4Ta[S_2P(OPr^i)_2]$ (3)	99	0.0738 (0.0737)	33.85 (34.28)	6.61 (6.66)	28.71 (28.72)	10.31 (10.15)	623 (629.95)
0.823	Bu^i 0.418	$(Pr^iO)_4Ta[S_2P(OBu^i)_2]$ (4)	86	0.0972 (0.103)	-	-	29.56 (27.50)	9.81 (9.72)	- (657.95)
0.648	Ph 0.384	$(Pr^iO)_4Ta[S_2P(OPh)_2]$ (5)	97	0.0815 (0.0816)	-	-	26.50 (25.92)	9.16 (9.16)	660 (697.95)

complexes are highly sensitive even to atomospheric moisture. However, they can be stored unchanged for long periods under anhydrous conditions.

Further replacement of isopropoxy groups in $(Pr^iO)_4Ta[S_2P(OR)_2]$ by dithiophosphate moieties does not appear to take place in refluxing benzene and even with excess of dithiophosphoric acids, the monosubstituted derivatives are the final products.

IR SPECTRA

The absorption due to ν —SH in the region 2500–2400 cm^{-1} in the parent dialkyl dithiophosphoric acids is absent in the spectra of the corresponding complexes, indicating formation of the Ta—S bond.[17–18] A new band due to ν Ta—S is present in the region 400–300 cm^{-1}. The bands present in the regions 1145–1020 cm^{-1} and 860–825 cm^{-1} may be assigned to ν (P)—O—C and ν P—O—(C), respectively.[19] The bands of variable intensity in the region 1240–1085 cm^{-1} have been ascribed to deformation vibrations involving the carbon atom. The ν P=S stretching frequency appears in the region 690–605 cm^{-1} and the bands for the ν P—S are present[20] in the region 600–500 cm^{-1} (Table II).

^{1}H NMR SPECTRA

All the tetraisopropoxytantalum(V) dialkyl dithiophosphates show only one set of signals (a multiplet for the —CHO proton in the region δ 4.50–5.15 ppm and a doublet for methyl proton in the region δ 1.20–1.30 ppm), thus showing equivalence of these groups. ^{1}H NMR spectra also show the disappearence of the —SH proton in the complexes which is present in the region δ 3.0–3.5 ppm in the parent dithio acids.[2,7] All other protons of dithiophosphate moieties are present at their expected positions (Table III).

^{13}C NMR SPECTRA

^{13}C NMR spectra do not show any notable change from the corresponding values from tantalum(V) isopropoxide and dithio ligand (Table IV). The carbon atoms of the dithio ligand being at least four bonds away from the metal atom, do not appear to be affected by complexation. All the isopropoxy groups in each compound appear to be equivalent as indicated by the presence of only one set of signals. The —CH_3 and —CHO carbons of isopropoxy groups are found at δ 23.00 and δ 76.00 ppm respectively in $Ta(OPr^i)_5$ and these are present in the region δ 24.43–25.73 ppm and δ 75.68–79.29 ppm, respectively in the dithiophosphato complexes.

^{31}P NMR SPECTRA

Only one peak for each compound is observed in the range δ 91.55–100.83 ppm (with a downfield shift of δ 15–20 ppm in comparison to the parent dithio acids)

TABLE II

I.R. Spectral data for tetraisopropoxytantalum(V) dialkyl dithiophosphates (cm^{-1})**

Product*	ν (P)–O–C	ν P–O–(C)	ν P=S	ν P–S	ν Ta–S
1	1020,s	850,m	605,m	550,m	390,m
2	990,s	860,m	660,s	550,w	350,m
3	925,s	790,m	665,m	550,w	340,w
4	995,b	850,m	660,m	560,w	350m
5	1270,b	1170,s	690,m	550,w	320,m

* Serial numbers refer to compounds listed in Table I.

** S = Strong, m = medium, b = broad and w = weak.

TABLE III

^{1}H and ^{31}P NMR spectral data for tetraisopropoxytantalum(V) dialkyldithiophosphates

Product*	^{1}H chemical shift** in δ ppm ($CDCl_3$)	^{31}P chemical shift in δ ppm (in C_6H_6)
1	1.33–1.43,d 6H(Me-C_2H_5) 1.77–1.27,d, 24H(Me-Pr^{i}O) 4.50–4.99,m, 4H(OCH_2-C_2H_5) 4.70–5.05,m, 4H(CHO-Pr^{i}O)	95.79
2	1.30–1.46,t, 6H(Me-Pr^{n}O) 1.14–1.30,d, 24H(Me-Pr^{i}O) 1.90–2.03,m, 4H(CH_2-Pr^{n}O) 3.91–4.26,m, 4H(OCH_2-Pr^{n}O) 4.77–5.05,m, 4H(CHO-Pr^{i}O)	99.37
3	1.11–1.24,d, 24(Me-Pr^{i}O) 1.24–1.39,d, 12H(Me-Pr^{i}O; dithio) 4.57–5.15,m, 2H(CHO-Pr^{i}O) 4.50–5.15,m, 4H(CHO-Pr^{i}O; dithio)	95.79
4	0.82–0.95,d, 12H(Me-Bu^{i}O) 1.14–1.24,d, 24H(Me-Pr^{i}O) 1.78–2.00,m, 2H(CH-Bu^{i}O) 3.68–3.87,t, 4H(CH_2-Bu^{i}O) 4.77–5.02,m, 4H(CHO-Pr^{i}O)	100.83
5	1.27–1.41,d, 24H(Me-Pr^{i}O) 4.72–5.05,m, 4H(CHO-Pr^{i}O) 6.86–7.28,m, 10H(C_6H_5)	91.55

* Serial numbers refer to the compounds listed in Table I.

** d = Doublet, t = triplet and m = multiplet.

(Table III). Glidewell[12] has correlated the ^{31}P chemical shift values with the mode of bonding (i.e., monodentate, bidentate and ionic) of dithiophosphato moieties. According to him, a downfield shift of 10 to 15 ppm in the metal complexes in comparison to the parent dithiophosphoric acid correspond to bidentate behaviour. The observed chemical shifts, thus, correspond to bidentate attachment of the ligand to the metal. The metal atom, therefore, should have a coordination number of six.

STRUCTURAL FEATURES

Molecular weight data and spectral studies like IR and NMR (^{1}H, ^{13}C and ^{31}P) indicate bidentate behaviour of dithiophosphate moieties and a monomeric nature of the new complexes. Accordingly, an octahedral geometry is proposed which has

TABLE IV

^{13}C NMR spectral data for some tetraisopropoxytantalum(V) dialkyl dithiophosphates*

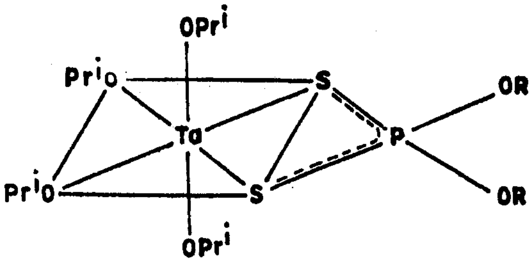
Product**	Isopropoxy (in δ ppm)		Dialkyldithiophosphates (in δ ppm)			
	$-CH_3$	$-OC$	$-CH_3$	$-CH_2$	$-CO$	$-C_6H_5$
2	24.43,d (J=6.10 Hz)	77.14,s	15.98,s	23.56,d (J=6.10 Hz)	63.44,d (J=6.10 Hz)	-
3	23.34,d (J=6.10 Hz)	76.22,s	24.05,d (J=3.60 Hz)	-	72.75,d (J=6.10 Hz)	-
4	25.73,d	75.68,s	18.90,s	29.30,d (J=9.76 Hz)	73.40,d (J=7.32 Hz)	-
5	23.60,d	77.29,s	-	-	-	≠ 162.29, 121.17 128.92, 119.49

* All the spectra were recorded in benzene except compound No. 5 which is in chloroform.

** Serial numbers refer the compound listed in Table I.

≠ Values are given in order of ipso, ortho, meta and para carbons.

four unidentate (isopropoxy) and one bidentate (dithio) moieties and the metal has coordination number of six.



As stated earlier, it has not been possible to distinguish between the two types of isopropoxy groups in the above plausible octahedral structure on the basis of room temperature NMR (^1H and ^{13}C) spectral studies.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture. Tantalum(V) isopropoxide and dialkyl dithiophosphoric acids[21,22] were prepared by methods reported in the literature. Tantalum and sulphur were estimated as oxide and barium sulphate (Messenger's Method), respectively. Isopropanol was estimated by the chromate oxidation method.[23] Benzene was dried by refluxing over sodium and finally azeotropically distillation over aluminium isopropoxide. IR spectra were recorded as Nujol mulls on a Perkin Elmer 577 spectrophotometer in the range of 4000–200 cm^{-1} using CsI cells and NMR spectra were recorded on a Jeol FX 90Q MHz spectrometer using TMS (for ^1H and ^{13}C) and TMP (for ^{31}P) as an external reference.

Reactions of tantalum(V) isopropoxide with dialkyl dithiophosphoric acids in 1:1 molar ratio. Equimolar quantities of tantalum(V) isopropoxide (1 mole) and dialkyl dithiophosphoric acids (1 mole) were mixed in benzene and refluxed on a fractionating column for ~3 hours. The isopropanol liberated during the reaction was collected azeotropically with benzene and estimated. Excess of solvent was evaporated under reduced pressure and the product was finally dried *in vacuo*. Analytical and other relevant data are given in Table I.

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