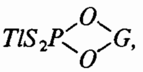
Inorganica Chimica Acta, *89* (1984) 41–46

Alkylenedithiophosphate Derivatives of Thallium

RAFI AHMAD, G. SRIVASTAVA and R. C. MEHROTRA*

Department of Chemistry, University of Rajasthan, Jaipur-302004, India

Received February 3, 1984

Tallium(I) alkylenedithiophosphates, 

$TlS_2P{<}\substack{O\\O}{>}G$,

[where G = $-CH_2C(CH_3)_2CH_2-$, $-CH_2C(C_2H_5)_2CH_2-$, $-C(CH_3)_2CH_2CH(CH_3)-$, $-C(CH_3)_2C(CH_3)_2-$ *and* $-CH(CH_3)CH(CH_3)$*] were synthesized by the reactions of* $TlOCOCH_3$ *or* Tl_2CO_3 *with the corresponding ammonium alkylenedithiophosphates in aqueous medium. These are high melting white solids, insoluble in common organic solvents but soluble in pyridine and DMF in which they show non-electrolytic behaviour. The compounds were characterized by elemental analyses, IR and NMR (*^1H *and* ^{31}P*) spectral data.*

Attempts to isolate Tl(III) derivatives were unsuccessful due to their ready decomposition into Tl(I) derivatives and alkylenethiophosphoryl disulphides.

Introduction

Thallium shows a marked tendency to form stable complexes with various sulphur ligands. Simple thiolates [1, 2], dithiocarbamates [3, 4], dithiophosphinates [5] and xanthates [6] of thallium(I) have been extensively explored. The crystal structure of Tl(I) diisopropyldithiocarbamate [7] shows dimeric units. Thallium(III) derivatives with sulphur ligands are less stable. Thallium(III) thiolates decompose [8] readily to a white solid (probably Tl(I) derivatives). On the other hand, thallium(III) derivatives [9] with chelating dithiols are comparatively stable. Thallium(III) dithiocarbamates [10, 11] are monomeric in solution and their infrared spectra suggest the presence of bidentate dithiocarbamate groups.

Conflicting reports have been published on the existence of Tl(III) tris(dialkyldithiophosphates). Bode *et al.* [11] claimed the isolation of $Tl[S_2P(OEt)_2]_3$ from the reaction of $TlCl_3$ with $NaS_2P(OEt)_2$, while Bonati *et al.* [12] found that the only product from the reaction of $TlCl_3$ and $KS_2P(OMe)_2$ is the corresponding Tl(I) compound. More recently, derivatives of thallium(I) [13] with a number of dialkyldithiophosphates have been characterized by their ultraviolet and vibrational spectra.

Alkylenedithiophosphoric acids and their ammonium salts have been synthesized [14] and their ligating behaviour towards the main group as well as transition elements is currently being investigated in our laboratories. In view of the contradictory findings about the existence of thallium(III) dialkyldithiophosphates, it was considered of interest to see if thallium(III) derivatives of alkylenedithiophosphates can be isolated, as these ligands could be expected to give more stable products than the simple dialkyldithiophosphates. However, in all cases only thallium(I) products were obtained with simultaneous separation of the disulphide derivatives of the ligands. A number of analogous reactions with simple dialkyldithiophosphoric acids were also investigated for comparison.

Experimental

Alkylenedithiosphosphoric acids and their ammonium salts were synthesized by the reported methods [14]. Thallium(III) chloride [15] was prepared *in situ* by passing dry chlorine gas through a suspension of thallium(I) chloride in dry acetonitrile. Thallium was estimated gravimetrically as Tl_2CrO_4 and sulphur was estimated gravimetrically as barium sulphate.

IR spectra were recorded as Nujol mulls or KBr pellets in the range of 400–4000 cm^{-1} on a Perkin-Elmer model 337 spectrometer. ^1H NMR spectra of a few compounds were determined on a Perkin-Elmer R12B spectrometer (60 MHz) in pyridine or carbon tetrachloride solutions, using TMS as external standard. ^{31}P NMR spectra were also recorded for a few compounds only on a Varian FT80A spectrometer (32.38 MHz) using 85% H_3PO_4 as reference. Molar conductance of thallium(I) alkylenedithiophosphates was measured using platinum electrodes in 0.001 *M* DMF solution.

1. *Thallium(I) Neopentylenedithiophosphate*

To a solution of thallous carbonate (2.04 g, 4.36 mmol) in ~30 ml water was added an aqueous solution (~20 ml) of ammonium neopentylenedithiophosphate (1.90 g, 8.82 mmol) at room temperature. A white precipitate was immediately formed. The reaction mixture was stirred for ~2 hr; the precipitate

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

© Elsevier Sequoia/Printed in Switzerland

was filtered and dried. The product (3.04 g, 87% yield) was soluble in pyridine and DMF. *Anal.* Calcd. for $C_5H_{10}O_2PS_2Tl$: Tl, 50.92; S, 15.94%. Found: Tl, 50.25; S, 15.70%. M.p. 260–63 °C dec.

Other Tl(1) alkylenedithiophosphates were synthesized by a similar method (Table I).

2. *Thallium(I) Diisopropyldithiophosphate*

A white precipitate was obtained on adding ~20 ml aqueous solution of $NaS_2P(OC_3H_7\text{-}i)_2$ (5.09 g, 21.50 mmol) to ~50 ml aqueous solution of $TlOCOCH_3$ (5.63 g, 21.37 mmol). The precipitate was filtered and dried under reduced pressure, yielding a white solid (7.70 g, 86% yield). On crystallization from toluene, needle shaped crystals were obtained. *Anal.* Calcd. for $C_6H_{14}O_2PS_2Tl$: Tl, 48.97; S, 15.33%. Found: Tl, 48.17; S, 14.92%. M.p. 124 °C.

Similar reactions were carried out to synthesize $TlS_2P(OEt)_2$ (Table I).

3. *Reaction of Thallium(III) Chloride with Sodium Diisopropyldithiophosphate in 1:3 Molar Ratio*

Thallium(III) chloride was prepared by passing dry chlorine gas (for ~40 minutes) through a suspension of TlCl (2.38 g, 9.92 mmol) in ~40 ml acetonitrile. Excess of chlorine (if any) was removed by passing a rapid stream of dry nitrogen gas through the reaction mixture. To the clear solution thus obtained was added a solution of sodium diisopropyldithiophosphate (7.09 g, 30.03 mmol) in ~50 ml acetonitrile dropwise with constant stirring. Precipitated sodium chloride (1.90 g) was removed by filtration. The yellow solid (7.91 g) obtained on removing the solvent from the filtrate was shaken with ~50 ml light petroleum (60–80°) leaving 3.53 g of grey residue which on crystallization from toluene (~30 ml) gave 2.70 g of white crystalline thallium(I) diisopropyldithiophosphate. *Anal.* Calcd. for $C_6H_{14}O_2PS_2Tl$: Tl, 48.97; S, 15.33%. Found: Tl, 48.17; S, 15.14%. M.p. 124 °C. The light petroleum filtrate was concentrated and left overnight, when a yellow solid diisopropylthiophosphoryl disulphide (2.81 g) crystallized. *Anal.* Calcd. for $C_{12}H_{28}O_4P_2S_4$: S, 30.05%. Found: S, 29.21%. M.p. 86 °C; reported [16] 86 °C.

4. *Reaction of $TlCl_3$ (from Tl_2O_3) with Ammonium Hexylenedithiophosphate in 1:3 Molar Ratio*

Tl_2O_3 (1.17 g, 2.56 mmol) was dissolved in the minimum volume of hydrochloric acid and was diluted with water (~80 ml). To this solution was added a solution of ammonium hexylenedithiophosphate (3.59 g, 15.68 mmol) in ~50 ml water. Initially a light yellow precipitate was obtained which became white after shaking for ~10 minutes. The white precipitate was stirred for ~3 hr and then filtered and dried. On shaking this solid with benzene (~60 ml), 1.65 g of the solid remained undissolved

TABLE I. Syntheses of Thallium(I) Alkylenedithiophosphates and Related Compounds.

Sl. No.	Reactants g	Products g	% Yield	m.p. (°C)	% Analyses Tl Found (Calcd)	% Analyses S Found (Calcd)
1	$Tl_2CO_3 + 2NH_4S_2\overline{POCH_2C(CH_3)_2CH_2O}$ 2.04 1.90	$2TlS_2\overline{POCH_2C(CH_3)_2CH_2O}$ 3.04	86	260–63 dec.	50.25 (50.92)	15.70 (15.94)
2	$Tl_2CO_3 + 2NH_4S_2\overline{POCH_2C(C_2H_5)_2CH_2O}$ 2.20 2.30	$2TlS_2\overline{POCH_2C(C_2H_5)_2CH_2O}$ 3.37	84	165–8 dec.	48.15 (47.60)	14.49 (14.90)
3	$Tl_2CO_3 + 2HS_2\overline{POCH(CH_3)(CH_3)CHO}$ 3.20 2.51	$2TlS_2\overline{POCH(CH_3)(CH_3)CHO}$ 4.50	85	184	51.51 (52.76)	16.27 (16.52)
4	$Tl_2CO_3 + 2NH_4S_2\overline{POC(CH_3)_2(CH_3)_2CO}$ 1.70 1.75	$2TlS_2\overline{POC(CH_3)_2(CH_3)_2CO}$ 2.63	87	186–90 dec.	49.60 (49.21)	15.27 (15.41)
5	$TlOCOCH_3 + NH_4S_2\overline{POC(CH_3)_2CH_2(CH_3)CHO}$ 1.95 1.80	$TlS_2\overline{POC(CH_3)_2CH_2(CH_3)CHO}$ 2.92	95	175 dec.	48.92 (49.21)	15.66 (15.41)

6	$TlOCOCH_3 + NaS_2P[OCH(CH_3)_2]_2$ 5.63 5.09		$TlS_2P[OCH(CH_3)_2]_2$ 7.70	86	124	48.17 (48.97)	14.89 (15.33)
7	$Tl_2CO_3 + 2NaS_2P(OC_2H_5)_2$ 2.20 2.00		$2TlS_2P(OC_2H_5)_2$ 3.05	85	86	51.77 (52.49)	16.17 (16.43)
8	$Tl_2O_3 + 6NH_4S_2\overline{POC(CH_3)_2CH_2(CH_3)CHO}$ 1.17 3.59	(i)	$2TlS_2\overline{POC(CH_3)_2CH_2(CH_3)CHO}$ 1.65	79	175 dec.	50.44 (49.21)	15.75 (15.41)
		(ii)	$2[S\overline{POC(CH_3)_2CH_2(CH_3)CHO}]_2S_2$ 2.00	92	148	–	30.83 (30.33)
9	$Tl_2O_3 + 6NH_4S_2\overline{POCH_2C(CH_3)_2CH_2O}$ 0.95 2.80	(i)	$2TlS_2\overline{POCH_2C(CH_3)_2CH_2O}$ 1.48	88	260–64 dec.	50.25 (50.67)	15.70 (15.94)
		(ii)	$2[S\overline{POCH_2C(CH_3)_2CH_2O}]_2S_2$ 1.35	82	63	–	32.18 (32.48)
10	$Tl_2O_3 + 6NH_4S_2\overline{POC(CH_3)_2(CH_3)CO}$ 0.50 1.84	(i)	$2TlS_2\overline{POC(CH_3)_2(CH_3)_2CO}$ 0.81	76	186–89 dec.	49.29 (49.21)	15.86 (15.41)
		(ii)	$2[S\overline{POC(CH_3)_2(CH_3)_2CO}]_2S_2$	78	135 dec.	–	30.70 (30.33)
11	$TlCl_3 + 3NaS_2P[OCH(CH_3)_2]_2$ (From 2.38 g TlCl) 7.09 3.08	(i)	$TlS_2P[OCH(CH_3)_2]_2$ 2.70 (crystallized)	67	124	48.17 (48.97)	15.14 (15.33)
		(ii)	$[SPCOCH(CH_3)_2]_2S_2$ 2.81 (crystallized)	79	86	–	29.17 (30.05)
12	$2NH_4S_2\overline{POCH_2C(CH_3)_2CH_2O} + I_2$ 3.02 1.82		$[S\overline{POCH_2C(CH_3)_2CH_2O}]_2S_2$ 2.55	92	63	–	31.02 (32.48)
13	$2NH_4S_2\overline{POC(CH_3)_2(CH_3)_2CO} + I_2$ 2.22 1.29		$[S\overline{POC(CH_3)_2(CH_3)_2CO}]_2S_2$ 1.70	83	135 dec.	–	29.44 (30.33)
14	$2NH_4S_2\overline{POC(CH_3)_2CH_2(CH_3)CHO} + Br_2$ 2.85 0.99		$[S\overline{POC(CH_3)_2CH_2(CH_3)CHO}]_2S_2$ 2.52	96	148	–	30.06 (30.33)
15	$AsCl_3 + TlS_2P(OC_2H_5)_2$ 1.22 2.63		$Cl_2AsS_2P(OC_2H_5)_2$ 2.20	99	yellow liquid	% As, 22.93 (22.67)	19.26 (19.34)
16	$AsCl_3 + 3TlS_2P(OC_2H_5)_2$ 0.41 2.63		$As[S_2P(OC_2H_5)_2]_3$ 1.40	99	52	% As, 11.62 (11.91)	30.32 (30.48)

which was obtained after filtration and drying. *Anal.* Calcd. for $C_6H_{12}O_2PS_2Tl$: Tl, 49.21; S, 15.41%. Found: Tl, 50.44; S, 15.75%. M.p. 175° dec. On drying, the benzene filtrate gave a light yellow solid (2.00 g) which was crystallized from mixture of chloroform and n-hexane. *Anal.* Calcd. for $C_{12}H_{24}O_4P_2S_4$: S, 30.33%. Found: S, 30.83%. M.p. 148 °C.

Similar reactions (Table I) were carried out with ammonium neopentylenedithiophosphate and pinacoldithiophosphate.

5. Preparation (for Comparison) of Hexylenethiophosphoryl Disulphide by the Reaction of Ammonium Hexylenedithiophosphate with Bromine in 2:1 Molar Ratio

To a suspension of ammonium hexylenedithiophosphate (2.85 g, 12.45 mmol) in ~40 ml chloroform, a solution of bromine (0.99 g, 6.19 mmol) in ~30 ml chloroform was added dropwise and the reaction mixture was stirred for ~2 hrs. The resulting white precipitate of NH_4Br (1.20 g) was filtered. Removal of the solvent from the filtrate under reduced pressure gave the desired compound (2.51 g) as a white solid. It was crystallized (80% yield) from a mixture of chloroform and n-hexane. *Anal.* Calcd. for $C_{12}H_{24}O_4P_2S_4$: S, 30.33%. Found: S, 30.06%. M.p. 148 °C.

Disulphides of ammonium pinacoldithiophosphate and neopentylenedithiophosphate were also prepared using iodine as an oxidizing agent (Table I).

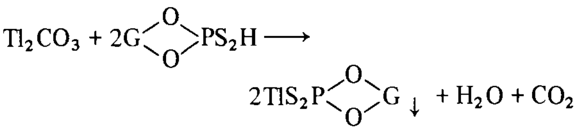
6. Ligand Exchange Reaction of Thallium(I) Diethyldithiophosphate with $AsCl_3$ in 1:1 Molar Ratio

To arsenic trichloride (1.22 g, 6.71 mmol) dissolved in benzene (~30 ml), a solution of thallium(I) diethyldithiophosphate (2.63 g, 6.73 mmol) in hot toluene (~30 ml) was added when TlCl (1.60 g) was immediately precipitated. The supernatant light yellow liquid was decanted, the precipitate was washed with benzene and the washings were mixed with the decanted liquid. The solvent was removed under reduced pressure leaving a light yellow liquid (2.22 g, 99% yield) which on analysis corresponded to $Cl_2AsS_2P(OEt)_2$. *Anal.* Calcd. for $C_4H_{10}O_2PS_2AsCl_2$: As, 22.64; S, 19.34%. Found: As, 22.92; S 19.26.

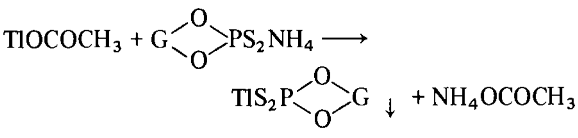
The reaction was also carried out in 1:3 molar ratio yielding $As[S_2P(OEt)_2]_3$ and TlCl (Table I).

Results and Discussion

Thallium(I) alkylenedithiophosphates are precipitated in almost quantitative yields by reactions of thallium(I) acetate or carbonate with ammonium alkylenedithiophosphates in aqueous medium or the parent acids in alcoholic solution:



$$Tl_2CO_3 + 2G\langle{}^{O}_{O}\rangle PS_2H \longrightarrow 2TlS_2P\langle{}^{O}_{O}\rangle G \downarrow + H_2O + CO_2$$



$$TlOCOCH_3 + G\langle{}^{O}_{O}\rangle PS_2NH_4 \longrightarrow TlS_2P\langle{}^{O}_{O}\rangle G \downarrow + NH_4OCOCH_3$$

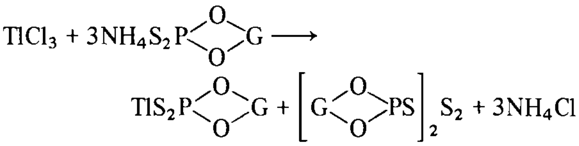
[where G = $-CH_2C(CH_3)_2CH_2-$, $-CH_2C(C_2H_5)_2CH_2-$, $-CHCH_3CHCH_3$, $-C(CH_3)_2C(CH_3)_2$ and $-C(CH_3)_2CH_2CHCH_3-$].

All these compounds are white, high melting point solids fairly stable in air and water. The compounds are insoluble in common organic solvents like benzene, n-hexane, light petroleum and chloroform, but dissolve in pyridine and DMF from which they can be recovered unchanged. Molar conductances of the derivatives in DMF were found in the range 3–8 ohm^{-1} cm^2 mol^{-1}, indicating their non-ionic nature [17, 18].

In view of conflicting reports in the literature on the stability of thallium(III) dialkyldithiophosphate [11, 12], we have re-investigated the reaction of $TlCl_3$ with $(i\text{-}C_3H_7O)_2PS_2Na$ in 1:3 molar ratio in CH_3CN. The products obtained from this reaction at room temperature are thallium(I) diisopropyldithiophosphate and diisopropylthiophosphoryl disulphide:

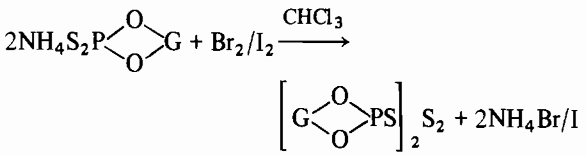
$$TlCl_3 + 3(i\text{-}C_3H_7O)_2PS_2Na \xrightarrow{CH_3CN} TlS_2P(OC_3H_7\text{-}i)_2 + [(i\text{-}C_3H_7O)_2PS]_2S_2 + 3NaCl$$

The same thallium(I) derivative could be prepared by a reaction of thallium(I) acetate with sodium diisopropyldithiophosphate in aqueous medium. Similar attempts to synthesize Tl(III) alkylenedithiophosphates (from Tl_2O_3 in HCl) were also unsuccessful and we could only isolate Tl(I) alkylenedithiophosphates and the corresponding disulphides which were separated by treating the mixture with benzene, in which only the disulphide portion dissolved. The disulphides were characterized and compared with authentic samples obtained by oxidizing the corresponding ammonium alkylenedithiophosphates directly with iodine/bromine in $CHCl_3$ solution:



$$TlCl_3 + 3NH_4S_2P\langle{}^{O}_{O}\rangle G \longrightarrow TlS_2P\langle{}^{O}_{O}\rangle G + \left[G\langle{}^{O}_{O}\rangle PS\right]_2 S_2 + 3NH_4Cl$$

[where G = $-C(CH_3)_2CH_2CHCH_3-$, $-C(CH_3)_2C(CH_3)_2-$ and $-CH_2C(CH_3)_2CH_2-$]



[where G = $-C(CH_3)_2CH_2CHCH_3-$, $-C(CH_3)_2C(CH_3)_2-$ and $-CH_2C(CH_3)_2CH_2-$]

The formation of the disulphide in the reaction of $TlCl_3$ with 3 mole of ammonium alkylenedithiophosphates indicates that the Tl(III) derivative is formed first, and then dissociates into the Tl(I) derivative and the corresponding disulphide. No indication of any reverse reaction could be observed on prolonged heating of a mixture of Tl(I) diisopropyldithiophosphate and corresponding disulphide in toluene; a similar reaction converting Tl(I) to Tl(III) has been reported [10] in the dithiocarbamate series:

$$TlS_2CNR_2 + [R_2NCS]_2S_2 \longrightarrow Tl[S_2CNR]_3$$

The utility of Tl(I) dialkyldithiophosphates in synthesizing other metal dialkyldithiophosphates has been demonstrated. The advantage over choosing Tl(I) dialkyldithiophosphates in place of alkali metal dialkyldithiophosphates is the immediate precipitation of granular TlCl which settles in the reaction mixture and can be more easily separated:

$$AsCl_3 + n(C_2H_5O)_2PS_2Tl \longrightarrow Cl_{3-n}As[S_2P(OC_2H_5)_2]_n + nTlCl$$

(where n = 1 and 3)

Spectroscopic Studies

The bands present in the regions 1060–1000 cm^{-1} and 895–810 cm^{-1} in the IR spectra of thallium(I) alkylenedithiophosphates may be assigned to (P)–O–C and P–O–(C) stretching vibrations respectively [19]. The bands in the region 990–900 cm^{-1} may be attributed to the ring vibrations of the dioxaphospholanes and dioxaphosphorinanes [20, 21] which are probably coupled with C–C stretching vibrations. A sharp peak present in the region 700–620 cm^{-1} is due to $\nu_{P=S}$ vibrations and the bands present in the region 630–490 cm^{-1} may be assigned to P–S asymmetric and symmetric vibrations [22].

^1H NMR spectra of representative compounds, recorded in pyridine (Table II), were in accordance with the proposed formulae. NMR signals for protons at the α-carbon of P–O–C skeleton are doubled, due to coupling with ^{31}P nucleus. Decoupled ^{31}P NMR spectra of Tl(I) alkylenedithiophosphates (in DMF) and Tl(I) dialkyldithiophosphates (as well as disulphides in $CDCl_3/CCl_4$) show a singlet at 80–117 δ ppm (Table II). It was observed that ^{31}P NMR chemical shifts are higher for compounds having dioxaphospholane rings than in compounds having dioxaphosphorinane rings. Glidewell's [23] classification does not appear to hold in the case of thallium(I) alkylenedithiophosphates, as the ^{31}P chemical shifts in these cases lie in the range indicative of an ionic nature of the derivatives, which is not corroborated by their low molar conductance in DMF. The insolubility of these derivatives (in contrast to open chain compounds) in organic solvents could there-

TABLE II. Molar Conductance and NMR (^1H and ^{31}P) Studies of Some Tl(I) Alkylenedithiophosphates and Disulphides.

Sl. No.	Compound	Molar conductance in 0.001 *M* DMF soln. ($ohm^{-1}\ cm^2\ mol^{-1}$)	^{31}P NMR (decoupled) chemical shifts δ ppm	^1H NMR chemical shifts, δ ppm
1	$TlS_2\overline{POCH_2C(CH_3)_2CH_2O}$	7.94		
2	$TlS_2\overline{POCH_2C(C_2H_5)_2CH_2O}$	8.14	112.74	
3	$TlS_2\overline{POCH(CH_3)(CH_3)CHO}$	8.88	115.83	0.40–0.50d, $6H(-CH_3)$; 3.28–3.48m, 2H(OCH)
4	$TlS_2\overline{POC(CH_3)_2(CH_3)_2CO}$	5.92	117.65	0.75s $(-CH_3)_2$
5	$TlS_2\overline{POC(CH_3)_2CH_2(CH_3)CHO}$	3.70	97.33	
6	$TlS_2P(OC_2H_5)_2$		98.62	1.24–1.50t, $6H(-CH_3)$, 3.90–4.40q, $4H(-OCH_2)-$
7	$TlS_2P[OCH(CH_3)_2]_2$		96.01	1.30–1.60d, $12H(-CH_3)$; 4.40–5.20m, 2H(-OCH)
8	$[S\overline{POCH_2C(CH_3)_2CH_2O}]_2S_2$		80.83	0.90s, $12H(-CH_3)$; 3.10–4.10m, $8H(OCH_2)$
9	$[S\overline{POC(CH_3)_2(CH_3)_2CO}]_2S_2$		97.99	1.35s $(CH_3)_2$
10	$[S\overline{POC(CH_3)_2CH_2(CH_3)CHO}]_2S_2$		80.04	1.15–1.70m, $22H[C(CH_3)_2CH_2(CH_3)C]$, 4.80–5.10m, 2H(OCH)

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

fore be ascribed to the chelating character of the ligands.

Acknowledgement

One of the authors (R.A.) is grateful to the University Grants Commission, New Delhi, for awarding senior research fellowship.

References

1 H. Gilman and R. K. Abbott, *J. Am. Chem. Soc., 71*, 657 (1939).

2 C. R. Lucas and M. E. Peach, *Inorg. Nucl. Chem. Lett., 5*, 73 (1969).

3 S. Akerstrom, *Acta Chem. Scand., 18*, 824 (1964).

4 F. M. Tulyupa, Yu. I. Usatenko and V. S. Berkalov, *Zhur. Neorg. Khim., 13*, 3227 (1968).

5 F. Bonati, S. Cenini and R. Ugo, *J. Organomet. Chem., 2*, 395 (1967).

6 J. R. A. Anderson, *Roy. Australian Chem. Inst. J. and Proc., 17*, 120 (1950).

7 L. Nilson and R. Hesse, *Acta Chem. Scand., 23*, 951 (1969).

8 F. Feigl, *Nature, 161*, 436 (1948).

9 E. Hoyer, W. Dietzsch, H. Muller, A. Zschunke and W. Schroth, *Inorg. Nucl. Chem. Lett., 3*, 457 (1967).

10 S. Akerstrom, *Arkiv. Kemi., 24*, 495 (1965).

11 H. Bode and W. Arnswald, *Z. Anal. Chem., 185*, 179 (1962).

12 F. Bonati and G. Mingetti, *Inorg. Chim. Acta, 3*, 161 (1969).

13 W. Szezepamiak, B. Juskowiak and K. Ran, *Pol. J. Chem., 53*, 755 (1979).

14 H. P. S. Chauhan, C. P. Bhasin, G. Srivastava and R. C. Mehrotra, *Phosphorus and Sulphur, 15*, 99 (1983).

15 F. A. Cotton, B. F. G. Johnson and R. M. Wing, *Inorg. Chem., 4*, 502 (1977).

16 C. N. Rowe, J. J. Diekert, *ASLE Trans., 10*, 85 (1967).

17 J. A. Walmsley and S. Y. Tyree, *Inorg. Chem., 2*, 312 (1963).

18 D. J. Phillips and S. Y. Tyree, *J. Am. Chem. Soc., 83*, 1806 (1961).

19 D. E. C. Corbridge, 'Topics in Phosphorus Chemistry', *6*, 235 (1969).

20 J. Casdeon, W. N. Baxter and W. DeAcetis, *J. Org. Chem., 24*, 247 (1959).

21 R. A. Y. Jones and A. R. Katritzky, *J. Chem. Soc.*, 4376 (1960).

22 C. P. Bhasin, G. Srivastava and R. C. Mehrotra, *Inorg. Chim. Acta, 77*, L131 (1983).

23 C. Glidewell, *Inorg. Chim. Acta, 25*, 159 (1977).