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Metal and Organometal Complexes of Oxy- and Thiophosphorus Acids IV*. *O,O*-Alkylene and Dialkyl Dithiophosphates of Zirconium(IV)

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Abstract

O,O-Alkylene and dialkyl dithiophosphates of zirconium(IV), $Cl_{4-n}Zr(dtp)_n$ [dtp = $S(S)\overline{POC(Me)_2C(Me)_2O}$, n = 1, 2, 3 and 4; dtp = $S(S)\overline{POCH_2C(Me_2)CH_2O}$ or $S(S)P(OPr^i)_2$, n = 2, 3 and 4] have been synthesised by the reactions of zirconium tetrachloride with ammonium salts of *O,O*-alkylene and dialkyl dithiophosphoric acids in appropriate stoichiometric ratios in refluxing dichloromethane. All these compounds are hydrolysable white powdery or waxy solids and soluble in common organic solvents. These derivatives have been characterised on the basis of elemental analyses, IR and NMR (^1H, ^{13}C and ^{31}P) spectral studies. A chelating bidentate behaviour of dithiophosphato moieties has been proposed. The NMR data indicate stereochemical nonrigidity in solution.

Introduction

O,O-Alkylene dithiophosphoric acids, $\overline{OGOP}(S)SH$ and their open chain analogues, $(RO)_2P(S)SH$ constitute an important series of 1,1-dithio ligands which show considerable versatility in their bonding modes with metallic and organometallic species [1–3]. In continuation of our studies on dialkyl (and alkylene) dithiophosphates of titanium(IV) [4, 5], the present communication deals with the corresponding derivatives of zirconium(IV).

The sulphur ligand chemistry of zirconium has been little explored as yet and the published work in this area is mainly concerned with cyclopentadienyl–zirconium moieties [6]. The zirconium(IV) derivatives of 1:1 dithio ligands have been restricted mainly to *N,N*-dialkyl dithiocarbamates, which have been obtained either by CS_2 insertion into Zr–N bonds [7–9] or by the reaction of zirconium halides (e.g. $ZrCl_4$, ZrF_4, $(PhO)_2ZrCl_2$ etc.) with sodium dialkyl dithiocarbamates [10–13]. The dithiocarbamato moieties are invariably bidentate in these compounds and the tetrakis derivatives show rapid intramolecular rearrangement on the NMR time scale [14, 15].

Except for the isolation of two examples of the tetrakis derivatives [16, 17], $Zr[S(S)P(OR)_2]_4$, R = Et, Pr^i and the crystal structure determination of the latter [17], no work appears to have been carried out on dithiophosphato derivatives of zirconium(IV).

Results and Discussion

Reactions of zirconium tetrachloride with ammonium alkylene (and dialkyl) dithiophosphates in appropriate molar ratios proceed readily in refluxing dichloromethane with stepwise replacement of the chlorine atoms by dithiophosphato moieties. The products which are soluble in dichloromethane are obtained after filtering off the precipitated ammonium chloride and removal of the solvent. Employing this route, three series of complexes, derived from open chain as well as five- and six-membered cyclic dithiophosphoric acids, have been isolated.

$$ZrCl_4 + nNH_4(dtp) \longrightarrow Cl_{4-n}Zr(dtp)_n + nNH_4Cl\downarrow$$

dtp = $S(S)\overline{POC(Me)_2C(Me)_2O}$, n = 1 (**1**); n = 2 (**2**);
n = 3 (**3**) and n = 4 (**4**)

dtp = $S(S)\overline{POCH_2C(Me)_2CH_2O}$, n = 2 (**5**); n = 3 (**6**);
n = 4 (**7**)

dtp = $S(S)P(OPr^i)_2$, n = 2 (**8**); n = 3 (**9**); n = 4 (**10**)

dtp = $S(S)P(OEt)_2$, n = 4 (**11**).

The above reactions appear to be more facile than the corresponding reactions of titanium tetrachloride [4]. However, for the synthesis of the tetrakis derivatives (**4**, **7**, **10** and **11**), the amount of ammonium dithiophosphate taken was in slight excess than required, as a precautionary measure (Although compounds **10** and **11** are not new, their spectroscopic behaviour has not been described.)

All the above products are obtained in quantitative yields except derivative **1**, the yield of which could be raised only to ~50% even after extending the re-

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TABLE 1. Synthetic and analytical data of zirconium(IV) *O,O*-alkylene and dialkyl dithiophosphates

Compound no.	Reactants (g)		Molar ratio	Product/physical state	Melting point (°C)	Yield (%)	Analysis (%) found (calc.)		
	$ZrCl_4$	Ammonium dithiophosphate					Zr	S	Cl
1	0.96	$NH_4S(S)\overline{POC(Me)_2C(Me)_2O}$ 0.96	1:1	$Cl_3ZrS(S)\overline{POC(Me)_2C(Me)_2O}$ white grey microcrystalline solid	92	51	22.44 (22.33)	15.77 (16.66)	25.87 (26.02)
2	0.58	1.15	1:2	$Cl_2Zr[S(S)\overline{POC(Me)_2C(Me)_2O}]_2$ white microcrystalline solid	98	91	15.68 (15.62)	22.07 (21.91)	11.87 (12.14)
3	0.63	1.88	1:3	$ClZr[S(S)\overline{POC(Me)_2C(Me)_2O}]_3$ white microcrystalline solid	126	88	12.08 (12.01)	25.30 (25.27)	4.37 (4.66)
4	0.41	1.97	1:4	$Zr[S(S)\overline{POC(Me)_2C(Me)_2O}]_4$ white microcrystalline solid	142	84	9.85 (9.75)	27.46 (27.37)	
5	0.75	$NH_4S(S)\overline{POCH_2C(Me)_2CH_2O}$ 1.39	1:2	$Cl_2Zr[S(S)\overline{POCH_2C(Me)_2CH_2O}]_2$ white microcrystalline solid	96	75	16.54 (16.40)	23.09 (23.02)	12.60 (12.75)
6	0.21	0.60	1:3	$ClZr[S(S)\overline{POCH_2C(Me)_2CH_2O}]_3$ white microcrystalline solid	162 - 165	80	12.79 (12.71)	26.77 (26.75)	4.81 (4.94)
7	0.62	2.67	1:4	$Zr[S(S)\overline{POCH_2C(Me)_2CH_2O}]_4$ white microcrystalline solid	255	71	10.51 (10.37)	29.16 (29.12)	
8	0.51	$NH_4S(S)P(OPr^i)_2$ 1.03	1:2	$Cl_2Zr[S(S)P(OPr^i)_2]_2$ grey sticky solid		80	15.60 (15.51)	21.83 (21.76)	11.85 (12.05)
9	0.76	2.27	1:3	$ClZr[S(S)P(OPr^i)_2]_3$ grey sticky solid		93	11.97 (11.91)	25.41 (25.91)	4.56 (4.63)
10	0.42	1.95	1:4	$Zr[S(S)P(OPr^i)_2]_4$ white waxy solid		89	9.84 (9.67)	27.05 (27.14)	
11	0.49	$NH_4S(S)P(OEt)_2$ 1.98	1:4	$Zr[S(S)P(OEt)_2]_4$ white grey crystalline solid	172	94	11.03 (10.97)	30.93 (30.78)	

fluxing period of the reaction mixture for ~8 h. It seems that on mixing $ZrCl_4$ and ammonium tetramethylethylene dithiophosphate in equimolar ratio, a stable insoluble complex, ammonium tetramethylethylene dithiophosphatotetrachlorozirconate, $[NH_4]^+[\overline{OC(Me)_2C(Me)_2OP}(S)S\ ZrCl_4]^-$, is formed which, under the reaction conditions, decomposes reluctantly to form **1**. A similar stable insoluble complex has been described in the case of titanium also [4].

Zirconium alkylene dithiophosphates are white microcrystalline solids whereas the dialkyl dithiophosphates are white grey microcrystalline or wax like in nature (Table 1). This is in contrast to the corresponding titanium derivatives which are orange or deep yellow semi-solids [4]. All the zirconium derivatives are soluble in common organic solvents such as benzene, dichloromethane and chloroform but insoluble in n-hexane. The compounds were, therefore, purified by washing with n-hexane. However, attempts to crystallise the solid compounds from benzene/n-hexane mixture were unsuccessful.

All the zirconium dithiophosphato derivatives show ageing phenomenon. On keeping for longer periods (i.e. 6–8 months) even in stoppered flasks at room temperature these became almost insoluble in common organic solvents (in which initially these are highly soluble). This is probably due to their slow polymerisation. This effect seems to be more pronounced in the open chain compounds. Zirconium dithiophosphates tend to hydrolyse slowly by moisture and both Zr–Cl as well as Zr–S linkages are broken.

The relevant infrared spectral data of zirconium alkylene and dialkyl dithiophosphates, with tentative assignments, on the basis of published literature on other metal dithiophosphates [1, 3, 18] and on zirconium–sulphur bonded compounds [8, 11], are given in Table 2. The bands present in the regions 1135–980 and 870–760 cm^{-1} may be assigned to ν(P)–O–C and νP–O–(C) vibrations and these do not show any shift from their position in parent acids. In the cyclic derivatives, broad bands present in the region 920–970 cm^{-1} are due to the ring vibrations of the dioxaphospholane and dioxaphosphorinane moieties and these are probably coupled with C–C stretching vibrations [19, 20]. The bands due to νP=S vibrations are present in the regions 675–660 and 670–640 cm^{-1} in cyclic [21] and acyclic [1] derivatives, respectively, and show a shift ($\delta\nu$ = 20–10 cm^{-1}) to lower frequency from their positions in the corresponding parent acids, thus indicating coordination of the metal atom with the phosphorothionyl sulphur. The bands attributable to νP–S vibrations [22] (symmetric and asymmetric) are present in the region 600–510 cm^{-1}. The bands of weak to medium intensity in the regions 375–360 and 335–300 cm^{-1} may be assigned to νZr–Cl and νZr–S vibrations, respectively [8, 11]. In zirconium tetramethylethylene dithiophosphates, the νZr–S vibrations show a regular lowering from mono to tetrakis derivatives (325, 310, 300 and 300 cm^{-1} respectively) which may be attributed to an increase in the coordination number of the zirconium atom [11, 23]. However, this lowering in other derivatives is not regular.

The ^{1}H NMR spectra (Table 3) of these derivatives show the characteristic proton resonances due to the corresponding glyoxy and alkoxy groups. The chemical shifts as well as the coupling constants are almost same as those observed for the corresponding ligand dithiophosphoric acids, thus indicating that com-

TABLE 2. Some relevant IR spectral data for zirconium(IV) *O,O*-alkylene and dialkyl dithiophosphates

Compound no.	ν(P)–O–C	νP–O–(C)	Ring vibration	νP=S	νP–S	νZr–Cl	νZr–S
1	1135s	850m	920s, br	675m	600s	350w	325w
2	1120s	860m	930s, br	665s	585s	355w	310m
3	1130s	850m	920m, br	660m	585s	355w	300w
4	1120s	850m	920m, br	670m	595s		300m
5	1035s	810m	970s, br	670s	550m, 510s	370w	320m
6	1030s	820m	970s, br	670s	545w, 510s	370w	320w
7	1030s	820m	960s, br	670s	550m		310w
8	970s	770s		670s, 645m	560s	375w	290m
9	980s, br	760s		665s, 640s	560s	370w	290m
10	970s	755s		670w, 645s	555m		300m

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

TABLE 3. ^{1}H, ^{31}P and ^{13}C NMR chemical shifts (in δ ppm) of zirconium *O,O*-alkylene and dialkyl dithiophosphates

Compound no.	^{1}H NMR (in $CDCl_3$)	^{31}P NMR (in $CHCl_3$)	^{13}C NMR (in $CHCl_3$)
1	1.40s	94.8	
2	1.50s	94.3	23.94d(J = 4.88 Hz), (CH_3) 90.73d(J = 2.44 Hz), (CO)
3	1.40s	93.9	23.94d(J = 6.11 Hz), (CH_3) 90.73d(J = 2.44 Hz), (CO)
4	1.55s	95.2	23.96d(J = 6.11 Hz), (CH_3) 90.74s(CO)
5	1.05s, 12H(Me) 4.04d(J = 16 Hz), 8H($-CH_2O$)	87.3	
6	1.10s, 18H(Me) 4.05d(J = 16 Hz), 12H($-CH_2O$)	87.6	
7	1.15s, 24H(Me) 4.08d(J = 16 Hz), 16H($-CH_2O$)	88.0	21.40s(CH_3) 32.47d(J = 4.11 Hz, $(\rangle\overset{|}{\underset{|}{C}})$ 76.25(CO)
8	1.32d(J = 7 Hz), 24H(Me) 4.53–5.06m, 4H(–CH)	87.6	
9	1.36d(J = 7 Hz), 36H(Me) 4.57–5.14m, 6H(–CH)	88.2	
10	1.44d(J = 7 Hz), 48H(Me) 5.06–5.54m, 8H(–CH)	88.7	
11		91.2	

plexation with the metal atom does not have any pronounced effect on these. This is probably due to the long distance of the protons from the metal atom. The protons on the α-carbon atoms of the alkoxy and glycoxy groups show three bond coupling with phosphorus with *J* values in the range of 10–15 Hz.

The ^{13}C NMR spectra of only tetramethylethylene and 2,2-dimethyltrimethylene dithiophosphato derivatives of zirconium (compounds **2**, **3**, **4** and **7**) were recorded in chloroform (Table 3). These are also remarkably similar to those of the ligand dithiophosphoric acids except for some variations in the ^{3}J-(^{13}C–^{31}P) values. The ^{1}H as well as ^{13}C NMR spectra, however, indicate the equivalence of all the dithiophosphato moieties in each compound.

The ^{31}P NMR spectra (Table 3) show only one signal for each compound and the phosphorus atom is invariably deshielded in comparison to its position in the corresponding parent dithio acid. The extent of deshielding, however, varies in the three series of compounds; being 4.7–6.3 ppm in open chain dithiophosphates (compounds **8**–**11**), 8.7–9.4 ppm in six-membered cyclic dithiophosphates (compounds **5**–**7**) and only 2.4–3.7 ppm in five-membered cyclic dithiophosphates (compounds **1**–**4**). In each series, on the other hand, there seems to be little variation.

Even though the overall bonding mode of different dithiophosphato ligands may be the same, the minor differences in the bonding angles around phosphorus may affect the ^{31}P chemical shifts considerably [24, 25] and therefore, it is difficult to comment on these ^{31}P chemical shift differences unless detailed structural data (e.g. from X-ray crystallography) are obtained.

The multinuclear NMR data (^{1}H, ^{13}C and ^{31}P) described above do not throw much light on the structural features of zirconium dithiophosphates, although these do indicate the equivalence of all the dithiophosphate moieties in each compound, which must be due to stereochemical nonrigidity of these zirconium complexes. Unfortunately low temperature NMR work could not be carried out due to lack of facilities. In fact variable temperature NMR studies on $Zr(dtc)_4$ by Muetterties [14, 15] and on $Cl_{4-n}Ti(dtc)_n$ (n = 2, 3) by Fay *et al.* [26] clearly indicate that stereochemical nonrigidity is a common feature of all such derivatives of titanium and zirconium.

The IR spectral data point towards bidentate attachment of the dithiophosphato ligands to the zirconium atom. The bigger size of zirconium in comparison to titanium and its pronounced tendency to expand the coordination number may ensure the bidentate attachment of dithiophosphato ligands in each case. Thus trigonal bipyramidal, octahedral, pentagonal bipyramidal and dodecahedral structures may be suggested tentatively for 5-, 6-, 7- and 8-coordinated mono, bis, tris and tetrakis dithiophosphates of zirconium, $Cl_{4-n}Zr(dtp)_n$, on the basis of their expected similarity with the corresponding zirconium *N,N*-dialkyl dithiocarbamates [11] as well as titanium alkylene and dialkyl dithiophosphates [4]. It may be pointed out that according to the crystal structure studies, $Zr[S(S)P(OPr^i)_2]_4$ [17] and $Ti(S_2CNEt_2)_4$ [27] are dodecahedral and $CpZr(S_2CNMe_2)_3$ [28] and $ClTi(S_2CNMe_2)_3$ [29] are pentagonal bipyramidal. The derivative $Cl_2Ti(dtc)_2$ has been assigned *cis*-octahedral structure on the basis of dipole moment data [26].

Interestingly, the trichlorozirconium alkylene dithiophosphate (**1**) seems to be the first example of derivatives of the type Cl_3ZrL (where L is a bidentate ligand). The four-membered ZrS_2P ring in this compound may force the dithiophosphato moiety to occupy the equitorial-axial position in a trigonal-bipyramidal structure.

The cyclic dithiophosphato derivatives of zirconium are expected to show interesting structural variations from the corresponding open chain derivatives (e.g. structures of $Ph_3SnS(S)P(OEt)_2$ [30] and $Ph_3SnS(S)\overline{POC(Me)_2C(Me)_2O}$ [31]). Unfortunately, our attempts to get suitable crystals of any of these compounds have been unsuccessful so far.

Experimental

Owing to the extremely hydrolysable nature of the starting materials as well as the newly synthesised zirconium(IV) dithiophosphates, stringent precautions were taken to exclude moisture. Solvents (dichloromethane and chloroform) and alcohols (ethanol and isopropanol) were dried by standard methods. Zirconium tetrachloride (Fluka) was sublimed before use. *O-O*-Dialkyl [32] and alkylene [21] dithiophosphoric acids and their ammonium salts were prepared by methods reported in the literature. Sulphur and zirconium were estimated as barium sulphate (Messenger's method) and zirconium oxide (cupferron method), respectively. Chlorine was estimated by Volhard's method.

IR spectra were recorded as Nujol mulls using CsI pellets on a Perkin-Elmer 577 spectrophotometer in the range 4000–200 cm^{-1}. The ^1H NMR spectra were recorded in $CDCl_3$ using TMS as external reference on a Jeol FX 90 Q at 89.55 MHz. ^{13}C and ^{31}P NMR spectra were recorded in chloroform using TMS and H_3PO_4 as external references on the same instrument at 22.49 and 36.23 MHz, respectively.

Reaction of Zirconium Tetrachloride with Ammonium O,O-Tetramethylethylene Dithiophosphate in 1:1 Molar Ratio

To a suspension of ammonium *O,O*-tetramethylethylene dithiophosphate (0.96 g) in ~50 ml dichloromethane, was added zirconium tetrachloride (0.96 g) in ~20 ml of the same solvent. The mixture was refluxed for ~8 h, with constant stirring. The insoluble portion was filtered off. Removal of the solvent from the filtrate under reduced pressure gave a white grey powdery solid (yield: 0.98 g; 51%), which was purified by washing with n-hexane. *Anal.* Found: Zr, 22.44; S, 15.53; Cl, 25.87. Calc. for $C_6H_{12}Cl_3O_2PS_2Zr$; Zr, 22.31; S, 15.66; Cl, 26.02%.

Reactions of Zirconium Tetrachloride with Ammonium O,O-Alkylene and Dialkyl Dithiophosphate in 1:≥2 Molar Ratios

Zirconium tetrachloride in dichloromethane was added to a suspension of ammonium alkylene or dialkyl dithiophosphate in dichloromethane in different molar ratios (1:2, 1:3 and 1:4). The reactants were refluxed for ~6 h with constant stirring and precipitated ammonium chloride was removed by filtration, followed by removal of solvent under reduced pressure. The products were finally purified by washing with n-hexane and dried.

Pertinent experimental and analytical data for these experiments are summarised in Table 1.

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