



Synthesis and Spectroscopic Characterization of Lead(II)bis{*O,O'*-ditolyldithiophosphates} and their Adducts with 2,2'-Bipyridyl and 1,10-Phenanthroline

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Abstract: The reaction of lead(II) dichloride with ammonium salts of *O,O'*-ditolyldithiophosphoric acid have been carried out in 1:2 molar ratio by refluxing in benzene. These compounds have been further used to synthesize the adduct of the type lead(II)bis{*O,O'*-ditolyldithiophosphates}.2,2'-bipyridyl and lead(II)bis {*O,O'*-ditolyldithiophosphates}.1,10-phenanthroline by the reaction of lead(II)bis{*O,O'*-ditolyldithiophosphates} and 2,2'-bipyridyl and 1,10-phenanthroline in the presence of unimolar dichloromethane and ethanol. All these complexes have been characterized by spectroscopic techniques such as IR, ¹H NMR and ³¹P NMR. On the basis of spectroscopic studies tetraordinated nature of lead atom in ditolyldithiophosphates complexes and hexacoordinated nature in their adducts have been established.

Keywords: Lead chloride, *O,O'*-di(*o*-, *m*-, *p*- tolyl)dithiophosphates, 1,10-Phenanthroline, 2,2'Bipyridyl

Introduction

The synthesis of coordination compounds with sulphur containing ligands has been an active area of research. Dialkyl and alkylene dithiophosphates have been widely used in industrial area¹⁻² and agricultural field³ such as pesticides⁴, herbicides, lubricative oil additives *etc.* They also show biological activity *i.e.* antitumour properties⁵. These ligands behave both as bridging as well as chelating ligands.

Dithiophosphates of lead complexes are also widely used in nature such as bis (2-ethylhexyldithiophosphate)lead is used as lubricating oil. Lead atom present in complexes in two oxidation state *i.e.* (II) and (IV). S atom of dithiophosphates donates it's lone pair of electrons to the lead atom and increases the oxidation state of lead. Thus, the dithiophosphates of

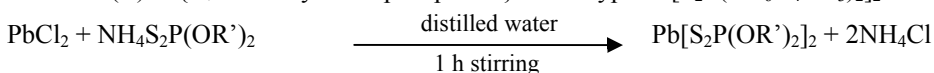
lead complexes formed mono-, bi-, tetra- and polynuclear complexes such as bis(diethylphosphorodithioato)lead(II)⁶ is tetragonal pyramid, bis(diisobutylphosphorodithioato)lead(II)⁶ forms dimer, bis(diisopropylphosphorodithioato) lead(II)⁷ is pentagonal pyramid.

Lead(IV) complexes present generally tetrahedral or distorted tetrahedral complexes *eg.* Ph₃PbSPh⁸ but some exceptions are also observed like Ph₃PbS₂P(OEt)₂⁸ forms trigonal bipyramidal and Ph₂Pb[S₂P(OPh)₂]₂⁸ forms distorted octahedral.

Lead complexes also form adducts. The structure of these adducts are either dimer or polymer depending upon stereochemical arrangements *eg.* Pb[S₂P(OEt)₂]₂.en⁹ (en = ethylene) {Pb[S₂P(OEt)₂]₂}₂.en⁹, Pb[S₂P(OEt)₂]₂.bipy⁹. (bipy. = bipyridine)

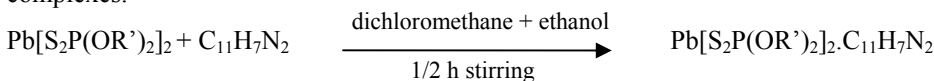
Experimental

Reactions of lead chloride and ammonium salts of *O,O'*-di(*o*-, *m*-, *p*- tolyl) dithiophosphates in 1:2 molar ratio in distilled water were carried out by stirring the mixture for about 1 h to form lead(II)bis{*O,O'*-ditolyldithiophosphates} of the type Pb[S₂P(OC₆H₄CH₃)₂]₂.

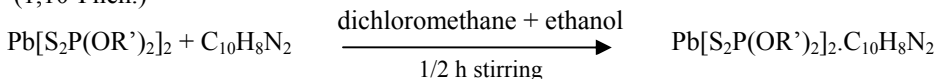


(R' = *o*-, *m*-, *p*- C₆H₄CH₃)

The newly synthesized compounds have been used to form corresponding adducts with 2,2'-bipyridyl and 1,10-Phenanthroline. Reaction of these lead complexes with amine in the presence of equimolar quantity of ethanol and dichloromethane yield the adduct of lead complexes.



(1,10-Phen.)



(2,2'-bipy.) (R' = *o*-, *m*-, *p*- C₆H₄CH₃)

Synthesis of lead(II)bis{*O,O'*-ditolyldithiophosphates} complexes

A mixture of lead(II) dichloride(0.23 g, 0.827 mmole) and ammonium salts of *O,O'*-ditolyldithiophosphoric acid(0.54 g, 1.67 mmole) is mixed in 1:2 molar ratio in minimum amount of distilled water and stirred about half an hour then filtered and dried. A yellow crystalline solid (0.64 g, 94%) was formed which was purified 3-4 times with dichloromethane. (Calcd. for C₂₈H₂₈O₄S₄P₂Pb: S, 39.09; C, 40.72; H, 3.39; Found: S, 38.92; C, 40.38; H, 3.26) All members of this series were synthesized in the same manner.

Synthesis of 1,10 phen. adducts of lead(II)bis{*O,O'*-ditolyldithiophosphates} complexes

A mixture of prepared lead complexes (0.61 g, 0.740 mmole) and amine {(1,10-phen.) (0.14 g, 0.740 mmole)} is mixed in 1:1 molar ratio in the equal amount of dichloromethane and ethanol and stirred at about half an hour and kept stand for about 24 h. White crystalline solid (0.69 g, 92%) was formed which was purified by ethanol. (Calcd. for C₄₀H₄₀O₄S₄P₂N₂Pb: S, 39.09; C, 46.92; H, 3.51; Found: S, 38.96; C, 46.42; H, 3.46) All members of this series were synthesized in the same manner.

Synthesis of 2,2'-bipy adducts of lead(II)bis{O,O'-ditolyldithio-phosphates} complexes

A mixture of prepared lead complexes (0.65 g, 0.793 mmole) and amine {(2,2'-bipy.) (0.12 g, 0.808 mmole)} is mixed in 1:1 molar ratio in the equal amount of dichloromethane and ethanol and stirred about half an hour which was kept stand about 24 h. White crystalline solid (0.75 g, 97%) formed which was purified by ethanol. (Calcd. for $C_{38}H_{36}O_4S_4P_2N_2Pb$: S, 39.09; C, 48.92; H, 3.51; Found: S, 39.01; C, 48.80; H, 3.45) All members of this series were synthesized in the same manner.

Results and Discussion

IR spectra

IR spectra of these compounds are assigned with the comparison of salts of O,O'-di(*o*-,*m*-,*p*-tolyl)dithiophosphates¹⁰⁻¹¹. Two strong intensity bands which are present in the region 1108-1274 cm^{-1} and 903-945 cm^{-1} are assigned to $\nu[(P)-O-C]$ and $\nu[P-O-(C)]$ stretching vibrations. Bands due to $\nu(P=S)$ or $\nu(P-S)$ asymmetric and $\nu(P=S)$ or $\nu(P-S)$ symmetric are observed at 670-530 and 550-450 cm^{-1} respectively. The lower shifting of 40-50 cm^{-1} as compared to corresponding O,O'-di(*o*-,*m*-,*p*-tolyl)dithiophosphoric acid indicates the coordination to the metal atom. The appearance of a new sharp band at 339.2-445 cm^{-1} , is assigned to $\nu(Pb-S)$ linkage.

Table 1. IR spectral data of lead(II)bis{O,O'-ditolyldithiophosphates} complexes

Compounds	$\nu[(P)-O-C]$	$\nu[P-O-(C)]$	$\nu(P=S)$	$\nu(P-S)$	$\nu(Pb-S)$
$Pb[S_2P(OC_6H_4CH_3-o)_2]_2$	1108(s)	910 (s)	680,596(m)	556 (m)	445(s)
$Pb[S_2P(OC_6H_4CH_3-m)_2]_2$	1121 (s)	928 (m)	690,598 (s)	450 (m)	440(s)
$Pb[S_2P(OC_6H_4CH_3-p)_2]_2$	1274 (s)	938 (s)	680,590(m)	473 (m)	444(s)
$Pb[S_2P(OC_6H_4CH_3-o)_2]_2$ $C_{11}H_7N_2$	1245 (s)	945 (s)	674,576 (s)	432 (m)	442(s)
$Pb[S_2P(OC_6H_4CH_3-m)_2]_2$ $C_{11}H_7N_2$	1250 (s)	931 (m)	667,569 (s)	417 (m)	445(s)
$Pb[S_2P(OC_6H_4CH_3-p)_2]_2$ $C_{11}H_7N_2$	1180 (b)	903 (b)	708,680(m)	442 (m)	440(s)
$Pb[S_2P(OC_6H_4CH_3-o)_2]_2$ $C_{10}H_8N_2$	1234 (s)	927 (s)	654,598(m)	462 (b)	339.5(s)
$Pb[S_2P(OC_6H_4CH_3-m)_2]_2$ $C_{10}H_8N_2$	1250 (s)	944 (s)	667,597(m)	417 (m)	339.2(s)
$Pb[S_2P(OC_6H_4CH_3-p)_2]_2$ $C_{10}H_8N_2$	1194 (s)	930 (m)	667,528(m)	472 (m)	443.8(s)

¹H NMR spectra

The ¹H NMR spectra was recorded in CDCl₃ solution. Data of lead(II)bis{O,O'-ditolyldithiophosphates} were similar to those of corresponding salts of dithiophosphates¹⁰⁻¹¹. The singlet of 2.0-2.2 ppm indicates the methyl proton which are attach to the benzene ring. The phenyl protons show multiplet at ~ 7.0 ppm.

Similarly the adduct of lead(II)bis{ditolyldithiophosphates}.2,2'-bipyridyl shows multiplet due to different type of hydrogen in the region 8.4-8.6 ppm in the pyridyl ring. The 1,10-phen. Adduct of these complexes also shows multiplet. The NMR signal is shift to the low field compare to the dithiophosphoric acid which shows the linkage of lead atom to the dithiophosphates.

Table 2. ^1H NMR and ^{31}P NMR spectral data of lead(II)bis{*O,O'*-ditolyldithiophosphates} complexes

Compound	^1H NMR (δ) ppm	^{31}P NMR (δ) ppm
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_2]_2$	2.2(s,6H,CH ₃),7.3(m,8H,C ₆ H ₄),	93.12
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}m)_2]_2$	2.2(s,6H,CH ₃),7.1(m,8H,C ₆ H ₄)	93.34
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_2$	2.2(s,6H,CH ₃),7.0(m,8H,C ₆ H ₄)	94.50
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_2]_2 \cdot \text{C}_{11}\text{H}_7\text{N}_2$	2.2(s,6H,CH ₃),7.0(m,8H,C ₆ H ₄) 8.5(m,7H, C ₁₁ H ₇ N ₂)	95.42
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}m)_2]_2 \cdot \text{C}_{11}\text{H}_7\text{N}_2$	2.2(s,6H,CH ₃),7.0(m,8H,C ₆ H ₄) 8.6(m,7H, C ₁₁ H ₇ N ₂)	99.09
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_2 \cdot \text{C}_{11}\text{H}_7\text{N}_2$	2.1(s,6H,CH ₃),7.1(m,8H,C ₆ H ₄) 8.4(m,7H, C ₁₁ H ₇ N ₂)	96.89
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_2]_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2$	2.1(s,6H,CH ₃),6.9(m,8H,C ₆ H ₄) 8.0(m,7H, C ₁₀ H ₈ N ₂)	98.83
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}m)_2]_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2$	2.1(s,6H,CH ₃),6.9(m,8H,C ₆ H ₄) 8.4(m,7H, C ₁₀ H ₈ N ₂)	100.16
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2$	2.1(s,6H,CH ₃),7.0(m,8H,C ₆ H ₄) 8.5(m,7H, C ₁₀ H ₈ N ₂)	98.38

 ^{31}P NMR

^{31}P NMR spectra were recorded in CDCl_3 . There is only one signal of the phosphorous atom which indicates that only one resonance peak of phosphorous is present in all of these complexes. ^{31}P NMR shows 93.12-100.16 ppm indicates the coordination of the dithiophosphates group to the metal centre in the molecule¹². The ^{31}P NMR of all these complexes is shifted to 11-15 ppm downfield as compare to the corresponding dithiophosphates indicates the anisobidentate nature of the dithiophosphate moieties.

Table 3. Synthesis and analytical data of ditolyldithiophosphatolead(II)complexes

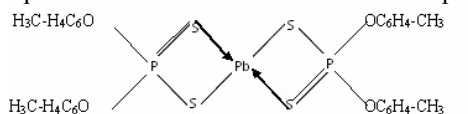
Reactant		Molar ratio	Product, g, %	Analysis		
(g, mmole)	(g, mmole)			Found C%	S%	(Calcd.) H%
$\text{NH}_4[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_2] + \text{PbCl}_2$	(0.54, 1.67) (0.23, 0.827)	1:2	$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_2]_2$ (0.64, 94%)	40.38 (40.72)	3.26 (3.39)	38.92 (39.09)
$\text{NH}_4[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}m)_2] + \text{PbCl}_2$	(0.61, 1.87) (0.26, 0.938)	1:2	$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}m)_2]_2$ (0.71, 92%)	40.45 (40.72)	3.21 (3.39)	38.89 (39.09)
$\text{NH}_4[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2] + \text{PbCl}_2$	(0.57, 1.74) (0.24, 0.870)	1:2	$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_2$ (0.68, 94%)	40.42 (40.72)	3.18 (3.39)	38.96 (39.09)
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_2] + \text{C}_{11}\text{H}_7\text{N}_2$	(0.61, 0.740) (0.14, 0.740)	1:1	$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_2]_2 \cdot \text{C}_{11}\text{H}_7\text{N}_2$ (0.69, 92%)	46.42 (46.92)	3.46 (3.51)	38.96 (39.09)
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}m)_2] + \text{C}_{11}\text{H}_7\text{N}_2$	(0.26, 0.320) (0.06, 0.320)	1:1	$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}m)_2]_2 \cdot \text{C}_{11}\text{H}_7\text{N}_2$ (0.30, 94%)	46.70 (46.92)	3.38 (3.51)	3.38 (3.51)

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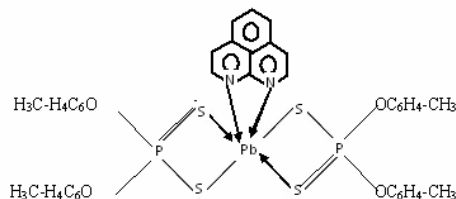
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_2^{+}$ $\text{C}_{11}\text{H}_7\text{N}_2(0.19, 0.240)$ (.04, 0.239)	1:1	$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_2$ $\text{C}_{11}\text{H}_7\text{N}_2(0.22, 92\%)$	46.58 (46.92)	3.29 (3.51)	38.85 (39.09)
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_2]_2^{+}$ $\text{C}_{10}\text{H}_8\text{N}_2(0.65, 0.793)$ (0.12, 0.808)	1:1	$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_2]_2$ $\text{C}_{10}\text{H}_8\text{N}_2(0.75, 97\%)$	48.80 (48.92)	3.45 (3.51)	39.01 (39.09)
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}m)_2]_2^{+}$ $\text{C}_{10}\text{H}_8\text{N}_2(0.37, 0.456)$ (0.07, 0.458)	1:1	$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}m)_2]_2$ $\text{C}_{10}\text{H}_8\text{N}_2(0.44, 93\%)$	48.46 (48.92)	3.21 (3.51)	38.94 (39.09)
$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_2^{+}$ $\text{C}_{10}\text{H}_8\text{N}_2(0.20, 0.246)$ (0.03, 0.246)	1:1	$\text{Pb}[\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_2$ $\text{C}_{10}\text{H}_8\text{N}_2(0.23, 96\%)$	48.65 (48.92)	3.54 (3.51)	39.03 (39.09)

Conclusion

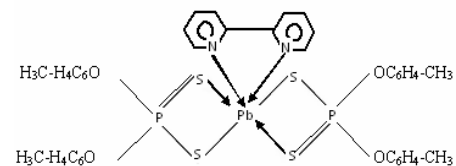
On the basis of spectroscopical data the structure of all these complexes are as follows:



Lead(II)bis{*O,O'*-ditolyldithiophosphates}



1,10-Phenanthroline adduct of lead(II)bis{*O,O'*-ditolyldithiophosphates}



2,2'-Bipyridyl adduct of lead(II)bis{*O,O'*-ditolyldithiophosphates}

Lead(II)bis{*O,O'*-ditolyldithiophosphates} complexes show distorted tetrahedral geometry and their adducts show distorted octahedral geometry.

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