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TRI- AND DI-PHENYL LEAD (IV) O,O-ALKYLENEDITHIOPHOSPHATES

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Tri- and di-phenyl lead (IV) O,O-alkylenedithiophosphates, $\text{Ph}_{4-n}\text{Pb}(\text{S}_2\text{PO}_2\text{G})_n$ (Where $\text{G} = -\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2-$, $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2-$, and $-\text{CHCH}_3\text{CH}_2\text{C}(\text{CH}_3)_2-$; $n = 1, 2$) were synthesized by treatment of organolead (IV) chlorides with ammonium O,O-alkylenedithiophosphates in benzene. These are white solids. All of these are miscible in common organic solvents and monomeric in refluxing benzene. Like dialkyldithiophosphate derivatives of organolead these also appear to be tetrahedral with ligands behaving in a unidentate manner.

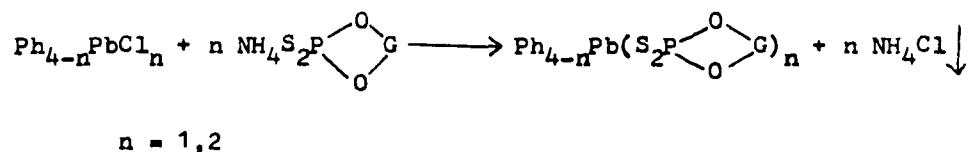
Key words: Organolead; dithiophosphate; unidentate; tetrahedral; spectral studies.

INTRODUCTION

A considerable amount of work carried out on O,O-alkylenedithiophosphate derivatives of organotin(IV), -silicon(IV) and -germanium(IV) in recent years¹⁻⁵ has revealed interesting coordination modes of the dithioligands, e.g. they have been shown to behave as monodentate species towards organosilicon⁴ and -germanium⁵ and triorganotin(IV) moieties¹ whereas these bind diorganotin(IV) as well as mono-organotin(IV) moieties in a bidentate manner. In view of their interesting structural properties, we have extended these investigations to the corresponding alkylene-dithiophosphates of organolead(IV) moieties. In continuation of our earlier work, we report the synthesis and structural investigations of some organolead(IV) O,O-alkylenedithiophosphates in this communication.

RESULTS AND DISCUSSION

Tri- and di-phenyl lead(IV) O,O-alkylenedithiophosphates have been prepared by the mathematical reaction between phenyl lead(IV) chlorides and the ammonium salt of O,O-alkylenedithiophosphates in benzene.

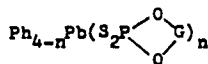


$\text{G} = -\text{CHCH}_3\text{CH}_2\text{C}(\text{CH}_3)_2-$, $-\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2-$ and $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2-$

TABLE I
Reactions of phenyl lead(IV) chlorides with ammonium O,O-alkylenedithiophosphates reaction to (g)

$\text{Ph}_4\text{-n PbCl}_n$	$\text{H}_4\text{NS-P-O-G}$ G=	Molar ratio	Product, m.p. (Physical state)	Yield (%)	Analysis Found (calcd)	%Pb	% S
$(\text{C}_6\text{H}_5)_3\text{PbCl}$ 1.64	$-\text{C}(\text{CH}_3)_2\overset{\text{I}}{\text{C}}(\text{CH}_3)_2$ 0.82	1:1	$(\text{C}_6\text{H}_5)_3\text{PbS}_2\text{POC}(\text{CH}_3)_2\overset{\text{I}}{\text{C}}(\text{CH}_3)_2\text{O}$ 139-141 (White solid)	89	31.74 (31.88)	9.70 (9.85)	
$(\text{C}_6\text{H}_5)_3\text{PbCl}$ 1.21	$-\text{C}(\text{CH}_3)_2\text{CH}_2\overset{\text{I}}{\text{CHCH}_3}$ 0.64	1:1	$(\text{C}_6\text{H}_5)_3\text{PbS}_2\text{POC}(\text{CH}_3)_2\text{CH}_2\overset{\text{I}}{\text{CHCH}_3}\text{O}$ 140-145 (White solid)	81	31.68 (31.88)	9.62 (9.85)	
$(\text{C}_6\text{H}_5)_3\text{PbCl}$ 1.13	$-\text{CH}_2\overset{\text{I}}{\text{C}}(\text{CH}_3)_2\text{CH}_2$ 0.56	1:1	$(\text{C}_6\text{H}_5)_3\text{PbS}_2\text{POCH}_2\overset{\text{I}}{\text{C}}(\text{CH}_3)_2\text{CH}_2\text{O}$ 119-121 (White solid)	94	33.18 (32.58)	9.94 (10.07)	
$(\text{C}_6\text{H}_5)_2\text{PbCl}_2$ 0.66	$-\text{C}(\text{CH}_3)_2\overset{\text{I}}{\text{C}}(\text{CH}_3)_2$ 0.76	1:2	$(\text{C}_6\text{H}_5)_2\text{Pb[S}_2\text{POC}(\text{CH}_3)_2\overset{\text{I}}{\text{C}}(\text{CH}_3)_2\text{O}]_2$ 112-115 (White solid)	74	26.48 (26.43)	16.22 (16.34)	
$(\text{C}_6\text{H}_5)_2\text{PbCl}_2$ 0.61	$-\text{C}(\text{CH}_3)_2\text{CH}_2\overset{\text{I}}{\text{CHCH}_3}$ 0.66	1:2	$(\text{C}_6\text{H}_5)_2\text{Pb[S}_2\text{POC}(\text{CH}_3)_2\text{CH}_2\overset{\text{I}}{\text{CHCH}_3}\text{O}]_2$ 145-146 (White solid)	92	26.29 (26.43)	16.34 (16.34)	
$(\text{C}_6\text{H}_5)_2\text{PbCl}_2$ 0.49	$-\text{CH}_2\overset{\text{I}}{\text{C}}(\text{CH}_3)_2\text{CH}_2$ 0.49	1:2	$(\text{C}_6\text{H}_5)_2\text{Pb[S}_2\text{POCH}_2\overset{\text{I}}{\text{C}}(\text{CH}_3)_2\text{CH}_2\text{O}]_2$ 154-155 (White solid)	79	27.40 (27.41)	16.67 (16.94)	

TABLE II
Infrared spectral data (cm^{-1}) of Phenyl lead(IV) O,O-alkylenedithiophosphates



Compound	$\nu(\text{P})-\text{O}-\text{C}$	$\nu\text{P}-\text{O}-(\text{C})$	Ring vibration.	$\nu(\text{P}-\text{S})$	$\nu(\text{P}-\text{S})$	$\nu(\text{Pb}-\text{C})$	$\nu(\text{Pb}-\text{S})$
$(\text{C}_6\text{H}_5)_3\text{PbS}_2\overline{\text{POCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}}$	1070	810	980	710	-	500	430
$(\text{C}_6\text{H}_5)_3\text{PbS}_2\overline{\text{POC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}}$	1070	850	920	730	630	-	450
$(\text{C}_6\text{H}_5)_3\text{PbS}_2\overline{\text{POC}(\text{CH}_3)_2\text{CH}_2\text{CHCH}_3\text{O}}$	1050	890	960	700	600	520	450
$(\text{C}_6\text{H}_5)_2\text{Pb}[\text{S}_2\overline{\text{POC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}}]_2$	-	850	925	720	605	490	440
$(\text{C}_6\text{H}_5)_2\text{Pb}[\text{S}_2\overline{\text{POC}(\text{CH}_3)_2\text{CH}_2\text{CHCH}_3\text{O}}]_2$	1050	890	960	700	600	525	450
$(\text{C}_6\text{H}_5)_2\text{Pb}[\text{S}_2\overline{\text{POCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}}]_2$	1070	820	960	690	-	550	460

The reactions are quite facile and can be completed in 3–4 hours at room temperature by stirring the reactants. The yields of the products are almost quantitative.

These derivatives are white crystalline solids with sharp melting points. They are stable at room temperature, insensitive to atmospheric oxygen and moisture. All the derivatives are sparingly soluble in common organic solvents. The molecular weight in refluxing benzene, indicate their monomeric nature in solution.

INFRARED SPECTRA

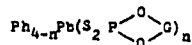
The infrared spectra of these phenyl lead(IV) O,O-alkylene-dithiophosphates have been recorded as nujol mulls in the region $4000\text{--}200\text{ cm}^{-1}$. The absorption frequencies (cm^{-1}) of diagnostic value and possible assignments are listed in Table II.

The bands appearing in the region $1050\text{--}1070$ and $810\text{--}890\text{ cm}^{-1}$ may be assignable to $\nu(\text{P})-\text{O}-\text{C}$ and $\nu\text{P}-\text{O}-(\text{C})$ stretching vibrations respectively on the basis of earlier assignments.^{6–8} Generally these stretching vibrations are coupled with the motions of the atoms in the vicinity.⁹

A sharp band in the region $690\text{--}720\text{ cm}^{-1}$ may be due to $\nu(\text{P}-\text{S})$ stretching vibrations,¹⁰ which overlaps with $\text{Pb}-\text{C}_6\text{H}_5$ vibrations in these phenyl lead(IV) O,O-alkylenedithiophosphates. The bands present in the region $600\text{--}630\text{ cm}^{-1}$ are due to $\nu(\text{P}-\text{S})$ vibrations.⁶ The bands in the region $920\text{--}980\text{ cm}^{-1}$ are due to dioxaphospholane and dioxaphosphorinane ring vibrations.^{11–12} These bands are generally present at the same position as in ligands.

In the far IR region $\text{Pb}-\text{S}$ stretching bands appear at $430\text{--}460\text{ cm}^{-1}$ in agreement with earlier findings.^{13,14} All these assignments were made tentatively on the basis of earlier reports.^{7,8,15,16}

TABLE III
Proton nuclear magnetic resonance spectra of few phenyl lead(IV) O,O-alkylenedithiophosphate



Compound	Chemical Shift δ (ppm)
$(\text{C}_6\text{H}_5)_3\text{PbS}_2\text{POCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}$	7.1-8.1, m, 15H (Pb-C ₆ H ₅) 3.7-4.2, d, 4H (OCH ₂) 1.0, s, 6H (CH ₃)
$(\text{C}_6\text{H}_5)_3\text{PbS}_2\text{POC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}$	7.8-8.1, m, 15H (Pb-C ₆ H ₅) 1.2, s, 12H (CH ₃)
$(\text{C}_6\text{H}_5)_3\text{PbS}_2\text{POC}(\text{CH}_3)_2\text{CH}_2\text{CHCH}_3\text{O}$	7.2-8.0, m, 15H (Pb-C ₆ H ₅) 1.1-1.9, m, 11H (CH ₃ , CH ₂)
$(\text{C}_6\text{H}_5)_2\text{Pb}[\text{S}_2\text{POC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}]_2$	7.2-8.5, m, 10H (Pb-C ₆ H ₅) 1.5, s, 24H (CH ₃)

NUCLEAR MAGNETIC RESONANCE SPECTRA

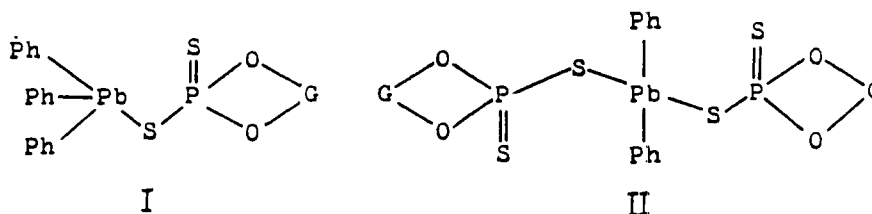
The ¹H NMR spectra of the new derivatives have been recorded in CDCl₃ and values of observed chemical shifts are tabulated in Table III.

Proton NMR spectra of some representative derivatives exhibit two groups of signals; a multiplet due to phenyl protons at 7.1-8.5 ppm and singlet or multiplet due to alkylene protons. The protons attached to oxygen atom appear at lower field than the other alkylene protons.

The ³¹P NMR spectrum of one representative compound i.e. Ph₃PbS₂P(=O)(OMe)₂ was recorded and chemical shift value occur at 111.52 ppm. The chemical shift difference between ligand and the complex is less i.e., 16 ppm. Such small changes can be attributed to bond polarity and to the electron withdrawing nature of the phenyl group, which effects —bonding with phosphorus. It is therefore difficult to comment on the nature of ligand in these phenyl lead(IV) O,O-alkylenedithiophosphates only on the basis of such small chemical shifts differences.

STRUCTURAL INFORMATION

These organolead(IV) O,O-alkylenedithiophosphates do not exhibit any remarkable shift from the $\nu(\text{P}=\text{S})$ absorption of the corresponding ligand, as observed in the case of other chelated derivatives of O,O-alkylenedithiophosphoric acid of other metals.¹⁷⁻²⁰ In view of the above and monomeric nature of these derivatives the following ester type structures have been proposed tentatively:



These structures were further supported by the fact that corresponding organolead(IV) dithiocarbamates,¹³ -dithiocarboxylates¹⁴ and -dithiophosphates²¹ were given similar structures on the basis of IR and NMR spectral studies.

EXPERIMENTAL

The O,O-alkylenedithiophosphoric acids and their ammonium salts were prepared by a reported method.¹⁰ Sulfur was estimated as barium sulfate and lead as the lead sulfate.

Molecular weights were determined ebullioscopically. ¹H and ³¹P NMR spectra in CDCl₃ were recorded using TMS and H₃PO₄ as references, respectively. IR spectra were recorded as nujol mulls.

Reaction of phenyl lead(IV) chloride with ammonium O,O-alkylenedithiophosphate in desired molar ratio. A solution of phenyl lead(IV) chloride was added to the suspension of ammonium O,O-alkylene dithiophosphate in benzene. The mixture was stirred for 3–4 hrs, then the solid was allowed to settle. After filtration, the solvent was evaporated under reduced pressure to leave a solid, which was purified by crystallization using benzene-Petroleum ether (40°–60°) mixture.

Details of synthesis of the individual compounds are listed in Table I.

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REFERENCES

1. R. J. Rao, G. Srivastava and R. C. Mehrotra, *J. Organometal Chem.*, **258**, 155 (1983).
2. R. J. Rao, G. Srivastava, R. C. Mehrotra, B. S. Saraswat and J. Mason, *Polyhedron*, **3**, 485 (1984).
3. R. J. Rao, G. Srivastava and R. C. Mehrotra, *Phosphorus and Sulfur*, **25**, 183 (1985).
4. R. J. Rao, G. Srivastava and R. C. Mehrotra, *Inorg. Chim. Acta*, **111**, 163 (1985).
5. R. J. Rao, *Phosphorus, Sulfur and Silicon*, **53**, 203 (1990).
6. B. P. Singh, G. Srivastava and R. C. Mehrotra, *Synth. React. Inorg. Met. Org. Chem.*, **12**, 145 (1982).
7. O. M. Adam and J. B. Cornell, *J. Chem. Soc. A.*, 1299 (1968).
8. D. E. C. Gorbridge "Topics in Phosphorus Chemistry," **6**, 235 (1969).
9. W. Rudzinski, G. T. Behnke and Q. Fernando, *Inorg. Chem.*, **16**, 1206 (1977).
10. H. P. S. Chauhan, C. P. Bhasin, G. Srivastava and R. C. Mehrotra, *Phosphorus and Sulfur*, **15**, 99 (1983).
11. J. Cason, W. N. Paxter and W. De Acetis, *J. Org. Chem.*, **24**, 247 (1959).
12. R. A. Y. Jones and A. R. Katritsky, *J. Chem. Soc.*, 4376 (1960).
13. T. N. Srivastava, V. Kumar and A. Bhargava, *J. Inorg. Nucl. Chem.*, **40**, 347 (1978).
14. S. Kato, A. Hori, M. Sheotani, M. Mizuta, N. Hayashi and T. Takakuwa, *J. Organometal Chem.*, **82**, 223 (1974).
15. J. R. Wasson, C. M. Wolterman and H. J. Stoklosa, *Top Curr. Chem.*, **35**, 65 (1973).
16. L. J. Bellamy, *Infrared Spectra of Complex Molecules*, p. 311, Methuen & Co., Ltd., London (1966).
17. R. K. Gupta, A. K. Rai and R. C. Mehrotra, *Inorg. Chim. Acta*, **88**, 197 (1984).
18. C. P. Bhasin, G. Srivastava and R. C. Mehrotra, *Inorg. Chim. Acta*, **77**, 131 (1983).
19. C. P. Bhasin, G. Srivastava and R. C. Mehrotra, *Inorg. Chim. Acta*, **128**, 69 (1987).
20. C. P. Bhasin, G. Srivastava and R. C. Mehrotra, *Inorg. Chim. Acta*, **131**, 195 (1987).
21. A. N. Pudovik, R. A. Cherkasov and I. V. Shergina, *Zh. Obshch. Khim.*, **41**, 1472; *Chem. Abstr.*, **75**, 140947 (1971).