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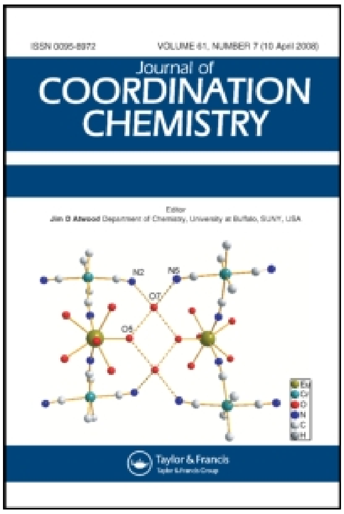

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Trichloro- and triisopropoxy-niobium(V) and tantalum(V) <i>bis</i>-(<i>O</i>,<i>O</i>'-alkylene dithiophosphates): synthesis and characterization

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Trichloro- and triisopropoxy-niobium(V) and tantalum(V) *bis*-(*O*,*O*′-alkylene dithiophosphates): synthesis and characterization

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Trichloro- and triisopropoxy-niobium(V) and tantalum(V) alkylene dithiophosphates, $X_3M(S_2\overline{POGO})_2$, (M = Nb(V) or Ta(V); G = –CHMeCHMe–, $–CMe_2CMe_2–$, $–CH_2CMe_2CH_2–$, $–CH_2CEt_2CH_2–$ or $–CMe_2CH_2CHMe–$ and X = Cl or OPr^i) have been synthesized by reaction of metal(V) chloride, MCl_5, or triisopropoxymetal(V) dichloride, $(Pr^iO)_3MCl_2$, with the sodium salts of O,O′-alkylene dithiophosphoric acids, $NaS_2\overline{POGO}$, in 1 : 2 molar ratio in THF under anhydrous conditions. These pink-purple or light-yellow compounds are viscous, semi-solid or solid, hydrolyzable and soluble in common organic solvents. These compounds have been characterized by elemental analyses, molecular weight determinations and spectral studies like IR and heteronuclear NMR (^1H, ^{13}C and ^{31}P), which indicated a bidentate mode of chelation of dithio ligands, leading to a pentagonal bipyramidal geometry around the niobium(V) or tantalum(V) centers.

Keywords: Alkylene; Dithiophosphates; Niobium; Tantalum; Triisopropoxy; Trichloro

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1. Introduction

Both the *O*,*O*′-dialkyl and O,O′-alkylene dithiophosphate ligands are versatile chelating ligands [1–4]. A variety of complexes has been reported with these dithio ligands in which dithio moiety behaved, normally, in a bidentate manner [5–8]. However, less common monodentate behavior of dithiophosphate moieties was observed in the case of nickel [9], trialkyl (R_3Sn) and triphenyltin (Ar_3Sn) derivatives of dialkyl dithiophosphates [10], which created considerable interest since bidentate ligands with diorganotin was established [11–15]. This might be due to lower electrophilicity of trialkyltin compared to dialkyltin. Several dithiophosphato derivatives have found extensive applications in agriculture [16], in industry as oil additives [17–20] and regeneration of cracking catalysts [21, 22], and also in extraction and analytical processes [23, 24]. Only a few reports are available on dialkyl and alkylene

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dithiophosphate derivatives of niobium(V) and tantalum(V) [5]. Monomeric compounds $MX(OMe)_2\{S_2P(OR)_2\}_2$ (M = Nb or Ta, X = Cl or Br) have been isolated by reaction of MCl_5 with $(OR)_2PS_2Na$ in methonolic solution [25]. Cavell *et al.* have shown that two moles of HCl are evolved on reaction of MCl_5 with F_2PS_2H while not more than one mole of HCl is evolved on reaction of $NbCl_4$ with F_2PS_2H, yielding $Cl_3Nb^V(S_2PF_2)_2$ and $Cl_3Nb^{IV}(S_2PF_2)$, respectively [26]. We reported some O,O′-dialkyl and alkylene dithiophosphates [5]. We report herein the synthesis of the title compounds by reaction of sodium salts of the alkylene dithiophosphoric acids, NaS_2POGO, with metal(V) chloride, MCl_5, and triisisopropoxymetal(V) dichloride, $(Pr^iO)_3MCl_2$.

2. Experimental

Moisture was excluded by using standard Schlenk technique and nitrogen atmosphere. Tetrahydrofuran was dried by refluxing over sodium followed by distillation. Triisopropoxyniobium(V)/tantalum(V) dichloride, $(Pr^iO)_3MCl_2$, was prepared by reaction of MCl_5 (M = Nb or Ta) with isopropanol (in excess). Sodium salts of *O*,*O*′-alkylene dithiophosphoric acids were prepared by the method described [27]. Two typical syntheses are described below. The remaining compounds reported herein were synthesized using similar methodology and stoichiometry. The relevant synthetic and analytical data are given in table 1.

2.1. *Reaction of niobium(V) chloride, $NbCl_5$, with sodium salt of 2,2-dimethyltrimethylene dithiophosphoric acid, $OCH_2CMe_2CH_2OPS_2Na$* (3)

THF solution (~30 mL) of niobium(V)chloride, $NbCl_5$, (0.468 g, 1.70 mmol) was added dropwise to a THF solution of sodium salt of 2,2-dimethyltrimethylene dithiophosphoric acid, $OCH_2CMe_2CH_2OPS_2Na$, (0.763 g, 3.46 mmol) with constant stirring at room temperature. The contents were then refluxed for 4–5 h during which the color changed from colorless to pink-purple. The sodium chloride was separated by filtration using Schlenk funnel fitted with a G-4 sintered disc; excess solvent from the filtrate was evaporated under reduced pressure followed by drying *in vacuo* for 3–4 h, giving trichloroniobium(V) *bis*-(2,2-dimethyltrimethylene dithiophosphate), $Cl_3Nb(S_2POCMe_2CMe_2O)_2$ (**3**) as an orange solid in 89% yield.

2.2. *Reaction of triisopropoxyniobium(V) dichloride, $(Pr^iO)_3NbCl_2$, with sodium salt of 2,2-dimethyltrimethylene dithiophosphoric acid, $OCH_2CMe_2CH_2OPS_2Na$* (11)

THF solution (~30 mL) of triisopropoxyniobium(V)dichloride, $(Pr^iO)_3NbCl_2$, (0.582 g, 1.70 mmol) was added dropwise to a THF solution of the sodium salt of 2,2-dimethyltrimethylene dithiophosphoric acid, $OCH_2CMe_2CH_2OPS_2Na$, (0.751 g, 3.41 mmol) with constant stirring at room temperature. The contents were then refluxed for 4–5 h during which the color changed from colorless to pink-purple. The sodium chloride formed was separated by filtration using a Schlenk funnel fitted

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Table 1. Synthetic and analytical data of trichloro- and triisopropoxy-niobium(V) and tantalum(V) alkylene dithiophosphates.

	Reactants (gm mmol^{-1})						Analysis (%)	Found (Calcd.)		
Compound no.	X_3MCl_2	$M'S_2POGO$ (g mmol^{-1})	Compound (physical state)	Yield (%)	M.W. (Found (Calcd))	Nb/Ta	Cl	S	C	H
1	0.269/1.34	–CHMeCHMe–0.411/2.68	$Cl_3Nb(S_2POCHMeCHMeO)_2$ (Orange Solid)	90	–	16.50 (16.42)	18.10 (18.80)	22.35 (22.67)	16.78 (16.98)	2.70 (2.80)
2	0.696/1.48	$–CMe_2CMe_2–$ 1.205/2.96	$Cl_3Nb(S_2POCMe_2CMe_2O)_2$ (Orange Solid)	87	612 (621.41)	15.06 (14.94)	16.90 (17.11)	22.50 (20.63)	23.12 (23.17)	3.80 (3.89)
3	0.468/1.70	$–CH_2CMe_2CH_2–$ 0.762/3.40	$Cl_3Nb(S_2POCH_2CMe_2CH_2O)_2$ (Orange Solid)	89	–	15.10 (15.65)	17.20 (17.11)	21.40 (21.60)	22.12 (22.22)	3.38 (3.39)
4	0.626/3.75	$–CMe_2CH_2CHMe–$* 1.06/7.50	$Cl_3Nb(S_2POCMe_2CH_2CHMeO)_2$ (Purple Semi-solid)	92	–	14.44 (14.94)	16.89 (17.11)	20.42 (20.63)	23.15 (23.17)	3.81 (3.89)
5	0.414/1.17	–CHMeCHMe– 0.476/2.34	$Cl_3Ta(S_2POCHMeCHMeO)_2$ (Yellow Viscous)	93	–	27.72 (27.68)	16.22 (16.27)	19.59 (19.62)	19.50 (19.69)	2.41 (2.46)
6	0.696/1.30	$–CMe_2CMe_2–$ 0.909/2.60	$Cl_3Ta(S_2POCMe_2CMe_2O)_2$ (Yellow Solid)	86	705 (709.45)	25.65 (25.52)	14.94 (15.01)	18.34 (18.01)	20.13 (20.29)	3.28 (3.40)
7	0.752/1.26	$–H_2CMe_2CH_2–$ 0.924/2.52	$Cl_3Ta(S_2POCH_2CMe_2CH_2O)_2$ (Yellow Solid)	80	–	26.18 (26.54)	15.50 (15.60)	18.72 (18.81)	17.42 (17.62)	2.60 (2.95)
8	0.511/1.42	$–CMe_2CH_2CHMe–$* 0.653/2.40	$Cl_3Ta(S_2POCMe_2CH_2CHMeO)_2$ (Yellow Viscous)	92	–	25.69 (25.49)	14.93 (14.98)	18.35 (18.07)	20.20 (20.29)	3.20 (3.40)

(Continued)

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Table 1. Continued.

	Reactants (gm mmol^{-1})					Analysis (%)		Found (Calcd.)		
Compound no.	X_3MCl_2	$M'S_2POGO$ (g mmol^{-1})	Compound (physical state)	Yield (%)	M.W. (Found (Calcd))	Nb/Ta	Cl	S	C	H
9	0.459/1.34	–CHMeCHMe– 0.554/2.68	$(Pr^iO)_3Nb(S_2POCHMeCHMeO)_2$ (Pink-purple Viscous)	93	–	14.69 (14.59)	–	20.09 (20.15)	31.95 (32.08)	5.80 (5.85)
10	0.505/1.48	$–CMe_2CMe_2–$ 0.678/2.96	$(Pr^iO)_3Nb(S_2POCMe_2CMe_2O)_2$ (Pink-purple Viscous)	87	702 (691.91)	13.20 (13.41)	–	18.10 (18.52)	35.90 (36.43)	6.40 (6.54)
11	0.582/1.70	$–CH_2CMe_2CH_2–$ 0.751/3.41	$(Pr^iO)_3Nb(S_2POCH_2CMe_2CH_2O)_2$ (Pink Viscous)	92	–	13.10 (13.98)	–	19.20 (19.30)	34.20 (34.33)	6.18 (6.22)
12	0.430/1.26	$–CH_2CEt_2CH_2–$ 0.625/2.52	$(Pr^iO)_3Nb(S_2POCH_2CEt_2CH_2O)_2$ (Pink Viscous)	87	735 (719.91)	13.09 (12.89)	–	17.44 (17.80)	38.83 (38.33)	6.78 (6.85)
13	1.266/3.75	$–CMe_2CH_2CHMe–$* 1.727/7.50	$(Pr^iO)_3Nb(S_2POCMe_2CH_2CHMeO)_2$ (Purple Semi-solid)	90	–	13.44 (13.41)	–	18.42 (18.52)	30.40 (36.41)	6.38 (6.55)
14	0.506/1.17	–CHMeCHMe– 0.486/2.34	$(Pr^iO)_3Ta(S_2POCHMeCHMeO)_2$ (Light-yellow Semi-solid)	95	–	25.04 (24.97)	–	17.57 (17.70)	28.20 (28.18)	5.12 (5.15)
15	0.559/1.30	$–CMe_2CMe_2–$ 0.610/2.60	$(Pr^iO)_3Ta(S_2POCMe_2CMe_2O)_2$ (Light-yellow Semi-solid)	95	805 (779.71)	23.37 (23.18)	–	16.38 (16.63)	32.86 (32.31)	5.78 (5.81)
16	0.541/1.26	$–CH_2CMe_2CH_2–$ 0.555/2.52	$(Pr^iO)_3Ta(S_2POCH_2CMe_2CH_2O)_2$ (Light-yellow Viscous)	94	–	24.41 (24.04)	–	17.03 (17.04)	30.62 (30.32)	5.54 (5.49)
17	0.383/0.89	$–CH_2CEt_2CH_2–$ 0.443/1.78	$(Pr^iO)_3Ta(S_2POCH_2CEt_2CH_2O)_2$ (Light yellow Semi-solid)	94	835 (807.71)	22.60 (22.37)	–	15.98 (15.86)	34.21 (34.16)	6.20 (6.11)
18	0.566/1.20	$–Me_2CH_2CHMe–$* 0.608/2.40	$(Pr^iO)_3Ta(S_2POCMe_2CH_2CHMeO_2$ (Light-yellow Solid)	91	–	23.35 (23.18)	–	16.38 (16.43)	32.40 (32.31)	5.52 (5.58)

M = Nb or Ta and M′ = Na or NH_4^*; X = OPr^i or Cl.

Table 2. IR spectral data of trichloro- and triisopropoxy-niobium(V) and tantalum(V) alkylene dithiophosphates (in cm^{-1}).

Compound no.	ν(P)–O–C	νP–O–(C)	Ring vibrations	νP=S	νP–S	νM–S	νM–Cl
1	1040, m	870, m	950, m	670, m	610, m	380, w	460, m
2	1000, m	865, m	955, s	650, m	570, m	360, w	460, w
3	990, b	855, m	955, m	675, m	520, m	380, m	470, m
4	1020, m	860, m	870, m	675, s	590, m	350, m	450, m
5	1020, m	860, m	870, m	675, s	590 m	350, m,	450, m
6	1010, b	860, m	960, m	670, m	530, m	380, m	470, w
7	990, s	860, m	960, s	670, s	520, m	360, m	470, m
8	1000, m	870, m	960, m	650, m	580, m	340, m	460, m
9	1035, m	855, m	955, m	700, s	620, m	380, w	–
10	1010, m	865, m	985, s	680, m	620, m	379, m	–
11	1000, b	840, m	970, m	670, m	525, m	385, w	–
12	1040, s	850, m	970, s	675, s	530,m	370,w	–
13	1010, m	850, m	900, m	680, m	575, m	377, m	–
14	1035, b	850, m	945, m	660, m	610, m	360, w	–
15	1015, s	855, s	955, s	700, m	600, s	382, m	–
16	1000, m	855, m	960, s	670, s	510, m	399, w	–
17	1032, s	857, m	971, s	675, s	525, m	369, m	–
18	1000, m	855, m	915, m	670, m	510, m	387, m	–

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

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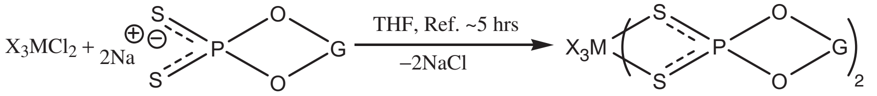
with a G-4 sintered disc and excess solvent was evaporated under reduced pressure. This was followed by drying *in vacuo* for 3–4 h, which gave triisopropoxyniobium(V) *bis*-(2-dimethyltrimethylene dithiophosphate), $(Pr^iO)_3Nb(S_2\overline{POCMe_2CMe_2O})_2$, (**11**) as a light pink, viscous mass in 92% yield.

3. Measurements

Infrared spectra were recorded on a Perkin-Elmer-577 spectrophotometer in the range 4000–200 cm^{-1} as nujol mulls between cesium iodide windows. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ on either a Bruker DRX 300 (120 MHz) or a Jeol 90Q (90 MHz) spectrometer using tetramethylsilane as the internal reference for ^1H NMR and 85% H_3PO_4 as an external reference for ^{31}P NMR. Niobium and tantalum were estimated as their metal oxides after ignition of hydrous oxide formed by hydrolysis. Sulfur was estimated as barium sulfate according to the Messenger's method. Molecular weight determinations of these compounds were measured by the cryoscopic method.

4. Results and discussion

Although reactions of $(Pr^iO)_3MCl_2$ (M = Nb or Ta) with $NaS_2\overline{POGO}$ (where G = –CHMe CHMe–, $–CMe_2CMe_2–$, $–CH_2CMe_2CH_2–$, $–CH_2CEt_2CH_2–$ or $–CMe_2CH_2CHMe–$) could be expected to be more facile due to the anionic nature of dithiophosphate nucleophile, they were found to be rather sluggish, perhaps from steric factors revealed in the substitution reactions of $M(OPr^i)_5$ with excess free ligand, $HS_2\overline{POGO}$, which did not proceed beyond the formation of monosubstituted products i.e., $(\mathrm{Pr^iO})_4\mathrm{MS_2POGO}$ [5]. However, trichloro- and triisopropoxy-niobium(V) and tantalum(V) *bis*-(*O*,*O*′-alkylene dithiophosphates), $\mathrm{X_3M(S_2POGO)_2}$ (where X=Cl or $\mathrm{OPr^i}$), have been isolated after refluxing for ~5 h in 87–95% yield by reaction of $\mathrm{MCl_5}$ or $(\mathrm{Pr^iO})_3\mathrm{MCl_2}$ with $\mathrm{POGOS_2Na}$ in 1 : 2 molar ratio in tetrahydrofuran (scheme 1).



(M = Nb, Ta; X = Cl or OPri, G = $-\mathrm{CHMeCHMe}-$, $-\mathrm{CMe_2CMe_2}-$, $-\mathrm{CH_2CMe_2CH_2}-$, $-\mathrm{CH_2CEt_2CH_2}-$, $-\mathrm{CHMeCH_2CMe_2}-$)

Scheme 1. Reactions of $\mathrm{X_3MCL_2}$ with sodium salt of alkalene dithiophosphoric acids.

The color of the reaction mixture changes with progress of the reaction from colorless to pink-purple and light-yellow for niobium and tantalum complexes, respectively. These complexes were obtained as viscous, semi-solids or solids and are soluble in both hydrocarbon and coordinating solvents. The complexes appeared to be highly moisture sensitive but can be kept unchanged either *in vacuo* or in an inert atmosphere. These compounds were non-volatile and decomposed to dark brown products on heating even under reduced pressure. The solid trichloro- derivatives decomposed in the range 120–145°C at atmospheric pressure to uncharacterized products. The elemental analyses, particularly, C, H, Nb, Ta and S were consistent with the molecular composition of these complexes. Molecular weight determination of representative compounds in freezing benzene indicated the monomeric nature of these complexes. The compounds $\mathrm{Cl_3M(S_2POGO)_2}$ and $(\mathrm{Pr^iO})_3\mathrm{M(S_2POGO)_2}$ were the final products even when the reactions were carried out in 1 : 1 molar stoichiometry.

In the IR spectra of these complexes (4000–200 cm^{-1}), the band for νM–S and νM–Cl stretching vibrations were found at 399–340 cm^{-1} and 470–450 cm^{-1} [5, 27–28]. The bands in the region 1040–990 cm^{-1} and 870–855 cm^{-1} may be assigned to ν(P)–O–C and νP–O–(C) stretching vibrations, respectively. The ring vibrations of dioxaphosphorinanes and dioxaphospholanes appeared in the region 985–870 cm^{-1}. Strong to medium intensity bands in the region 700–650 cm^{-1} and 620–510 cm^{-1} are from νP = S and νP–S (symmetric and asymmetric) vibrations, respectively [1] (table 2). The band for νP–S vibrations occurred with a slight shift of 15–20 cm^{-1} (compared to parent dithiophosphate ligands), indicative of bidentate bonding [15, 27, 28].

The ^{1}H NMR spectra of these complexes have shown characteristic resonances due to both glycoxy and isopropoxy protons. The $-\mathrm{OCH_2}$ protons are doublets in the region δ 3.72–4.26 ppm with coupling constant J(^{1}H–^{31}P) of 16–17 Hz (**3**, **7**, **11**, **12**, **16**, **17**). The protons of the methyl groups of both dithiophosphate and isopropoxy moiety were found in the region δ 0.85–1.84 ppm (**1**–**18**) and δ 1.20–1.88 ppm (**9**–**18**), respectively. The chemical shift for the methyl protons of the dithio moiety in **1**, **5**, **9** and **14** are doublets and triplets for **12** and **17** in the range of δ 1.39–1.52 ppm and δ 0.89–1.06 ppm, respectively. The chemical shift for the –OCH protons of the dithio moiety in **1**, **5**, **9** and **14** occurred in the region δ 3.75–4.42 ppm. A multiplet was found for the –CHO protons

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Table 3. ^{1}H and ^{31}P NMR spectral data of trichloro- and triisopropoxy-niobium(V) and tantalum(V) alkylene dithiophosphates (in δ ppm).

Compound no.	^{1}H Chemical shift	^{31}P Chemical shift
1	1.49, d, 12H (Me) ($J = 9$ Hz); 4.26 m, 4H (–OCH)	97.20, s
2	1.49, s, 24H (Me)	94.14,s
3	1.11, s, 12H (Me); 4.16, d, 8H (–OCH$_2$) ($J = 17$ Hz)	77.95, s
4	1.59, s, 12H (Me); 1.76, q, 6H; 3.02–3.21, m, 4H (–H$_2$); 4.70–5.02, m,	95.42, s
5	1.52, d, 12H (Me) ($J = 9$ Hz); 4.45, m, 4H (–OCH)	97.11, s
6	1.46, s, 24H (Me)	93.95, s
7	1.08, s, 12H (Me); 4.13, d, 8H (–OCH$_2$) ($J = 17$ Hz)	78.16, s
8	1.49, s, 12H (Me); 1.84, q, 6H (Me); 3.49–3.78, m, 4H (–CH$_2$); 4.70–5.08, m, 2H (–OCH)	74.30, s
9	1.39, d, 12H (Me) ($J = 9$ Hz); 1.82, d, 18H (Me); 4.22, m, 4H (–OCH); 4.72–5.26, m, 3H (–OCH)	95.03, s
10	1.27, d, 18H (Me); 1.40, s, 24H (Me); 4.78–5.20, m, 3H(–OCH)	103.06,s
11	0.89, s, 12H (Me); 1.20, d, 18H (Me); 3.72, d, 8H (–OCH$_2$) ($J = 17$ Hz); 4.77–5.27, m, 3H (–CHO)	92.980, s
12	0.85, t, 12H (Me) ($J = 6$ Hz); 1.35, d, 18H (Me); 1.82, q, 8H (–CH$_2$); 4.08, d, 8H (–OCH$_2$) ($J = 16$ Hz); 4.75–5.18, m, 3H (–CHO)	92.20, s
13	1.23, d, 6H (Me);1.40, s, 12H (Me); 1.59, d, 18H (Me); 1.90, t, 4H (–CH$_2$); 3.75–3.84, m, 2H (–OCH); 4.77–5.05, m, 3H (–CHO)	105.06, s
14	1.49, d, 12H (Me) ($J = 9$ Hz); 1.88, d, 18H (Me); 4.19–4.42, m, 4H (–OCH); 4.78–5.20, m, 3H (–CHO)	107.88, s
15	1.49, s, 24H (Me); 1.33, d, 18H (Me); 4.77–5.02, m, 3H (–OCH)	108.80, s
16	0.95, s, 12 H (Me); 1.27, d, 18H (Me); 4.10, d, 8H (–OCH$_2$) ($J = 17$ Hz); 4.78–5.22, m, 3H (–CHO)	92.21, s
17	1.06, t, 12H (Me) ($J = 6$ Hz); 1.38, d, 18H (Me); 1.80, q, 8H (–CH$_2$); 4.16, d, 8H (–OCH$_2$) ($J = 16$ Hz); 4.83–5.19, m, 3H (–CHO)	92.91, s
18	1.28, d, 6H (Me); 1.43, s, 12H (Me); 1.49, d, 18H (Me); 1.87, t, 4H (–CH$_2$); 3.81–3.94, m, 2H (–OCH)4.70–5.02, m, 3H (–CHO)	110.31, s

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

of isopropoxy in each case (**9–18**) in the region δ 4.45–5.27 ppm. The presence of only one multiplet for isopropoxy proton supports the monomeric nature of the complexes. The ^{1}H NMR spectral data are given in table 3.

The ^{13}C NMR spectra of some of these complexes at ambient temperature do not show any appreciable change in their chemical shift compared to the parent dithiophosphate ligands or triisopropoxyniobium(V)/tantalum(V) dichloride (table 4). The carbon atoms of the ligand are at least four bonds from the metal and are unaffected by complexation. As for the ^{1}H NMR, all the isopropoxy groups are equivalent with only one set of signals. For $(Pr^{i}O)_3MCl_2$, the –CH$_3$ and –CHO carbons of isopropoxy groups were at δ 21.45–23.46 ppm and δ 74.17–76.19 ppm, respectively. The secondary carbon of isopropoxy group in the compounds was observed in the range δ 75.41–78.00 ppm while primary carbon nuclei have chemical shifts in the range δ 21.88–25.40 ppm. The reason for the deshielding of this carbon in dithiophosphato derivatives is not clear.

The ^{31}P NMR spectra of complexes **1–18** have shown only one singlet for each compound, indicating equivalent and symmetric nature of phosphorus nuclei (table 3). The chemical shifts for five-membered parent dithiophosphoric acids (**1**, **2**, **5**, **6**, **9**, **10**, **14**, **15**) were at δ 92–94 ppm while six-membered parent dithiophosphoric acids (**3**, **4**, **7**, **8**, **11–13**, **16–18**) were in the range δ 75–78 ppm, exhibiting a pronounced effect of the ring size. These complexes of niobium and tantalum show a downfield shift of δ 13–18 ppm (δ 95.03–108.80 ppm for five-membered and δ 92.20–110.30 ppm for

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Table 4. ^{13}C NMR spectral data of some trichloro- and triisopropoxy-niobium(V) and tantalum(V) alkylene dithiophosphates in $CDCl_3$ (in δ ppm).

	Isopropoxy		Alkylene dithiophosphate				
Compound no.	$-CH_3$	$-CH$	$-Me_2$	$-CO$	$-C-$	$-CH_2$	$-CH_3$
1	–	–	–	82.56	–	–	17.55
2	–	–	–	94.03	–	–	24.42
3	–	–	21.33	78.05	32.81	–	–
7	–	–	–	78.05	32.76	–	21.28
8	–	–	29.09	49.02	–	33.69	22.53
10	24.05	76.00	24.27	79.58	–	–	–
11	21.88	75.52	21.08	75.52	32.77	–	–
12	23.29	76.27	–	74.70	37.22	23.59	6.88
13	25.10	75.85	23.25	44.86	32.34	–	28.02
16	22.05	76.31	21.12	75.42	32.67	–	–
17	23.29	75.41	–	74.33	37.44	22.59	7.10
18	22.48	75.95	22.32	77.38	44.58	–	27.41

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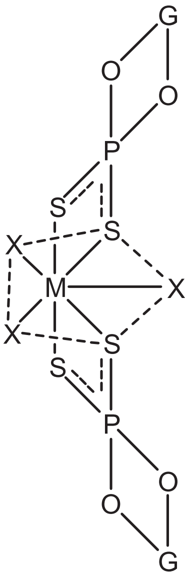

Figure 1. Proposed pentagonal bipyramidal geometry of the complexes $[X_3MS_2\overline{POGO}]$, where $M = Nb$ or Ta; $G = -CMe_2CMe_2-, -CHMeCHMe-, -CH_2CMe_2CH_2-, -CH_2CEt_2CH_2-$ or $-CHMeCH_2CMe_2-$; $X = Cl$ or pr^iO.

six-membered) with respect to the corresponding dithiophosphoric acids. This deshielding of ^{31}P nucleus might be due to bidentate bonding of with niobium and tantalum atoms. Such deshielding in ^{31}P NMR spectra is observed by Glidewell [15].

5. Structural features

The proton NMR spectra show only one type of isopropoxy group, terminal (non-bridging) in nature. The bidentate mode of linkage of dithio ligand is supported by both

IR and NMR spectroscopy. Conjecture about the geometry of these derivatives would be rather speculative at this stage. However, on the basis of the above studies, seven-coordination could plausibly be assigned to the central metal atom in these complexes (figure 1), particularly, considering bidentate mode of attachment of the dithiophosphate ligand. For the sake of comparison, acyclic analogues and monochlorodimethoxy *bis*-(dialkydithiophosphates) of niobium(V) and tantalum(V), $MX(OMe)_2\{S_2P(OR)_2\}_2$, were found to be monomeric and proposed to have similar structure [5, 25, 26].

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