Asian Journal of Chemistry Vol. 16, Nos. 3–4 (2004), 1287–1293

Dialkyl and Alkylene Dithiophosphate of Selenium(IV) Derivatives

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Selenium tetrachloride reacts with O,O-dialkyl and alkylene dithiophosphoric acids in 1 : 4 molar ratio in refluxing benzene to yield $Se[S_2P(OR)_2]_4$, R = Et, Pr-*n*, *i*-Pr, *i*-Bu and Ph, and $Se[S_2\overline{POGO}]_4$ where G = $—CH_2CMe_2CH_2—$, $—CH_2CEt_2CH_2—$ and $—CMe_2CMe_2—$. The complexs are viscous liquids in open chain derivatives and red crystalline solids in cyclic derivatives, soluble in mixture solvents (DMSO and $CHCl_3$) and monomeric in nature. These have been characterized on the basis of elemental analysis, molecular weight determinations, IR and multinuclear NMR (^1H, ^{13}C and ^{31}P NMR).

Key Words: Dialkyl, Alkylene, Dithiophosphate, Selenium(IV).

INTRODUCTION

Selenium tetrachloride reacts readily with dialkyl and alkylene dithiophosphoric acids in 1 : 4 molar ratio in refluxing benzene with evolution of HCl. A survey of literature on dithiophosphato derivatives of group (16) showed that a few examples of tellurium(II)[1, 2], (IV)[3], organotellurium[4–9] and heterocyclic tellurium[10–12] are known.

Although Se—S bonded compounds, particularly selenium(II) dithiophosphate $[Se[S_2P(OEt)_2]_2]_n$ has been described by X-ray[13], the corresponding dialkyl and alkylene dithiophosphate derivatives of selenium(IV) are surprisingly still unknown. In view of this, it was thought worth while to study the reactions of $SeCl_4$ with open chain as well as cyclic dithiophosphoric acids with a view to isolate tetrakis dithiophosphate derivatives.

EXPERIMENTAL

Moisture was carefully excluded throughout the experimental manipulations.

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Dialkyl[14] and alkylene[15] dithiophosphoric acids were prepared by standard methods. Glycol was distilled before use, selenium tetrachloride (Aldrich) was used as such. Sulfur was determined by Messenger's method as barium sulfate. Selenium was determined by iodometric titration.

IR spectra were recorded as Nujol mulls using CsI cells in region 4000–200 cm^{-1} on an FT-IR 8201 PC spectrometer. ^1H, ^{13}C and ^{31}P spectra were recorded on a Jeol-FT-NMR spectrometer-LA300 using TMS as internal reference (for ^1H and ^{13}C) and H_3PO_4 (for ^{31}P) as external reference.

The following synthetic details for one specific 1 : 4 replacement reaction represent the procedure used to synthesize all compounds.

Reaction between Selenium Tetrachloride with Dialkyl (OPh) and Alkylene Dithiophosphoric Acid in 1 : 4 Molar Ratio

A benzene solution (*ca.* 30 mL) of $[HS_2P(OPh)_2]$ (0.710 g, 2.515 mmol) was added into a suspension of $SeCl_4$ (0.139 g, 0.63 mmol) in benzene (*ca.* 20 mL). The addition was dropwise with constant stirring at room temperature. The reaction mixture was refluxed for *ca.* 5 h. The excess solvent was removed under reduced pressure and the product washed repeatedly by *n*-hexane and the product was finally dried under reduced pressure to give yellow viscous liquids, but after a long time (*ca.* 20 days) form red needle crystals. In cyclic derivatives the red needle crystals formed during reaction mixture; after cooling at room temperature more red needle crystals formed.

RESULTS AND DICUSSION

The reactions of selenium tetrachloride with dialkyl and alkylene dithiophosphoric acids in refluxing benzene with constant stirring resulted in the formation of replacement reaction of 1 : 4 stoichiometry.

$$SeCl_4 + 4HS_2P(OR)_2 \longrightarrow Se[S_2P(OR)_2]_4 + 4HCl\uparrow$$

where R = Et, *n*-Pr, *i*-Pr, *i*-Bu and Ph.

$$SeCl_4 + 4HS_2\overline{POGO} \longrightarrow Se[S_2\overline{POGO}]_4 + 4HCl\uparrow$$

G = $—CH_2CMe_2CH_2—$, $—CH_2CEt_2CH_2—$ and $—CMe_2CMe_2—$.

The colour of the reaction medium changes from yellow to red with the progress of the reaction. Selenium tetrakis (O,O-dialkyl and alkylene dithiophosphate) derivatives are viscous liquids in open derivatives and solid crystals in cyclic derivatives. The products were washed with *n*-hexane several times and finally dried under reduced pressure. The open derivatives are soluble in common organic solvents, like benzene, dichloromethane and chloroform and cyclic derivatives soluble in mixture solvents (DMSO and $CHCl_3$). The molecular weights (Table-1) of all these derivatives determined by cryoscopic method indicated the monomeric nature of these products.

TABLE-1

SYNTHESIS AND PHYSICAL PROPERTIES OF DIALKYL AND ALKYLENE DITHIOPHOSPHATE OF SELENIUM(IV) DERIVATIVES

Sl. No.	Reactants g (mmol)		Products g (mmol)	Yield (%)	m.p. (°C)	Physical state	m.w. Found (Calcd.)	Elemental analysis (%), Found (Calcd.)	
	$SeCl_4$	Dithiophosphoric acids						Se	S
1.	0.480 (2.170)	$HS_2P(OEt)_2$ 1.619 (8.690)	$Se[S_2P(OEt)_2]_4$ 1.590 (1.939)	89	—	Reddish brown V.L.*	802 (819.88)	10.23 (9.63)	30.43 (31.29)
2.	0.391 (1.769)	$HS_2P(n\text{-}OPr)_2$ 1.516 (7.074)	$Se[S_2(n\text{-}OPr)_2]_4$ 1.520 (1.631)	92	—	Yellowish brown V.L.*	919 (932.10)	7.53 (8.47)	26.56 (27.52)
3.	0.369 (1.675)	$HS_2P(i\text{-}OPr)_2$ 1.436 (6.700)	$Se[S_2P(i\text{-}OPr)_2]_4$ 1.422 (1.525)	91	80	Reddish brown solid	921 (932.10)	7.79 (8.47)	26.50 (27.52)
4.	0.596 (2.698)	$HS_2P(i\text{-}OBu)_2$ 2.616 (10.790)	$Se[S_2P(i\text{-}OBu)_2]_4$ 2.430 (2.327)	86	—	Yellowish brown V.L.*	1028 (1044.32)	8.34 (7.56)	25.25 (24.56)
5.	0.139 (0.629)	$HS_2P(OPh)_2$ 0.710 (2.515)	$Se[S_2P(OPh)_2]_4$ 0.632 (0.525)	83	—	Yellow V.L.*	1188 (1204.25)	5.62 (6.57)	22.08 (21.30)
6.	0.349 (1.583)	$HS_2POCH_2CMe_2CH_2O$ 1.254 (6.328)	$Se[S_2POCH_2CMe_2CH_2O]_4$ 1.154 (1.330)	84	130	Red crystal	— (867.56)	8.92 (9.10)	28.62 (29.57)
7.	0.547 (2.478)	$HS_2POCH_2CEt_2CH_2O$ 2.243 (9.916)	$Se[S_2POCH_2CEt_2CH_2O]_4$ 2.186 (2.231)	90	122	Red crystal	— (979.76)	7.76 (8.06)	25.49 (26.18)
8.	0.339 (1.533)	$HS_2POCMe_2CMe_2O$ 1.302 (6.134)	$Se[S_2POCMe_2CMe_2O]_4$ 1.310 (1.418)	92	108	Red crystal	— (923.86)	7.97 (8.55)	26.57 (27.77)

*VL = viscous liquid.

The IR spectra of these derivatives (Table-2) exhibit bands in the regions 1159–972 cm^{-1} and 880–802 cm^{-1} which may be assigned to ν(P)—O—C and νP—O—(C) stretching modes respectively[16, 17]. The bands present in the region 985–837 cm^{-1} may be ascribed to dioxaphospholane and dioxaphosphorinane ring vibrations[18, 19]. The bands due to ν(P=S) vibrations[20–22] are observed in the region 694–638 cm^{-1}, show notable small shift ($\Delta = 10.60\ cm^{-1}$) towards lower frequency. This shifting is probably due to coordination of sulfur of the (P=S) group to selenium atom. The bands attributable to ν(P—S) vibrations[21, 22] are present in the region 572–500 cm^{-1}. These bands in all compounds gave notable shifting ($\Delta = 10.71\ cm^{-1}$) towards lower frequency.

TABLE-2
IR SPECTRAL DATA (cm^{-1}) OF DIALKYL AND ALKYLENE DITHIOPHOSPHATE OF SELENIUM(IV) DERIVATIVES

Compounds	ν(P)–O–C	νP–O–(C)	Ring vibration	ν(P=S)	ν(P–S)	ν(Se–S)
$Se[S_2P(OEt)_2]_4$	1016.7 s	850.5 m	—	650.6 s	510.4 m	372.3 w
$Se[S_2P(n\text{-}OPr)_2]_4$	991.3 s	858.3 s	—	648.0 s	513.0 m	371.2 m
$Se[S_2(i\text{-}OPr)_2]_4$	972.1 sb	894.9 m	—	638.4 s	499.5 m	373.3 m
$Se[S_2P(i\text{-}OBu)_2]_4$	999.1 s	862.1 s	—	661.5 s	505.3 m	369.0 m
$Se[S_2P(OPh)_2]_4$	1159.1 s	908.4 s	—	688.5 s	511.1 m	372.7 w
$Se[S_2P\overline{OCH_2CMe_2CH_2O}]_4$	1043.1 s	819.7 s	985.6 s	675.0 s	500.5 s	375.8 m
$Se[S_2\overline{POCH_2CEt_2CH_2O}]_4$	1062.7 s	823.5 m	973.3 s	671.2 s	506.3 m	376.8 w
$Se[S_2\overline{POCMe_2CMe_2O}]_4$	1052.3 m	819.7 m	937.3 s	694.3 m	572.8 m	373.9 m

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

The band at 2550–2400 cm^{-1}, due to ν(S—H) vibrations in parent acids, disappears in selenium tetrakis (O,O-dialkyl and alkylene dithiophosphates) confirming deprotonation of ligand and metal-sulfur bond formation. New bands are shown in the region 380–365 cm^{-1} due to ν(Se—S) stretching vibration[23, 24].

The ^1H NMR spectra (Table-3) of these derivatives show the characteristic proton resonance of the corresponding dialkyl protons as well as alkylene protons. The peaks due to (S—H) proton (found at δ 3.01–3.64 ppm in the spectra of parent dithiophosphoric acids) are expectedly absent in the corresponding derivatives showing the formation of (Se—S) bond by deprotonation. The chemical shifts are almost same as those observed for the corresponding ligand dithiophosphoric acids, thus indicating that complexation with the metal atom does not have any pronounced effect on these.

TABLE-3

^{1}H AND ^{31}P NMR SPECTRAL DATA OF DIALKYL AND ALKYLENE DITHIOPHOSPHATE OF SELENIUM(IV) DERIVATIVES

Sl. No.	Compounds	^{1}H chemical shift in δ ppm in $CDCl_3$	^{31}P chemical shift in δ ppm (parent acid)
1.	$Se[S_2P(OEt)_2]_4$	1.247–1.515, m, 24H(CH_3) 3.931–4.165, m, 16 (OCH_2)	82.7 and 85.3 (85.70)
2.	$Se[S_2P(n\text{-}OPr)_2]_4$	0.986–1.123, m, 24H(CH_3) 1.65–1.79, m, 16H(CH_2) 4.175–4.264, m, 16H(OCH_2)	84.9 and 82.4 (86.10)
3.	$Se[S_2P(i\text{-}OPr)_2]_4$	1.145–1.582, m, 48H(CH_3) 4.671–4.910, m, 8H(OCH)	82.2 and 81.3 (82.30)
4.	$Se[S_2P(i\text{-}OBu)_2]_4$	0.912–1.178, m, 48H(CH_3) 1.919–2.082, m, 8H(CH) 3.767–3.958, m, 16H(OCH_2)	83.5 and 86.2 (85.70)
5.	$Se[S_2P(OPh)_2]_4$	7.403–7.578, m, 40H(OC_6H_5)	80.1 and 78.2 (79.90)
6.	$Se[S_2\overline{POCH_2CMe_2CH_2O}]_4$	1.07, s, 24H(CH_3) 4.026–4.078, d, (J = 15.6 Hz), 16H(OCH_2)	77.7 and 76.1 (77.30)
7.	$Se[S_2\overline{POCH_2CEt_2CH_2O}]_4$	0.866–1.598 m, 40H(CH_3, CH_2) 4.109–4.160, d (J = 15.3 Hz), 16H(OCH_2)	78.6 and 77.0 (78.50)
8.	$Se[S_2\overline{POCMe_2CMe_2O}]_4$	1.46, s, 48H(CH_3)	93.4 and 91.9 (93.10)

s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and J = $^3J_{(H,P)}$.

^{13}C NMR Spectra

The ^{13}C NMR spectra of the parent dithio acids and a few represented complexes were recorded in deuterated chloroform at ambient temperature (Table-4). The signals for dialkyl and alkylene carbons were observed at expected position.

TABLE-4

^{13}C NMR SPECTRAL DATA OF SOME DIALKYL AND ALKYLENE DITHIOPHOSPHATE OF SELENIUM(IV) DERIVATIVES (δ PPM)

Sl. No.	Compound	Dialkyl and alkylene dithiophosphate				
		CH_3	CH_2	CH	C	CO
1.	$Se[S_2P(OEt)_2]_4$	16.01, s	—	—	—	65.04, s
2.	$Se[S_2P(i\text{-}OPr)_2]_4$	23.98, s	—	—	—	75.00, s
3.	$Se[S_2P(i\text{-}OBu)_2]_4$	23.66, s	—	30.74, s	—	74.76, s

s = singlet and d = doublet.

The proton decoupled ^{31}P NMR spectra of selenium tetrakis (O,O-dialkyl and alkylene dithiophosphates) have been recorded in $CDCl_3$ (Table-3). It shows two signals for each compound in the region (93.4–76.1 ppm). This is support to the observations of Pudovick *et al.*[25] who reported two signals (at δ 85 and 86 ppm) for $Cl_2Sn[S_2P(i\text{-}OPr)_2]_2$ and inferred two types of dithiophosphato groups in solution, one is monodentate and the other is bidentate.

Structural Elucidation

On the basis of the above studies and considering the normal mode of bonding of dithiophosphate with the metal as mono- and bidentate chelating ligand, we conclude that the metal atom in selenium tetrakis derivative is seven coordinated. Fig. 1 due to (i) the presence of two signals of ^{31}P which infer two types of dithiophosphato groups in solution, one monodentate and another bidentate and this supports Pudovick's observations, (ii) lone pair of electron: ML_6, that occupy the seventh position[26] around selenium. The position of the lone pair of electrons may be present in different sites (axial or equatorial)—the equatorial described with dithiophosphate complexes[27] but the axial reported for dithiocarbamate[28] and xanthate[29, 30] complexes. Unfortunately our attempts to get a suitable crystal of any of these compounds have been unsuccessful so far.

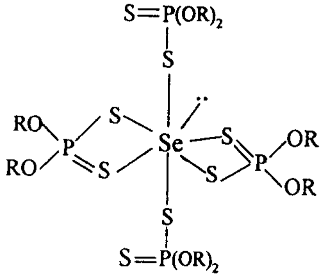

Fig. 1. (I) Suggested structures of selenium tetrakis(dialkyl and alkylene dithiophosphates).

ACKNOWLEDGEMENTS

We thank Amsterdam University, Department of Chemical Engineering and Institute of Molecular Chemistry. Thanks are also due to Prof. J.M. Ernsting and Mr. A.F. El-Qidrea for their cooperation.

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(*Received*: 5 August 2003; *Accepted*: 3 March 2004) AJC-3359