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Mixed Chloro Derivatives of Vanadium Dialkyl and Alkylene Dithiophosphates

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Mixed chloro vanadium derivatives of dialkyl and alkylene dithiophosphates of general formula $ClV[S_2P(OR)_2]_2$ where $R = Pr^n$ and Ph and cyclic $ClV[\overline{S_2POGO}]_2$ where $G = —CH_2—CMe_2—CH_2—$, $CMe_2CMe_2—$ and $—CH_2CEt_2CH_2—$ have been synthesized by the reaction of vanadium trichloride with dithiophosphoric acids in 1 : 1 and 1 : 2 molar ratio in suitable organic solvents. These new derivatives have been characterized by elemental analysis, molecular weight determinations as well as spectroscopic (IR, ^1H, ^{13}C and ^{31}P NMR) studies. On the basis of these data chelated structures with bidentate dialkyl and alkylene dithiophosphate groups have been proposed for these monomeric derivatives.

Key Words: Chloro derivatives, Vanadium dialkyl, Alkylene dithiophosphates.

INTRODUCTION

Various metal dithiophosphates have been reported in the literature[1, 2]. The dithiophosphate ligand exhibits differing bonding modes such as monodentate[3, 4], bidentate[5–7] or bridging[8, 9]. Occasionally, both mono and bidentate[10] or bridging and bidentate ligands[11] have been found in the same complex. The crystal structure of $V[S_2P(OEt)_2]_3$ has been reported[12]. We have recently reported the synthesis of organovanadium cyclic and acyclic dithiophosphate derivatives[13]. The corresponding halide dialkyl and alkylene dithiophosphate derivatives of vanadium(III) are still unknown. In view of the exciting chemistry of mixed halide dialkyl and alkylene dithiophosphate derivatives of vanadium, it was considered worthwhile to synthesize a number of these derivatives and investigate their physico-chemical properties.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture from the experimental set-up. Solvents (benzene, chloroform and *n*-hexane) were dried by standard methods. Alcohols and glycols were purified by distillation before use. VCl_3 (Aldrich) was used as such. The dialkyl dithiophosphoric acids were prepared using literature method[14,15]. Phosphorus was estimated as ammonium magnesium phosphate hexahydrate and chlorine was determined by Volhard's method. Sulfur was estimated as barium sulfate[20]. Molecular weights were determined cryoscopically in benzene. IR spectra were recorded as KBr discs or Nujol mulls on Shimadzu FTIR-8201 PC spectrophotometer. NMR spectra were recorded in $CDCl_3$ using a Jeol JNM-LA 300-NMR spectrophotometer with TMS as an internal reference for ^1H, ^{13}C. ^{31}P NMR spectra were recorded in $CDCl_3$ using 85% H_3PO_4 as external reference on the same instrument.

Reaction of vanadium(III) trichloride with di-*n*-propyl dithiophosphoric acids in 1 : 1 molar ratio

Di-*n*-propyl dithiophosphoric acid (1.32 g) in benzene (20 mL) was added dropwise with constant stirring to vanadium(III) trichloride (0.94 g,) in 20 mL benzene. The mixture was refluxed for *ca.* 6 h until liberation of hydrogen chloride gas ceased. Solvent was removed under reduced pressure; the desired product was purified by washing several times with *n*-hexane and dried under vacuum.

Reaction of vanadium(III) trichloride with pinacol dithiophosphoric acids in 1 : 2 molar ratio

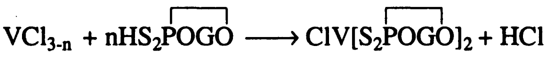
To benzene (20 mL) solution of pinacol dithiophosphoric acid (1.63 g) was added dropwise with constant stirring an equivalent amount of vanadium(III) trichloride (0.61 g) in (20 mL) benzene. The mixture was refluxed for *ca.* 6 h until liberation of hydrogen chloride gas ceased. The benzene solution was dried under reduced pressure; the desired product was purified by washing several times with n-hexane and dried under vacuum.

RESULTS AND DISCUSSION

Mixed chloro-dialkyl and alkylene dithiophosphates of vanadium have been prepared by the reaction of vanadium trichloride with dithiophosphoric acids in 1 : 2 and 1 : 1 molar ratio in refluxing benzene

$$VCl_{3-n} + nHS_2P(OR)_2 \longrightarrow ClV[S_2P(OR)_3]_2 + HCl$$

n = 1, 2, R = Pr^n and Ph



$$VCl_{3-n} + nHS_2\overline{POGO} \longrightarrow ClV[S_2\overline{POGO}]_2 + HCl$$

where n = 1, 2, G = CMe_2CMe_2, —$CH_2CMe_2CH_2$ and —$CH_2CEt_2CH_2$—

Most of these mixed derivatives are violet viscous liquids (Table-1) with the exception of corresponding diphenyl dithiophosphate derivative which is a brown powdery solid. These compounds are soluble in common organic solvents like benzene, carbon tetrachloride and chloroform but insoluble in *n*-hexane. These compounds could not be volatilized even under reduced pressure and tend to decompose at 130°C. However, attempts to crystallize the solid compounds from benzene/*n*-hexane mixture were unsuccessful. Molecular weight determinations in freezing benzene indicate the monomeric nature of these derivatives.

IR spectra of these new derivatives have been measured in the range 4000–200 cm^{-1} and assignments have been made on the basis of earlier reports[16, 17]. The strong intensity bands present in the region 1076–906 cm^{-1} and 885–769 cm^{-1} may be assigned to (P)—O—C and P—O—(C) vibrations respectively[16]. A strong band

TABLE-1: SYNTHESIS AND PHYSICAL PROPERTIES OF MIXED CHLORO-DIALKYL AND ALKYLENE DITHIOPHOSPHATE DERIVATIVES OF VANADIUM(III)

Compound No.	Reactants (g)		Molar ratio	Product/g	Yield (%)	Physical state (m.p. °C)	m.w.	Analysis, % Found (Calcd.)		
	VCl_3	Dithiophosphoric acid						P	S	Cl
1	0.94	$HS_2P(OPr^n)_2$ 1.32	1 : 1	$Cl_2V[S_2P(OPr^n)_2]$ 1.96	96.6	Violet viscous liquid	356.3 (334.84)	8.87 (9.22)	19.32 (19.11)	20.81 (21.20)
2	0.89	$HS_2P(OPr^n)_2$ 2.41	1 : 2	$ClV[S_2P(OPr^n)_2]_2$ 2.6	91.3	Violet viscous liquid	522.3 (512.24)	11.59 (12.06)	24.57 (24.98)	6.52 (6.93)
3	0.96	$HS_2P(OPh)_2$ 1.71	1 : 1	$Cl_2V[S_2P(OPh)_2]$ 2.17	88.7	Brown powdery solid (89)	436.8 (402.84)	7.92 (7.67)	15.37 (15.88)	16.85 (17.62)
4	0.64	$HS_2P(OPh)_2$ 2.28	1 : 2	$ClV[S_2P(OPh)_2]_2$ 2.19	83.4	Brown solid (103)	677.34 (648.24)	8.79 (9.03))	19.53 (19.74)	5.93 (5.47)
5	0.99	$HS_2POCMe_2CMe_2O$ 1.32	1 : 1	$Cl_2V[S_2POCMe_2CMe_2O]$ 1.97	94.6	Violet viscous liquid	311.7 (332.84)	8.95 (9.28)	19.77 (19.22)	21.37 (21.33)
6	0.61	$HS_2POCMe_2CMe_2O$ 1.63	1 : 2	$ClV[S_2POCMe_2CMe_2O]_2$ 1.79	91.8	Violet viscous liquid	527.56 (508.24)	12.64 (12.15)	25.76 (25.18)	6.91 (6.98)
7	0.84	$HS_2POCH_2CMe_2CH_2O$ 1.05	1 : 1	$Cl_2V[S_2POCH_2CMe_2CH_2O]$ 1.58	90.2	Violet viscous liquid	334.80 (318.84)	10.27 (9.69)	20.92 (20.07)	21.98 (22.26)
8	0.53	$HS_2POCH_2CMe_2CH_2O$ 1.32	1 : 2	$ClV[S_2POCH_2CMe_2CH_2O]_2$ 1.46	90.8	Vaint violet viscous liquid	498.34 (480.24)	12.52 (12.86)	26.43 (26.65)	7.83 (7.39)
9	0.65	$HS_2POCH_2CEt_2CH_2O$ 0.92	1 : 1	$Cl_2V[S_2POCH_2CEt_2CH_2O]$ 1.26	89.8	Violet viscous liquid	373.43 (346.84)	9.43 (8.90)	18.76 (18.45)	19.89 (20.47)
10	0.54	$HS_2POCH_2CEt_2CH_2O$ 1.54	1 : 2	$ClV[S_2POCH_2CEt_2CH_2O]_2$ 1.57	85.7	Violet viscous liquid	574.20 (586.30)	11.72 (11.52)	23.69 (23.86)	6.38 (6.62)

due to dioxaphospholane and dioxaphosphorinane ring vibrations is present in the region 985–914 cm^{-1} and these are probably coupled with C—C stretching vibrations[17]. A sharp band present in the region 663–601 cm^{-1} shows a notable shifting (= 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 sulfur of the P=S group to the metal atom. The bands of medium intensities in the region 571–536 cm^{-1} may be attributed to P—S asymmetric and symmetric vibrations. A number of new bands are observed in the region 486–301 cm^{-1} due to metal-chlorine and metal-sulfur stretching vibrations[18, 19]. The S—H vibration expected in the region 2500—2400 cm^{-1} could not be observed in the spectra of these compounds. Details regarding the individual peak have been given in Table-2.

TABLE-2
IR SPECTRAL DATA (cm^{-1}) FOR MIXED CHLORO-VANADIUM(III) DIALKYL AND ALKYLENE DITHIOPHOSPHATES

Comp. No.	Compound	ν[(P)—O—C]	ν[P—O—(C)]	Ring vibration	ν(P=S)	ν(P—S)	ν(V—S)	ν(V—Cl)
1	$Cl_2V[S_2P(OPr^n)_2]$	979 s	857 s	—	628 m	536 m	352 m	311 m
2	$ClV[S_2P(OPr^n)_2]_2$	977 s	847 s	—	624 m	541 m	417 m	350 m
3	$Cl_2V[S_2P(OPh)_2]$	907 s	846 m	—	663 m	566 m	491 w	305 m
4	$ClV[S_2P(OPh)_2]_2$	906 s	769 s	—	650 m	571 s	486 m	303 m
5	$Cl_2V[S_2\overline{POCMe_2CMe_2O}]$	1076 m	841 w	914 m	630 m	561 w	486 w	315 s
6	$ClV[S_2\overline{POCMe_2CMe_2O}]_2$	1003 m	849 m	953 s	629 s	581 m	482 w	301 m
7	$Cl_2V[S_2\overline{POCH_2CMe_2CH_2O}]$	1046 s	800 m	985 s	603 m	538 m	456 m	397 w
8	$ClV[S_2\overline{POCH_2CMe_2CH_2O}]_2$	1037 m	797 w	983 m	656 m	536 w	415 m	395 w
9	$Cl_2V[S_2\overline{POCH_2CEt_2CH_2O}]$	1066 s	802 m	982 m	604 m	542 s	451 w	370 w
10	$ClV[S_2\overline{POCH_2CEt_2CH_2O}]_2$	1064 m	885 m	966 s	601 m	546 m	456 m	374 m

The PMR spectra (Table-3) of chloro-vanadium dialkyl and alkylene dithiophosphates recorded in $CDCl_3$ show the expected peak patterns due to the corresponding glycoxy and alkoxy groups. The chemical shift as well as the coupling constants are almost same as those observed for the corresponding ligand dithiophosphoric acids, thus indicating that complexation with vanadium does not have any pronounced effect. The peak due to SH proton (present at 3.10–3.50 ppm) in the spectra of dithiophosphoric acids[20] is absent in the corresponding chloro-vanadium complexes showing the formation of (S—V) bond by deprotonation.

The ^{13}C NMR (Table-4) spectra of some representative compounds recorded in $CDCl_3$ show chemical shifts which are very close to those obtained for the parent compounds and indicate no substantial change in structural features.

^{31}P NMR spectra chemical shifts were measured in $CDCl_3$ and are summarized in Table-3. Only one peak for each compound was obtained in the range 82.03–

67.6 ppm, indicating only one type of phosphorus nucleus in the molecule. However, one noticeable difference was observed in comparison to parent acids. It appears that a minor difference in the bond angles around phosphorus may affect the ^{31}P chemical shift considerably. Considering the normal mode of bonding of dithiophosphate with the metal as a bidentate chelating ligand[21, 22], we conclude that the metal atom in mono- and dichloro-vanadium dialkyl and alkylene dithiophosphate are tetra- and penta-coordinated structures respectively.

TABLE-3

^{1}H AND ^{31}P NMR SPECTRAL DATA FOR SOME MIXED CHLORO-VANADIUM(III) DIALKYL AND ALKYLENEDITHIOPHOSPHATES

Comp. No.	Product/g	^{1}H Chemical shift (δ ppm) in $CDCl_3$	^{31}P Chemical shift in parent acid in $CDCl_3$	^{31}P Chemical shift (δ ppm) in $CDCl_3$
1	$Cl_2V[S_2P(OPr^n)_2]$	0.95–0.97, t, CH_3 (6H) 1.5–2.04, m, CH_2 (4H) 3.6–3.8, m, CH_2O (4H)	82.40	82.03
2	$ClV[S_2P(OPr^n)_2]_2$	0.96–.097, t, CH_3 (12H) 1.5–2.0, m, CH_2 (8H) 3.6–3.8, m, CH_2O (8H)	—	81.85
3	$Cl_2V[S_2P(OPh)_2]$	7.26–7.29, m, C_6H_5 (10H)	80.13	—
4	$ClV[S_2P(OPh)_2]_2$	6.42–7.25, m, C_6H_5 (20H)	80.13	67.61
5	$Cl_2V[S_2\overline{POCMe_2CMe_2O}]$	1.15–1.19, d, CH_3 (12H)	91.50	75.79
6	$ClV[S_2\overline{POCMe_2CMe_2O}]_2$	0.90, t, (J=7Hz), 12H(Me) 1.8, m, 8H (CH_2) 4.32, qd, 8H(CH_2O)	78.10	77.92
7	$ClV[S_2\overline{POCH_2CMe_2CH_2O}]_2$	0.95–0.97, d, CH_3 (12H) 3.6–3.9, d, CH_2O (8H)	78.60	73.05

TABLE-4

^{13}C NMR SPECTRAL DATA OF SOME MIXED CHLORO VANADIUM(III) DIALKY AND ALKYLENEDITHIOPHOSPHATES

Compound	CH_3	CH_2	^{13}C Chemical shift, in ppm	
			C	OC
$ClV[S_2P(OPr^n)_2]_2$	12.1 s	25.57d, (J = 6.1) Hz	70.6, d, (J = 6.1) Hz	
$ClV[S_2\overline{POCMe_2CMe_2O}]_2$	25.2, d, (J = 6.1) Hz		23.6, d, (J = 6.1) Hz	
$ClV[S_2\overline{POCH_2CEt_2CH_2O}]_2$	7.26, d, (J = 6.1) Hz	23.1, d, (JT= 6.1) Hz	23.6, d, (J = 7.3) Hz	37.80 s
$ClV[S_2\overline{POCH_2CMe_2CH_2O}]_2$	27.58 s		28.91, d, (J = 6.1) Hz	39.24 s

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