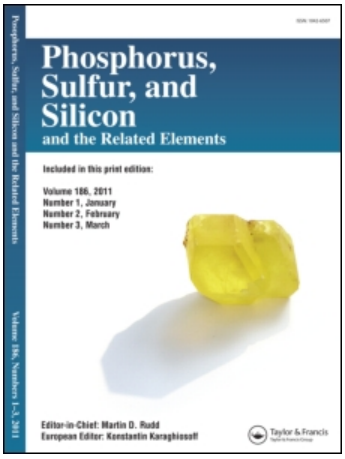

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Synthesis and Characterization of Some Novel Dialkyldithiophosphate Derivatives of Macrocyclic Complexes of Pb(II) Having N_2S_2 Potential Donors in 14- to 20-Membered Rings

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Dialkyldithiophosphate derivatives of macrocyclic complexes of Pb(II), having N_2S_2 potential donors, of the general formula, [Pb(L)S_2P(OR)$_2$] (where L = macrocyclic ligands L^1, L^2, L^3, L^4 & L^5 and R = CH_3-, $C_3H_7^n$- & $C_3H_7^i$-) have been Synthesized from the reactions of [Pb(L)X_2] (where X = Cl, NO_3, or CH_3COO) with sodium dialkyl dithiophosphates in 1:2 molar ratios in THF. Fifteen new derivatives have been synthesized by the combination of five macrocyclic complexes of 14–20 member rings with three different types of dialkyldithiophosphate. These compounds have been characterized by elemental analysis, molar conductance, molecular weight determination, IR, ^1H NMR, ^{13}C, and ^{31}P NMR. Molecular weight determinations of these complexes indicate their monomeric nature. An octahedral structure is proposed.

Keywords Dialkyldithiophosphates; macrocyclic complexes; mixed ligand complexes; Pb(II)

INTRODUCTION

The chemistry of macrocyclic ligands is a fascinating area of intense study for inorganic chemists. The possibility to tailor-make different types of macrocycles for specific use has promoted much of this interest. Among others, these uses include for biological systems, therapeutic reagents for the treatment of metal intoxication, synthetic ionophores, and the selective extraction of heavy and precious metals.[1–4] On the other hand, mixed ligand complexes have also played a vital role in burgeoning inorganic chemistry during the last few decades. Their uses in biological systems as a synthetic model; their novel structural

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features; and their unusual magnetic properties are the main focus of their importance.[5–15] In spite of vast innovation in macrocyclic chemistry and tremendous interest in mixed ligand complexes, no macrocyclic complex having mixed ligands system was reported until our publications. In the above publication we reported synthesis, characterization, biocidal, and catalytic aspects of mixed ligand macrocyclics complexes of Mn(II), Fe(III), Co(III), and Ni(II) with dialkyl- and alkylene dithiophosphates.[16–25]

Considering the interesting results obtained during the course of our previous investigations, we planned to extend the above work to the main group of metals, as well. Therefore, in continuation to our earlier work, we hereby report the synthesis, characterization and biocidal aspects of dialkyldithiophosphate derivatives of marcocyclic complexes of Pb(II), which are again the first example of mixed ligand macrocyclic complexes of main group metals.

EXPERIMENTAL

Materials

All of the lead salts and dicarboxylic acids of analytical reagent grade were obtained from S,d-fine chemicals (Mumbai, India) and were used without further purification. *o*-Aminothiophenol was used as obtained from Merck (Germany and U.K.). Solvents were purified and dried by standard methods.

Microanalysis for carbon, hydrogen, nitrogen and sulfur were determined from Sophisticated Instrumentation Center for Applied Research and Testing (SICART), VallabhVidhyanagar(India). Lead and phosphorus were estimated by standard methods.[5,4] The molecular weights were determined by Rast Camphor method. Infrared data were recorded on a Perkin-Elmer fouries(FTIR) spectrophotometer as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol 270 MHz spectrometer using DMSO-d_6 as a solvent and TMS as an internal standard. ^{31}P NMR were recorded on the same instrument using DMSO-d_6 as a solvent and H_3PO_4 as an external standard.

Synthesis of Macrocyclic Complexes and Its Derivatives

Macrocyclic complex were prepared by the methods as reported in our earlier communication.[17]

(i) Template synthesis of diethyldithiophosphate derivative of Dibenzo [7,8,15,16] [6,14] diaaza [1,9] dithiacyclohexadeca [2,5,10,13] tetraone. Chloride salt of the above mentioned macrocyclic complex

(1.084 g, 0.0015 mol) was dissolved in THF and was reacted with methanolic solution of sodium diethyldithiophosphate (0.627 g, 0.0030 mol) in 1:2 molar ratio. Reaction mixture was refluxed for 2 h. On cooling the off white crystals of dithiophosphate derivatives were separated out, which were filtered through filtering funnel. This crude product was washed several times with methanol, by vigorous shaking in filtration funnel, to remove the sodium chloride formed during the reaction. Product was dried under vacuum and was crystallized with THF/C_2H_5OH mixture.

(ii) Synthesis of di-n-propyldithiophosphate derivative of Dibenzo [6,7,13,14][5,12]diaza[1,8]dithiacyclotetradeca[2,4,9,11] tetraone.. Nitrate salt of the above mentioned macrocyclic complex (1.112 g,0.0016 mol) was dissolved in THF and was reacted with methanolic solution of sodium di-n-propyldithiophosphate (0.756 g, 0.0032 mol) in 1:2 molar ratio. Reaction mixture was refluxed for ~2 h. On cooling, the white crystals of dithiophosphate derivative were separated out, which were filtered through a filtering funnel. This crude product was washed several times with methanol by vigorous shaking in filtration funnel to remove the sodium nitrate formed during the reaction. Product was dried in vacuo and was crystallized with THF/C_2H_5OH mixture.

(iii) Synthesis of di-iso-propyldithiophosphate derivative of Tetrabenzo [3,4,7,8,11,12,15,16] [6,14] diaaza [1,9] dithiacyclohexadeca [2,5,10,13] tetraone.. Acetate salt of the above mentioned macrocyclic complex (1.202 g, 0.0014 mol) was dissolved in THF and was reacted with methanolic solution of sodium di-iso-propyldithio-phosphate (0.665 g, 0.0028 mol) in 1:2 molar ratio. Reaction mixture was refluxed for 2 hours. On cooling the white crystals of dithiophosphate derivative were separated out, which were filtered through filtering funnel. This crude product was washed several times with methanol, by vigorous shaking in filtration funnel, to remove the sodium acetate nitrate formed during the reaction. Product was dried under vacuo and was crystallized with THF/C_2H_5OH mixture. v Relevant data for the similar synthesis of other complexes are given in Table I. The analytical data of these complexes are given in Table II.

RESULTS AND DISCUSSION

Lead salts react with *o*-aminothiophenol and dicarboxylic acids in 1:2:2 molar ratios in methanol to afford white or off white complexes as shown in Figure 1.

TABLE I Reactions of Macrocyclic Complexes of Pb(II) with Sodium Dialkyldithiophosphates

Sr. no.	Macrocyclic complex [molecular formula] (empirical formula) g (mol)	Sodium dialkyl dithiophosphates g (mol)	Product yield (g) %
1	$[Pb(L^1).Cl_2]$ $(C_{18}H_{14}N_2S_2O_4.PbC_{12})$ 1.040 (0.0015)	$NaS_2P(OC_2H_5)$ 0.628 (0.0030)	$[Pb(L^1)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{26}H_{34}N_2P_2S_6.O_8Pb)$ (1.216) 81%
2	$[Pb(L^1).Cl_2]$ $(C_{18}H_{14}N_2S_2O_4.PbCl_2)$ 1.112 (0.0016)	$NaS_2P(OC_3H^n_7)_2$ 0.756 (0.0032)	$[Pb(L^1)\{S_2P(OC_3H^n_7)_2\}_2]$ $(C_{30}H_{42}N_2P_2S_6O_8Pb)$ (1.389) 80%
3	$[Pb(L^1).Cl_2]$ $(C_{18}H_{14}N_2S_2O_4.PbCl_2)$ 1.204 (0.0018)	$NaS_2P(OC_3H^i_7)_2$ 0.851 (0.0036)	$[Pb(L^1)\{S_2P(OC_3H^i_7)_2\}_2]$ $(C_{30}H_{42}N_2P_2S_6O_8Pb)$ (1.492) 81%
4	$[Pb(L^2).Cl_2]$ $(C_{20}H_{18}N_2S_2O_4.PbCl_2)$ 1.84 (0.0015)	$NaS_2P(OC_2H_5)$ 0.627 (0.0030)	$[Pb(L^2)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{28}H_{38}N_2P_2S_6O_8Pb)$ (1.183) 76%
5	$[Pb(L^2).Cl_2]$ $(C_{20}H_{18}N_2S_2O_4.PbCl_2)$ 1.264 (0.0018)	$NaS_2P(OC_3H^n_7)_2$ 0.857 (0.0036)	$[Pb(L^2)\{S_2P(OC_3H^n_7)_2\}_2]$ $(C_{32}H_{46}N_2P_2S_6.O_8Pb)$ (1.428) 75%
6	$[Pb(L^2).Cl_2]$ $(C_{20}H_{18}N_2S_2O_4.PbCl_2)$ 1.197 (0.0017)	$NaS_2P(OC_3H^i_7)_2$ 0.810 (0.0034)	$[Pb(L^2)\{S_2P(OC_3H^i_7)_2\}_2]$ $(C_{32}H_{36}N_2P_2S_6.O_8Pb)$ (1.286) 76%
7	$[Pb(L^3).Cl_2]$ $(C_{22}H_{22}N_2S_2O_4.PbCl_2)$ 1.209 (0.0016)	$NaS_2P(OC_2H_5)_2$ 0.668 (0.0032)	$[Pb(L^3)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{30}H_{42}N_2P_2S_6.O_8Pb)$ (1.284) 74%
8	$[Pb(L^3).Cl_2]$ $(C_{22}H_{22}N_2S_2O_4.PbCl_2)$ 1.182 (0.0016)	$NaS_2P(OC_3H^n_7)_2$ 0.762 (0.0032)	$[Pb(L^3)\{S_2P(OC_3H^n_7)_2\}_2]$ $(C_{34}H_{50}N_2P_2S_6.O_8Pb)$ (1.405) 80%
9	$[Pb(L^3).Cl_2]$ $(C_{22}H_{22}N_2S_2O_4.PbCl_2)$ 1.205 (0.0016)	$NaS_2P(OC_3H^i_7)_2$ 0.812 (0.0034)	$[Pb(L^3)\{S_2P(OC_3H^i_7)_2\}_2]$ $(C_{34}H_{50}N_2P_2S_6.O_8Pb)$ (1.302) 72%
10	$[Pb(L^4).Cl_2]$ $(C_{24}H_{26}N_2S_2O_4.PbCl_2)$ 1.045 (0.0014)	$NaS_2P(OC_2H_5)_2$ 0.585 (0.0028)	$[Pb(L^4)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{32}H_{46}N_2P_2S_6.O_8Pb)$ (1.113) 76%
11	$[Pb(L^4).Cl_2]$ $(C_{24}H_{26}N_2S_2O_4.PbCl_2)$ 1.75 (0.0014)	$NaS_2P(OC_3H^n_7)_2$ 0.670 (0.0028)	$[Pb(L^4)\{S_2P(OC_3H^n_7)_2\}_2]$ $(C_{36}H_{54}N_2P_2S_6.O_8Pb)$ (1.208) 76%
12	$[Pb(L^4).Cl_2]$ $(C_{24}H_{26}N_2S_2O_4.PbCl_2)$ 1.114 (0.0015)	$NaS_2P(OC_3H^i_7)_2$ 0.721 (0.0031)	$[Pb(L^4)\{S_2P(OC_3H^i_7)_2\}_2]$ $(C_{36}H_{54}N_2P_2S_6.O_8Pb)$ (1.252) 77%
13	$[Pb(L^5).Cl_2]$ $(C_{28}H_{18}N_2S_2O_4.PbCl_2)$ 1.209 (0.0015)	$NaS_2P(OC_2H_5)_2$ 0.629 (0.0030)	$[Pb(L^5)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{36}H_{38}N_2P_2S_6.O_8Pb)$ (1.356) 82%
14	$[Pb(L^5).Cl_2]$ $(C_{28}H_{18}N_2S_2O_4.PbCl_2)$ 1.108 (0.0014)	$NaS_2P(OC_3H^n_7)_2$ 0.662 (0.0029)	$[Pb(L^5)\{S_2P(OC_3H^n_7)_2\}_2]$ $(C_{40}H_{46}N_2P_2S_6.O_8Pb)$ (1.243) 78%

TABLE I Reactions of Macrocyclic Complexes of Pb(II) with Sodium Dialkyldithiophosphates *(Continued)*

Sr. no.	Macrocyclic complex [molecular formula] (empirical formula) g(mol)	Sodium dialkyl dithiophosphates g (mol)	Product yield (g) %
15	$[Pb(L^5).Cl_2]$ $(C_{28}H_{18}N_2S_2O_4.PbCl_2)$ 1.220 (0.0015)	$NaS_2P(OC_3H^i_7)_2$ 0.710 (0.0030)	$[Pb(L^5)\{S_2P(OC_3H^i_7)_2\}_2]$ $(C_{40}H_{46}N_2P_2S_6.O_8Pb)$ (1.325) 75%
16	$[Pb(L^1).(NO_3)_2]$ $(C_{18}H_{14}N_2S_2O_4.Pb(NO_3)_2)$ 0.970 (0.0013)	$NaS_2P(OC_2H_5)_2$ 0.541 (0.0026)	$[Pb(L^1)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{26}H_{34}N_2P_2S_6.O_8Pb)$ (1.064) 81%
17	$[Pb(L^2).(NO_3)_2]$ $(C_{20}H_{18}N_2S_2O_4.Pb(NO_3)_2)$ (0.0014)	$NaS_2P(OC_3H^n_7)_2$ 0.662 (0.0028)	$[Pb(L^2)\{S_2P(OC_3H^n_7)_2\}_2]$ $(C_{32}H_{46}N_2P_2S_6.O_8Pb)$ (1.184) 79%
18	$[Pb(L^5).(NO_3)_2]$ $(C_{28}H_{18}N_2S_2O_4.Pb(NO_3)_2)$ 1.202 (0.0014)	$NaS_2P(OC_3H^i_7)_2$ 0.665 (0.0028)	$[Pb(L^5)\{S_2P(OC_3H^i_7)_2\}_2]$ $(C_{40}H_{46}N_2P_2S_6.O_8Pb)$ (1.283) 79%
19	$[Pb(L^1).(CH_3COO)_2]$ $(C_{18}H_{14}N_2S_2O_4.Pb(CH_3COO)_2)$ 1.094 (0.0015)	$NaS_2P(OC_2H_5)_2$ 0.632 (0.0030)	$[Pb(L^1)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{26}H_{34}N_2P_2S_6.O_8Pb)$ (1.126) 76%
20	$[Pb(L^2).(CH_3COO)_2]$ $(C_{20}H_{18}N_2S_2O_4.Pb(CH_3COO)_2)$ 1.056 (0.0014)	$NaS_2P(OC_3H^i_7)_2$ 0.664 (0.0028)	$[Pb(L^2)\{S_2P(OC_3H^i_7)_2\}_2]$ $(C_{32}H_{46}N_2P_2S_6.O_8Pb)$ (1.082) 77%
21	$[Pb(L^5).(CH_3COO)_2]$ $(C_{28}H_{18}N_2S_2O_4.Pb(CH_3COO)_2)$ 1.246 (0.0015)	$NaS_2P(OC_3H^i_7)_2$ 0.712 (0.0030)	$[Pb(L^5)\{S_2P(OC_3H^i_7)_2\}_2]$ $(C_{40}H_{46}N_2P_2S_6.O_8Pb)$ (1.388) 82%

L^1 = Macrocyclic ligand derived from *o*-aminothiophenol & malonic acid. L^2 = Macrocyclic ligand derived from *o*-aminothiophenol & succinic acid. L^3 = Macrocyclic ligand derived from *o*-aminothiophenol & glutric acid.< L^4 = Macrocyclic ligand derived from *o*-aminothiophenol & adipic acid. L^5 = Macrocyclic ligand derived from *o*-aminothiophenol & phthalic acid.

L^1 = macrocyclic ligand derived from *o*-aminothiophenol and malonic acid (n = 1)*;

Dibenzo[6,7,13,14] [5,12] diaza [1,8] dithiacyclotetradeca [2,4,9,11] tetraone.

<* IUPAC names have been mentioned in parentheses in bold letters

L^2 = macrocyclic ligand derived from *o*-aminothiophenol and succinic acid (n = 2);

Dibenzo[7,8,15,16][6,14]diaaza[1,9]dithiacyclohexadeca[2,5,10, 13] tetraone.

L^3 = macrocyclic ligand derived from *o*-aminothiophenol and glutaric acid (n = 3);

Dibenzo[8,9,17,18][7,16]diaaza[1,10]dithiacyclooctadeca[2,6,11, 15] tetraone.

TABLE II Analytical Data of Dialkyldthiosphosphate Derivatives of Macrocyclic Complexes of Pb(II)

Sr. no.	Compound [molecular formula] (empirical formula)	Analysis % found (calcd.) C	H	N	P	S	Pb	Color	M.p. (°C)	Conductivity M ($ohm^{-1}cm^2\ mol^{-1}$)	M. wt. found (calcd.)
1	$[Pb(L^1)\{S_2P(OC_2H_5)_2\}_2]$	32.42	3.50	2.94	6.48	20.08	21.48	White	204	10	952.8
	$(C_{26}H_{34}N_2P_2S_6O_8Pb)$	(32.39)	(3.53)	(2.90)	(6.43)	(19.93)	(21.51)				(963.2)
2	$[Pb(L^1)\{S_2P(OC_3H_7^n)_2\}_2]$	35.99	4.16	2.77	6.12	18.79	20.39	Off	210	08	1028.4
	$(C_{30}H_{42}N_2P_2S_6O_8Pb)$	(35.32)	(4.12)	(2.74)	(6.08)	(18.83)	(20.32)	White			(1019.2)
3	$[Pb(L^1)\{S_2P(OC_3H_7^i)_2\}_2]$	35.27	4.09	2.78	6.12	18.79	20.39	Off	207	11	1030.6
	$(C_{30}H_{42}N_2P_2S_6O_8Pb)$	(35.32)	(4.12)	(2.74)	(6.08)	(18.83)	(20.32)	White			(1019.2)
4	$[Pb(L^2)\{S_2P(OC_2H_5)_2\}_2]$	33.94	3.86	2.87	6.28	19.40	20.88	Off	212	10	975.4
	$(C_{28}H_{38}N_2P_2S_6O_8Pb)$	(33.89)	(3.83)	(2.82)	(6.25)	(19.37)	(20.90)	White			(991.2)
5	$[Pb(L^2)\{S_2P(OC_3H_7^n)_2\}_2]$	36.72	4.42	2.63	5.96	18.29	19.84	White	218	12	1056.2
	$(C_{32}H_{46}N_2P_2S_6O_8Pb)$	(36.67)	(4.39)	(2.67)	(5.92)	(18.33)	(19.78)				(1047.2)
6	$[Pb(L^2)\{S_2P(OC_3H_7^i)_2\}_2]$	36.62	4.42	2.64	5.97	18.29	19.82	Off	206	13	1032.4
	$(C_{32}H_{36}N_2P_2S_6O_8Pb)$	(36.67)	(4.39)	(2.67)	(5.92)	(18.33)	(19.78)	White			(1037.2)
7	$[Pb(L^3)\{S_2P(OC_2H_5)_2\}_2]$	35.29	4.09	2.70	6.11	18.77	20.39	White	205	09	1031.6
	$(C_{30}H_{42}N_2P_2S_6O_8Pb)$	(35.32)	(4.12)	(2.74)	(6.08)	(18.83)	(20.32)				(1019.2)
8	$[Pb(L^3)\{S_2P(OC_3H_7^n)_2\}_2]$	37.85	4.70	2.57	5.81	17.72	19.34	White	208	10	1061.8
	$(C_{34}H_{50}N_2P_2S_6O_8Pb)$	(37.94)	(4.65)	(2.60)	(5.76)	(17.85)	(19.27)				(1075.2)
9	$[Pb(L^3)\{S_2P(OC_3H_7^i)_2\}_2]$	39.81	4.69	2.57	5.80	17.76	19.36	White	210	08	1092.4
	$(C_{34}H_{50}N_2P_2S_6O_8Pb)$	(37.94)	(4.65)	(2.60)	(5.76)	(17.85)	(19.27)				(1075.2)
10	$[Pb(L^4)\{S_2P(OC_2H_5)_2\}_2]$	36.74	4.43	2.61	5.89	18.39	19.68	White	206	10	1056.8

	$(C_{32}H_{46}N_2P_2S_6O_8Pb)$	(36.67)	(4.39)	(2.67)	(5.92)	(18.33)	(19.78)				(1047.2)
11	$[Pb(L^4)\{S_2P(OC_3H_7^n)_2\}_2]$	39.20	4.84	2.57	5.55	17.47	18.70	White	204	09	1114.4
	$(C_{36}H_{54}N_2P_2S_6O_8Pb)$	(39.15)	(4.89)	(2.53)	(5.62)	(17.40)	(18.78)				(1103.2)
12	$[Pb(L^4)\{S_2P(OC_3H_7^i)_2\}_2]$	39.20	4.91	2.57	5.67	17.33	18.66	Off	210	12	1116.2
	$(C_{36}H_{54}N_2P_2S_6O_8Pb)$	(39.15)	(4.89)	(2.53)	(5.62)	(17.40)	(18.78)	White			(1103.2)
13	$[Pb(L^5)\{S_2P(OC_2H_5)_2\}_2]$	39.68	3.51	2.54	5.78	17.71	19.12	Off	208	10	1098.6
	$(C_{36}H_{38}N_2P_2S_6O_8Pb)$	(39.73)	(3.49)	(2.57)	(5.70)	(17.66)	(19.05)	White			(1087.2)
14	$[Pb(L^5)\{S_2P(OC_3H_7^{mn})_2\}_2]$	41.88	4.08	2.41	5.59	16.74	18.08	Off	204	08	1155.4
	$(C_{40}H_{46}N_2P_2S_6O_8Pb)$	(41.98)	(4.02)	(2.44)	(5.42)	(16.79)	(18.12)	White			(1143.2)
15	$[Pb(L^5)\{S_2P(OC_3H_7^i)_2\}_2]$	41.84	3.39	2.47	5.38	16.87	18.04	White	211	09	1162.8
	$(C_{40}H_{46}N_2P_2S_6O_8Pb)$	(41.98)	(4.02)	(2.44)	(5.42)	(16.79)	(18.12)				(1143.2)
16	$[Pb(L^1)\{S_2P(OC_2H_5)_2\}_2]$	32.45	3.58	2.94	6.47	19.86	21.60	Off	208	08	972.4
	$(C_{26}H_{34}N_2P_2S_6O_8Pb)$	(32.39)	(3.53)	(2.90)	(6.43)	(19.93)	(21.51)	White			(963.2)
17	$[Pb(L^2)\{S_2P(OC_3H_7^n)_2\}_2]$	36.74	4.34	2.70	5.89	18.29	19.81	White	211	10	1039.8
	$(C_{32}H_{46}N_2P_2S_6O_8Pb)$	(36.67)	(4.39)	(2.67)	(5.92)	(18.33)	(19.78)				(1047.2)
18	$[Pb(L^5)\{S_2P(OC_3H_7^i)_2\}_2]$	42.04	4.07	2.48	5.48	16.86	18.05	White	211	03	1033.2
	$(C_{40}H_{46}N_2P_2S_6O_8Pb)$	(41.98)	(4.02)	(2.44)	(5.42)	(16.79)	(18.12)				(1143.2)
19	$[Pb(L^1)\{S_2P(OC_2H_5)_2\}_2]$	32.43	3.50	2.95	6.47	19.88	21.46	White	206	05	972.4
	$(C_{26}H_{34}N_2P_2S_6O_8Pb)$	(32.39)	(3.53)	(2.90)	(6.43)	(19.93)	(21.51)				(963.2)
20	$[Pb(L^2)\{S_2P(OC_3H_7^i)_2\}_2]$	36.58	4.42	2.63	5.88	18.27	19.84	Off	210	04	1046.0
	$(C_{32}H_{46}N_2P_2S_6O_8Pb)$	(36.67)	(4.39)	(2.67)	(5.92)	(18.33)	(19.78)	White			(991.2)
21	$[Pb(L^5)\{S_2P(OC_3H_7^i)_2\}_2]$	41.82	4.08	2.48	5.39	16.84	18.06	White	212	05	1151.6
	$(C_{40}H_{46}N_2P_2S_6O_8Pb)$	(41.98)	(4.02)	(2.44)	(5.42)	(16.79)	(18.12)				(1143.2)

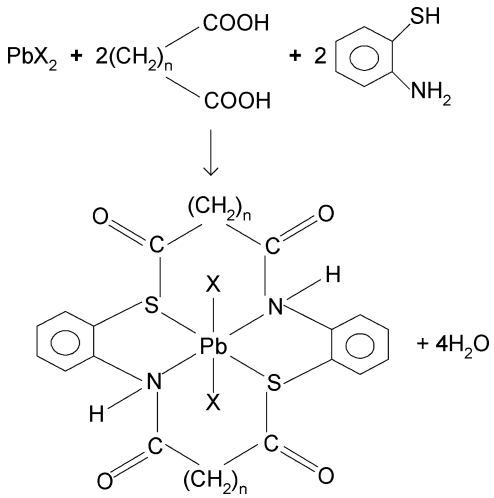


FIGURE 1 Tentative Structure of macrocyclic complexes of Pb(II).

L^4 = macrocyclic ligand derived from *o*-aminothiophenol and adipic acid (n = 4);

Dibenzo[9,10,19,20] [8,18] diaaza[1,11] dithiacycloicosa[2,7,12, 17] tetraone.

L^5 = macrocyclic ligand derived from *o*-aminothiophenol and phthalic acid $(CH_2)_n$ = o-C_6H_4-;

Tetrabenzo[3,4,7,8,11,12,15,16][6,14]diaaza[1,9]dithiacyclohexadeca[2,5,10,13] tetraone.

The above macrocyclic complexes of Pb(II) in THF react with methanolic solution of sodium dialkyldithiophosphates in 1:2 molar ratios to afford dialkyldithiophosphate derivatives of Pb(II) macrocyclic complexes as in Equation 1.

$$[Pb(L^{1--5})X_2] + 2NaS_2P(OR)_2 \longrightarrow [Pb(L^{1-5})\{S_2P(OR)_2\}_2] + 2NaX$$

$$R = C_2H_5-, C_3H_7^n - \text{or} C_3H_7^i - \text{and } X = Cl^-, NO_3^-, CH_3COO^- \qquad (1)$$

Except THF and DMSO, these derivatives are insoluble in organic solvents. The physical data of these derivatives are given in (Table II). All derivatives are white or off white in color. The molar conductance of 10^{-3} M solution in DMSO lies in the range 08–13 ohm^{-1} cm^2mol^{-1}showing that these complexes are non-electrolyte (Table II). The molecular weight determinations indicate their monomeric nature

(Table II). The analytical data of these derivatives are given in Table II.

Infrared Spectra

Characteristic IR absorption frequencies of these derivatives are given in Table III. As observed in the macrocyclic complexes, the four bands in the region 1658–1695(s), 1548–1578(m), 1250–1278(s) and 632–660(w) cm^{-1} have been ascribed to amide I, amide II, amide III and amide IV in plane deformation vibrations, respectively.[26,27] A broad band present in the region 3168–3270 cm^{-1} has been assigned to ν(NH) vibration of the secondary amino group. These bands do not show any significant change from their parent macro cyclic complexes. Two bands present in the region 1040–1070 and 865–890 cm^{-1} may be assigned to (P)–O–C and P–O–(C) stretching vibrations respectively.[28] A weak band present in the region 540–560 cm^{-1} has been attributed to P–S symmetric and asymmetric vibrations. A strong band observed in the region 670–700 cm^{-1}, which also appears in sodium dialkyldithiophosphates around the same region, is attributed to free P = S moiety. This indicates the unidentate behavior of dithiophosphate moieties.[29,30] The presence of sharp and weak bands in the region 418–470 cm^{-1} and 315–368 cm^{-1} respectively, have been assigned to ν(Pb-N) and ν(Pb-S) vibrations respectively.[31–33]

^{1}H NMR SPECTRAL DATA

The structures of dialkyldithiophosphate derivatives of macrocyclic complexes of Pb(II) have been confirmed by recording the ^{1}H NMR of these derivatives using DMSO-$d_6$as a solvent and TMS as an internal standard. In addition to the protons that appear in the parent macrocyclic complexes, the additional protons of dialkyldithiophosphate moieties appear in the spectra. The protons of CH_3- group of diethyldithiophosphate moieties appeared as a triplet in the range δ 1.38–1.59 ppm. Protons of CH_3- group of isopropyl moiety appeared as a doublet in the range δ 1.42–1.50 ppm and the protons of CH_3- group of n-propyl appeared as a triplet in the same range. Methylene and methine protons of the above three moieties appeared in the range δ 3.2–4.4 ppm. The broad singlet observed between, δ 8.14–8.42 ppm has been assigned the proton of –C(O)NH- group. The protons of -CH_2- group of malonic acid appear as a singlet in the range, δ 3.20–3.32 ppm. The methylene protons of – CH_2- CH_2- group of succinic acid appear as a singlet in the range of δ 3.16–3.20 ppm. The H-H coupling was not observed in

TABLE III IR Spectral Data of Dialkyldithiophosphate Derivatives of Macrocyclic Complexes of Pb(II)

Sr. No.	Compound	Amide-I	Amide-II	Amide-III	Amide-IV	ν(N—H)	(P)—O—C	P—O—(C)	P = S	P=S	ν(Pb—N)	ν(Pb—S)
1	$[Pb(L^1)\{S_2P(OC_2H_5)_2\}_2]$	1665s	1562m	1280s	630w	3200w	1050m	890m	700s	550w	460s	360m
2	$[Pb(L^1)\{S_2P(OC_3H^n_7)_2\}_2]$	1658s	1570m	1268s	640w	3240w	1045m	880m	690s	555w	430s	348w
3	$[Pb(L^1)\{S_2P(OC_3H^i_7)_2\}_2]$	1680s	1550m	1278s	658w	3190w	1040m	865m	670s	560w	420m	362w
4	$[Pb(L^2)\{S_2P(OC_2H_5)_2\}_2]$	1690s	1548m	1270s	640w	3220w	1050s	875m	700s	540w	428m	318w
5	$[Pb(L^2)\{S_2P(OC_3H^n_7)_2\}_2]$	1670m	1560m	1255m	648w	3260w	1055m	870m	680s	540w	460s	335w
6	$[Pb(L^2)\{S_2P(OC_3H^i_7)_2\}_2]$	1682s	1545m	1265s	650w	3270w	1060m	875m	670s	550w	470s	330w
7	$[Pb(L^3)\{S_2P(OC_2H_5)_2\}_2]$	1675m	1562m	1260s	640w	3258w	1050s	865m	690s	545w	458s	364w
8	$[Pb(L^3)\{S_2P(OC_3H^n_7)_2\}_2]$	1650m	1555m	1274w	648w	3250w	1065m	670m	700s	555w	465s	362w
9	$[Pb(L^3)\{S_2P(OC_3H^i_7)_2\}_2]$	1685s	1565m	1252w	650w	3190m	1050s	890m	710s	550w	428m	335w
10	$[Pb(L^4)\{S_2P(OC_2H_5)_2\}_2]$	1660s	1580m	1265s	640w	3180m	1068m	895m	690s	560w	445m	318w
11	$[Pb(L^4)\{S_2P(OC_3H^n_7)_2\}_2]$	1672s	1560m	1250s	648w	3265m	1052s	865m	685s	550w	430w	345w
12	$[Pb(L^4)\{S_2P(OC_3H^i_7)_2\}_2]$	1672m	1560m	1250m	648w	3255m	1052s	865m	685s	550w	460w	364w
13	$[Pb(L^5)\{S_2P(OC_2H_5)_2\}_2]$	1668m	1580m	1280s	660w	3255m	1046s	895m	680s	540w	460s	334w
14	$[Pb(L^5)\{S_2P(OC_3H^n_7)_2\}_2]$	1685m	1550m	1260s	655w	3190m	1045m	870m	675s	545w	420s	335m
15	$[Pb(L^5)\{S_2P(OC_3H^i_7)_2\}_2]$	1690s	1555m	1268s	638w	3265m	1060m	855m	670s	560w	430s	370w

s = strong; m = medium; and w = weak.

this case. The protons of α -C atoms of glutaric acid moiety were observed as a multiplet, δ 3.22 ppm, and β-C atoms of the above moiety appeared as a multiplet, δ 1.84 ppm. The protons of α-C atoms of adipic acid moiety appeared between, δ 3.20–3.32 ppm. The protons of β-C atoms appear in the δ 1.80–1.89 ppm as a multiplet. Aromatic protons of *o*-aminothiophenol moiety were observed as a multiplet in the range δ 7.12–7.78 ppm. The data have been depicted in Table IV. The values are in the expected region.[26]

^{13}C NMR Spectral Data

Structures of these derivatives have been further confirmed by recording ^{13}C NMR using DMSO-d_6 as a solvent and TMS as an internal standard. In addition to the carbons of parent macrocyclic complexes, the additional carbons of alkylene dithiophosphate moieties appear in the spectra. The carbons of CH_3- group of diethyl, di-n-propyl and di-isopropyl dithiophosphates appear in the region δ 13.08–14.08 ppm. The carbon of CH_3- group of diethyl, di-n-propyl and di-isopropyl lie in the range, δ 39.56–41.86 ppm. The carbon of -CH_2- group of malonic acid moiety lies in the range, δ 30.48–31.42 ppm. The carbons of –CH_2-CH_2- moiety appear in the range, δ 27.12–28.49 ppm. The α-carbon of glutaric acid moiety were observed in the range, δ 31.96–32.98 ppm and the β carbons in the range, δ 28.12–28.76 ppm, respectively. The α carbons of adipic acid moiety appeared at δ 32.98 ppm and β carbon at δ 27.14 ppm. The carbon of phthalic acid moiety observed at δ 71.04 ppm. Signals observed at δ 173.19–174.04 ppm have been assigned to the carbons of $>C=O$ group. The signals of the carbons of –C(O)NH- group appear in the range, δ 80. –82.26 ppm. The carbons of phenyl group of *o*-aminothiophenol moiety appeared in the range, δ 71.04–73.12 ppm. The values are in the expected range[26] and have been presented in Table V.

^{31}P NMR

^{31}P NMR spectra of a few representative compounds could be recorded. The spectra were recorded on 270 MHz spectrometer using DMSO-d_6 as a solvent and H_3PO_4 as an external standard. The values of chemical shifts of the newly synthesized compounds have been reported in Table VI. The chemical shift values do not show any significant change from their parent dialkyl dithiophosphoric acids. This indicates again the monodentate nature of dialkyl dithiophosphate moieties attached to the central lead ion.[29,30] The ^{31}P chemical shifts for the parent acids are given in parentheses in Table VI.

TABLE IV ^{1}H NMR Spectral Data of Dialkyldithiophosphate Derivatives of the Macrocyclic Complexes of Pb(II)

Sr. no.	Compound	-CH_3	/| -CH_2O- -CHO |	O || -C-NH-	-CO-(CH_2)-CO	—CO—$(CH_2)_2$—CO—	—CO—$(CH_2)_3$—CO	—CO—$(CH_2)_4$—CO	—CO—(C_6H_4)—CO	Aromatic
1	$[Pb(L^1)\{S_2P(OC_2H_5)_2\}_2]$ ($C_{26}H_{34}N_2P_2S_6.O_8Pb$)	1.40	4.02	8.22	3.22	—	—	—	—	7.48
2	$[Pb(L^1)\{S_2P(OC_3H_7^n)_2\}_2]$ ($C_{30}H_{42}N_2P_2S_6O_8Pb$)	1.48	3.82	8.30	3.20	—	—	—	—	7.66
3	$[Pb(L^1)\{S_2P(OC_3H_7^i)_2\}_2]$ ($C_{30}H_{42}N_2P_2S_6O_8Pb$)	1.52	3.24	8.22	3.32	—	—	—	—	7.78
4	$[Pb(L^2)\{S_2P(OC_2H_5)_2\}_2]$ ($C_{28}H_{38}N_2P_2S_6O_8Pb$)	1.50	4.42	8.14	—	3.16	—	—	—	7.60
5	$[Pb(L^2)\{S_2P(OC_3H_7^n)_2\}_2]$ ($C_{32}H_{46}N_2P_2S_6.O_8Pb$)	1.48	4.04	8.30	—	3.20	—	—	—	7.44
6	$[Pb(L^2)\{S_2P(OC_3H_7^i)_2\}_2]$ ($C_{32}H_{36}N_2P_2S_6.O_8Pb$)	1.59	3.88	8.42	—	3.22	—	—	—	7.12
7	$[Pb(L^3)\{S_2P(OC_2H_5)_2\}_2]$ ($C_{30}H_{42}N_2P_2S_6.O_8Pb$)	1.50	4.26	8.30	3.18	—	1.84	—	—	7.22
8	$[Pb(L^3)\{S_2P(OC_3H_7^n)_2\}_2]$ ($C_{34}H_{50}N_2P_2S_6.O_8Pb$)	1.38	4.23	8.32	3.12	—	1.86	—	—	7.30
9	$[Pb(L^3)\{S_2P(OC_3H_7^i)_2\}_2]$ ($C_{34}H_{50}N_2P_2S_6.O_8Pb$)	1.48	3.87	8.40	3.19	—	1.80	—	—	7.28
10	$[Pb(L^4)\{S_2P(OC_2H_5)_2\}_2]$ ($C_{32}H_{46}N_2P_2S_6.O_8Pb$)	1.44	4.06	8.24	3.20	—	—	1.80	—	7.54
11	$[Pb(L^4)\{S_2P(OC_3H_7^n)_2\}_2]$ ($C_{36}H_{54}N_2P_2S_6.O_8Pb$)	1.50	3.68	8.38	3.22	—	—	1.89	—	7.29
12	$[Pb(L^5)\{S_2P(OC_3H_7^n)_2\}_2]$ ($C_{40}H_{46}N_2P_2S_6.O_8Pb$)	1.48	3.74	8.32	—	—	—	—	8.02	7.12

TABLE V ^{13}C NMR Spectral Data of Dialkyldithiophosphate Derivatives of the Macrocyclic Complexes of Pb(II)

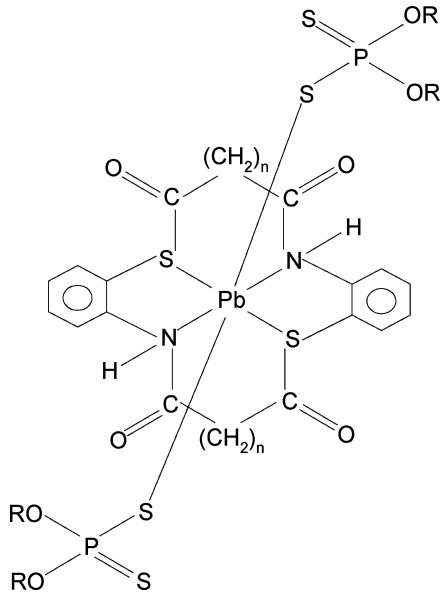
Sr. no.	Compound	—CH_3	/| -CH_2O- -CHO |	>C = O	—CO—(CH_2)—CO	—CO—(CH_2)$_2$—CO—	—CO—(CH_2)$_3$—CO	—CO—(CH_2)$_4$—CO	—CO—(C_6H_4)—CO	O || -C-NH-	Aromatic
1	[Pb(L^1){$S_2P(OC_2H_5)_2$}$_2$] ($C_{26}H_{34}N_2P_2S_6.O_8Pb$)	14.08	41.04	172.48	30.48	—	—	—	—	81.94	72.58
2	[Pb(L^1){$S_2P(OC_3H_7^n)_2$}$_2$] ($C_{30}H_{42}N_2P_2S_6O_8Pb$)	13.89	40.88	170.14	31.86	—	—	—	—	82.06	73.12
3	[Pb(L^1){$S_2P(OC_3H_7^i)_2$}$_2$] ($C_{30}H_{42}N_2P_2S_6O_8Pb$)	13.07	41.80	171.34	31.42	—	—	—	—	82.18	73.02
4	[Pb(L^2){$S_2P(OC_2H_5)_2$}$_2$] ($C_{28}H_{38}N_2P_2S_6O_8Pb$)	13.24	39.56	172.02	—	27.12	—	—	—	80.49	71.04
5	[Pb(L^2){$S_2P(OC_3H_7^n)_2$}$_2$] ($C_{32}H_{46}N_2P_2S_6.O_8Pb$)	13.18	41.02	173.19	—	28.04	—	—	—	81.32	72.08
6	[Pb(L^2){$S_2P(OC_3H_7^i)_2$}$_2$] ($C_{32}H_{36}N_2P_2S_6.O_8Pb$)	13.98	41.86	172.06	—	28.49	—	—	—	82.04	70.86
7	[Pb(L^3){$S_2P(OC_2H_5)_2$}$_2$] ($C_{30}H_{42}N_2P_2S_6.O_8Pb$)	13.09	40.04	173.58	32.84	—	28.12	—	—	81.14	71.62
8	[Pb(L^3){$S_2P(OC_3H_7^n)_2$}$_2$] ($C_{34}H_{50}N_2P_2S_6.O_8Pb$)	13.62	41.74	170.04	31.96	—	28.76	—	—	82.08	72.04
9	[Pb(L^4){$S_2P(OC_2H_5)_2$}$_2$] ($C_{32}H_{46}N_2P_2S_6.O_8Pb$)	13.14	41.07	173.08	32.98	—	—	27.14	—	81.68	71.84
10	[Pb(L^5){$S_2P(OC_3H_7^n)_2$}$_2$] ($C_{40}H_{46}N_2P_2S_6.O_8Pb$)	13.08	40.80	172.42	—	—	—	—	71.04	82.26	71.18

TABLE VI ^{31}P NMR Spectral Data of Dialkyldithiophosphate Derivatives of Macrocyclic Complexes of Pb(II)

Sr. no.	Compound [molecular formula] (empirical formula)	^{31}P NMR chemical shift (δ)
1	$[Pb(L^1)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{26}H_{34}N_2P_2S_6O_8Pb)$	91.24 (90.04)
2	$[Pb(L^2)\{S_2P(OC_3H_7^n)_2\}_2]$ $(C_{32}H_{46}N_2P_2S_6O_8Pb)$	88.39 (84.82)
3	$[Pb(L^3)\{S_2P(OC_3H_7^i)_2\}_2]$ $(C_{34}H_{50}N_2P_2S_6O_8Pb)$	89.12 (85.74)
4	$[Pb(L^4)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{32}H_{46}N_2P_2S_6O_8Pb)$	87.34 (90.04)
5	$[Pb(L^5)\{S_2P(OC_3H_7^i)_2\}_2]$ $(C_{40}H_{46}N_2P_2S_6O_8Pb)$	90.89 (88.32)

Structural Information

The following conclusion has been drawn from the above spectral data. The presence of four characteristic peaks of amide in the IR spectra indicates the formation of macrocycles having amido group. The



Where, $R = C_2H_5-$, $C_3H_7^i - or C_3H_7^n - n = 1, 1, 1 \, and \, 4$

FIGURE 2 General structure of mixed ligand complexes of dialkyldithiophosphates with macrocyclic complexes having N_2S_2 potential donor atoms in 14–20 membered rings.

chemical shift value in ^{1}H & ^{13}C NMR confirms the positions of hydrogens and carbons respectively in the expected region. A strong band observed in the region 670–700 cm^{-1} and which has been attributed to free P = S moiety, indicate the monodentate nature of dialkyldithiophosphate moieties. The position of chemical shifts in ^{31}P NMR also indicates the monodentate nature of the dithiophosphate ligands. Considering the previous data, the following octahedral geometry has been assigned for these derivatives in which two sulfur atoms and two nitrogen atoms of the macrocyclic ring coordinate to the central lead ion in the square planar form. Each dithiophosphate moiety occupies the axial position binding the central lead ion in unidentate manner through strong electrostatic attraction (Figure 2).

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