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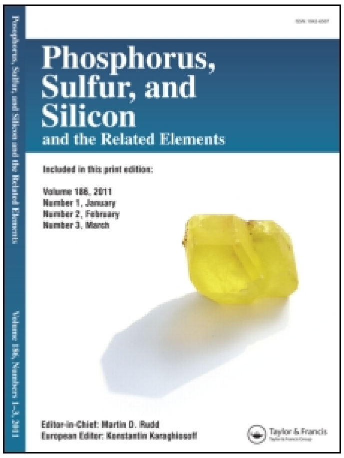

Phosphorus, Sulfur, and Silicon and the Related Elements

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF P,O' ALKYLENE DITHIOPHOSPHATO COMPLEXES OF METALLOCENES; CP_2ML_2[M = Ti OR Zr]

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF O,O′ ALKYLENE DITHIOPHOSPHATO COMPLEXES OF METALLOCENES; $CP_2ML_2[M = Ti\ OR\ Zr]^*$

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Complexes of the type $Cp_2M[S_2\overline{POGO}]_2$ [where $Cp = C_5H_5$, M=Ti or Zr; G = $-C(CH_3)CH_2CH(CH_3)$, $-CH_2C(CH_3)_2CH_2-$, $-C(CH_3)_2C(CH_3)_2-$ and $CH_2CH_2CH(CH_3)-$] were prepared by reaction of Cp_2MCl_2 and $NH_4[S_2\overline{POGO}]$ in 1:2 molar ratio in CH_2Cl_2. These newly synthesized compounds have been characterized by molecular weights, IR, ^1H and ^{31}P NMR spectral measurements. An octahedral geometry for both the metals have been proposed.

Keywords: Biscyclopentadienyl titanium(IV) chloride; biscyclopentadienyl zirconium(IV) chloride; metallocenes; alkylene dithiophosphates; spectral

Compared to the well developed chemistry of sulphur bonded derivative of Si, Ge, Sn and Pb, much less known about the corresponding compounds of transition elements, i.e. Ti and Zr. Due to hard acid character of Ti synthesis of simple thiolates of the type $Ti(SR)_4$ was not successful[1], but facile synthesis of $Cp_2Ti(SR)_2$ can be understood on the basis of enhanced electron density on the metal in latter derivatives[2]. Thiolates[2–5], dithiolates[3]and xanthates[6,7] of metallocenes were synthesized and their structures were determined by spectral and x-ray diffraction[5] techniques.

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[*] This paper is dedicated to Late (Drs.) G. Srivastava, Rajasthan University, Jaipur and R.J. Rao, Vikram University, Ujjain

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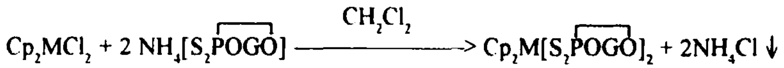
Many reports[8–15] are available on the synthesis and determination of mixed and pure dithiocarbamates of titanium and zirconium. A perusal of literature reveals the scanty appearance of reports on the corresponding dithiophosphates. The dithiophosphoric acids are versatile 1,1-dithio ligands which show varying modes of bonding with transition metals.[16–22] In view of biochemical reactivity of S,P donor ligands and in continuation to our earlier work[16–18]. It was considered worthwhile to extend the studies to some O,O′ alkylene dithiophosphato derivatives of metallocenes.

RESULTS AND DISCUSSION

All these derivatives have been synthesized by following matathetical reaction.



$$Cp_2MCl_2 + 2\,NH_4[S_2\overline{POGO}] \xrightarrow{CH_2Cl_2} Cp_2M[S_2\overline{POGO}]_2 + 2NH_4Cl\downarrow$$

[G = $-C(CH_3)_2CH_2CH(CH_3)-$, $CH_2C(CH_3)_2CH_2-$, $-C(CH_3)_2C(CH_3)_2-$ and $-CH_2\ CH_2CH(CH_3)$; M = Ti or Zr]. The derivatives of titanium are yellow orange and of zirconium are white crystalline solids. All these complexes are soluble in common (Benzene, Toluene, Chloroform, dichloromethane, Carbon tetrachloride etc.) and coordinating (DMSO, dioxane, THF etc.) solvents. Molecular weight determinations in dilute chloroform solution at 45°C show monomeric nature of these derivatives (Table I).

The IR spectra of complexes have been recorded in the region 4000–200 cm^{-1} and important bands are summarized in (Table II). The bands observed in the regions 1060–990 cm^{-1} and 990–860 cm^{-1} have been assigned to ν[(P)-O-C] and [P-O-(C)] respectively. The band present in the region 1000–910 cm^{-1} of sharp / medium intensity in these derivatives could be due to the ring vibration of dioxaphospholane or dioxaphosphorinane rings.[20–22] The ν[P=S] mode may be characterized by the presence of band in the region 660–600 cm^{-1} indicating the bidentate nature of dithiophosphate ligands[19–20]. The band present in the region 590–500 cm^{-1} may be ascribed to ν[P-S] stretching modes[23]. Appearance of a new band (in comparison to free ligand) in the region 380–320 cm^{-1} indicates the formation of metal sulphur bond[23].

TABLE I Synthetic and physical properties data of complexes

Compound	*Yield*	*M.P. (°C)*	*Mol.Wt. Found / Calcd*	*Analysis Found / (Calcd.)*		
				Metal	*S*	*C*
$(C_5H_5)_2Ti[S_2\overline{POC(CH_3)_2CH_2CH(CH_3)O}]_2$	87	152	610 (600.6)	7.8 (8.0)	21.7 (21.4)	44.2 (44.0)
$(C_5H_5)_2Ti[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$	85	148	559 (572.6)	8.5 (8.4)	22.1 (22.4)	42.1 (41.9)
$(C_5H_5)_2Ti[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$	83	165	610 (600.6)	8.1 (8.2)	21.6 (21.4)	43.8 (44.0)
$(C_5H_5)_2Ti[S_2\overline{POCH_2CH_2CH(CH_3)O}]_2$	81	155	540 (544.5)	8.9 (8.8)	23.4 (23.6)	40.0 (39.7)
$(C_5H_5)_2Zr[S_2\overline{POC(CH_3)_2CH_2CH(CH_3)O}]_2$	81	192	628 (643.9)	14.2 (14.2)	19.8 (19.9)	41.3 (41.0)
$(C_5H_5)_2Zr[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$	85	198	600 (615.9)	14.6 (14.8)	20.9 (20.8)	40.8 (39.0)
$(C_5H_5)_2Zr[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$	88	195	632 (643.9)	14.1 (14.2)	20.1 (19.9)	41.4 (41.0)
$(C_5H_5)_2Ti[S_2\overline{POCH_2CH_2CH(CH_3)O}]_2$	83	185	590 (587.8)	15.6 (15.5)	21.6 (21.8)	37.0 (36.8)

TABLE II Some relevant IR spectral bands (in cm^{-1}) of the complexes

Compound	ν*[(P)-O-C]*	ν*[P-O-(C)]*	*Ring Vibration*	ν*[P=S]*	ν*[P-S]*	ν*[*
$(C_5H_5)_2Ti[S_2\overline{POC(CH_3)_2CH_2CH(CH_3)O}]_2$	1040 m	990 w	1000 m	630 m	500 m	3
$(C_5H_5)_2Ti[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$	1050 m	960 m	990 s, br	600 s	590 s	3
$(C_5H_5)_2Ti[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$	1060 s	930 w	980 s	610 s	520 w	3
$(C_5H_5)_2Ti[S_2\overline{POCH_2CH_2CH(CH_3)O}]_2$	1030 m	920 m	970 m, br	600 m	510 m	3
$(C_5H_5)_2Zr[S_2\overline{POC(CH_3)_2CH_2CH(CH_3)O}]_2$	990 m	890 s	950 s, br	620 m	560 w	3
$(C_5H_5)_2Zr[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$	1010 s	860 s	910 s	660 m	540 w	3
$(C_5H_5)_2Zr[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$	990 s	870 s	960 m	620 s	540 m	3
$(C_5H_5)_2Ti[S_2\overline{POCH_2CH_2CH(CH_3)O}]_2$	1000 m	890 s	930 m, br	650 m	550 s	3

= medium, w = Weak, br = Broad.

TABLE III NMR spectral data of the complexes

Compound	*^1H NMR Spectral data in $CDCl_3$ (in δ ppm)*	*^{31}P NMR spectral data in C (in δ ppm)*
$_5H_5)_2Ti[S_2POC(CH_3)_2CH_2CH(CH_3)O]_2$	2.46–1.62, m, 22H ($-CH_3$, $-CH_2$); 4.92–4.25, m, 2H (-OCH), 6.93–6.50, s, 10H ($-C_5H_5$)	92.40 s
$H_5)_2Ti[S_2POCH_2C(CH_3)_2CH_2O]_2$	1.18, s, 12H ($-CH_3$); 4.15, d (^3J=16Hz), 8H($-OCH_2$); 6.73 – 6.48, s, 10H ($-C_5H_5$)	93.60 s
$H_5)_2Ti[S_2POC(CH_3)_2C(CH_3)_2O]_2$	1.32, s, 24H ($-CH_3$); 6.73–6.50, s, 10H ($-C_5H_5$)	110.30 s
$H_5)_2Ti[S_2POCH_2CH_2CH(CH_3)O]_2$	2.50–1.12, m, 10H ($-CH_3$, $-CH_2$); 4.02–3.60, m, 91.00 s ($-OCH_2$, -OCH), 7.02–6.66, s, 10H ($-C_5H_5$)	91.00 s
$H_5)_2Zr[S_2POC(CH_3)_2CH_2CH(CH_3)O]_2$	2.10–1.07, m, 22H ($-CH_3$, $-CH_2$); 5.01–4.60, m, 2H (-OCH), 6.93–6.63, s, 10H ($-C_5H_5$)	93.60 s
$H_5)_2Zr[S_2POCH_2C(CH_3)_2CH_2O]_2$	0.94, s, 12H ($-CH_3$); 4.01, d ($_3J$=17Hz), 8H($-OCH_2$); 6.48, s, 10H ($-C_5H_5$)	96.70 s
$C_5H_5)_2Zr[S_2POC(CH_3)_2C(CH_3)_2O]_2$	1.12, s, 24H ($-CH_3$); 6.93–6.64, s, 10H ($-C_5H_5$)	108.40 s
$_5H_5)_2Ti[S_2POCH_2CH_2CH(CH_3)O]_2$	2.31–1.02, m, 10H ($-CH_3$, $-CH_2$); 3.94–3.62, m, 6H ($-OCH_2$, -OCH), 6.97–6.54, s, 10H ($-C_5H_5$)	94.20 s

d = doublet, m = multiplet.

^1H NMR spectra of these new compounds have been recorded in $CDCl_3$ exhibiting the characteristic glycoxy and aromatic proton signals (Table III). The observed integration ratio corresponds well with the presence of both cyclopentadienyl rings as well as dithiophosphate groups. The aromatic protons of cyclopentadienyl rings have been observed as a singlet (broad) in the region 7.02–6.48 ppm.

The phosphorus atom of dithiophosphato moiety show one signal in the region δ 110.30–91.00 ppm for each compound. These signals are shifted downfield (δ 14–20 ppm) as compared to their respective positions in the free ligand spectra indicating the bidentate nature of the dithiophosphate ligand.[19,24,25]

On the basis of above studies, hexa-coordinated metal centre may tentitively be proposed in these newly synthesized derivatives.

EXPERIMENTAL

Ammonium salts of O,O′ alkylenedithiophosphoric acids were prepared as described earlier[19]. The compounds were synthesized by following general routes (Table I).

(1) Preparation of (C5H5)2 $Ti[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$

A CH_2Cl_2 (15 cm^3) solution of $(C_5H_5)_2$ $TiCl_2$ (1.94 g; 7.8 mmole) was mixed with the suspension of $NH_4[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$ (3.36 g; 15.6 mmole) in CH_2Cl_2(15 cm^3) and refluxed for 6 hours. The insolubles were removed by filtration and the volatiles were stripped off from filtrate under reduced pressure to get yellowish orange crystalline solid. It was washed by n-hexane repeatedly and dried under reduced pressure. Analytical results are summarized in Table I.

(2) Preparation of $(C_5H_5)_2$ $Zr[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$

A CH_2Cl_2 (10 cm^3) solution of $(C_5H_5)_2$ $ZrCl_2$ (1.06 g; 3.6 mmole) was mixed with the suspension of $NH_4[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$ (1.58 g; 7.3 mmole) in CH_2Cl_2 (20 cm^3) and refluxed for 8 hours to ensure completion of reaction. The insolubles were filtered off and the filtrate was concentrated down to 10 cm^3 under reduced pressure. Light petroleum (60–80°C) was mixed to it till the slight turbidity was seen. This mixture was left for over night. White crystalline solid thus deposited on walls was separated and recrystallised from dilute CH_2Cl_2 solution by slow evaporation of solvent at room temperature. The analytical results are summarized in Table I.

MEASUREMENTS

IR spectra were recorded as KBr pellets on Perkin-Elmer 577. ^1H NMR in $CDCl_3$ and ^{31}P NMR in CH_2Cl_2solution were recorded on a Jeol FX 90 Q spectrometer. Molecular weights were measured on a Knoauer vapour pressure Osmometer in $CHCl_3$ at 45°C, elemental analyses were carried out by standard procedures.[26,27]

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