



Synthesis, Characterization and Antimicrobial Aspects of Some Mixed Ligand Macrocyclic Complexes of Pb(II) Having N₄S₄ Potential Donors in 22-28 Membered Rings

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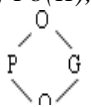
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ABSTRACT

Alkylene dithiophosphate derivatives of macrocyclic complexes of Pb(II), having N₄S₄ potential donors in

22 to 28 member rings of the general formula, [Pb(L){S₂F P  G }₂], Where L= macrocyclic

ligands L¹, L², L³, L⁴ and L⁵ and G = $\text{CH}_2\text{-}\overset{|}{\text{CH}}\text{-}\overset{|}{\text{CH}}\text{-CH}_2$ $\text{(CH}_3\text{)}_2\text{C-C(CH}_3\text{)}_2$ $\text{(CH}_3\text{)}_2\text{C-CH}_2\text{-CH(CH}_3\text{)-CH}_2\text{-C(CH}_3\text{)}_2\text{-CH}_2$

and $\text{CH}_2\text{-C(CH}_2\text{H}_5\text{)}_2\text{-CH}_2$ have been synthesized from the reactions of [Pb(L)X₂] (where X=Cl⁻, NO₃⁻

or CH₃COO⁻) with ammonium alkylene dithiophosphates in 1:2 molar ratio in THF. These complexes have

been characterized by elemental analysis, molar conductance, molecular weight determinations, IR, ¹H,

¹³C and ³¹P NMR. The anti-microbial activities of these derivatives have been studied by screening them

against fungi, like *Aspergillus flavus*, *Fusarium oxysporum*, *Alternaria alternata* and bacteria like

Salmonella typhi and *Bacillus subtili*. Alkylene dithiophosphate derivatives were found to be more

fungitoxic and antibacterial than their corresponding macrocyclic complexes.

Keywords: Macrocyclic complexes, bis-(2-aminophenyl)disulphide, 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]. In spite of vast innovation in macrocyclic chemistry and tremendous interest in mixed ligand complexes, no mixed ligand macrocyclic complex was reported till our publications. Alkylene dithiophosphates has been the area of our thrust since last 3 decades[5-14]. Considering the importance of mixed ligand macrocyclic complexes, we reported synthesis, characterization, antimicrobial and catalytic aspects of mixed ligand macrocyclic complexes of Cr^{III}, Mn^{II}, Fe^{III}, Co^{III}, Ni^{II}, Cu^{II}, Cd^{II}, Sn^{II} and Pb^{II} with dialkyl and alkylene dithiophosphates having N₂S₂ potential donors in 14 to 20 membered rings[15-29]. We have also reported the macrocyclic complexes of Ni^{II} and Sn^{II} with dialkyl and alkylene dithiophosphates having N₄S₄ potential donors in 22-28 membered rings[17,24,28]. In continuation to the above work we hereby report the synthesis, characterization and antimicrobial aspects of alkylene dithiophosphate derivatives of macrocyclic complexes of Pb^{II} having N₄S₄ potential donors in 22 to 28 membered rings.

MATERIALS AND METHODS

All of the lead salts and dicarboxylic acids of A.R. grade were obtained from s,d-fine chemicals and were used without further purification. *o*-Aminothiophenol was used as obtained from Merck. Solvents were purified and dried by standard methods. The chelating ligand *bis*-(2-aminophenyl)disulfide was synthesized by the dimerization of *o*-aminothiophenol by H₂O₂ as reported in the literature[30]. Ammonium alkylene dithiophosphates were prepared by the method as we reported in our earlier communication[6].

Microanalyses for carbon, hydrogen, nitrogen and sulphur were determined from SICART, Vallabh Vidyanagar. Lead and phosphorus were estimated by standard method[31]. The molecular weights were determined by Rast Camphor method. Infrared data were recorded on a *Perkin-Elmer* FT-IR spectrophotometer as KBr pellets. ¹H and ¹³C NMR spectra were recorded on a Jeol 270 MHz spectrometer using DMSO-*d*₆ as a solvent and TMS as an internal standard. ³¹P NMR were recorded on the same instrument using DMSO-*d*₆ as a solvent and H₃PO₄ as an external standard.

Synthesis Of Macrocyclic Complexes And Its Derivatives: Macrocyclic complexes were prepared by the method as reported in our earlier communication[18].

Synthesis of hexylene dithiophosphate derivative of {Tetrabenzo[2,3,11,12,15,16,24,25][4,10,17,23] tetraaza [1,13,14,26] tetrathiacyclohexaico-sane[5,9,18,22]tetraone} : Precursor macrocyclic complex, mentioned above in parenthesis (1.433g, 0.0015 mol) was dissolved in THF and was reacted with methanolic solution of ammonium hexylene dithiophosphate (0.674g, 0.0030 mol) in 1:2 molar ratio. Reaction mixture was refluxed for 6 h at 200°C. On cooling the light yellow crystals of dithiophosphate derivative separated out, which were filtered through G-3 filtering funnel. This crude product was washed several times with methanol, by vigorous shaking in filtration funnel, to remove the ammonium nitrate formed during the reaction. Product was dried under vacuum and was crystallized with THF/C₂H₅OH mixture.

RESULTS AND DISCUSSION

Reaction of metal lead salts with *bis*-(2-aminophenyl) disulfide and various dicarboxylic acids in 1:2:2 molar ratio in methanol to afford off white or light yellow complexes as shown below :

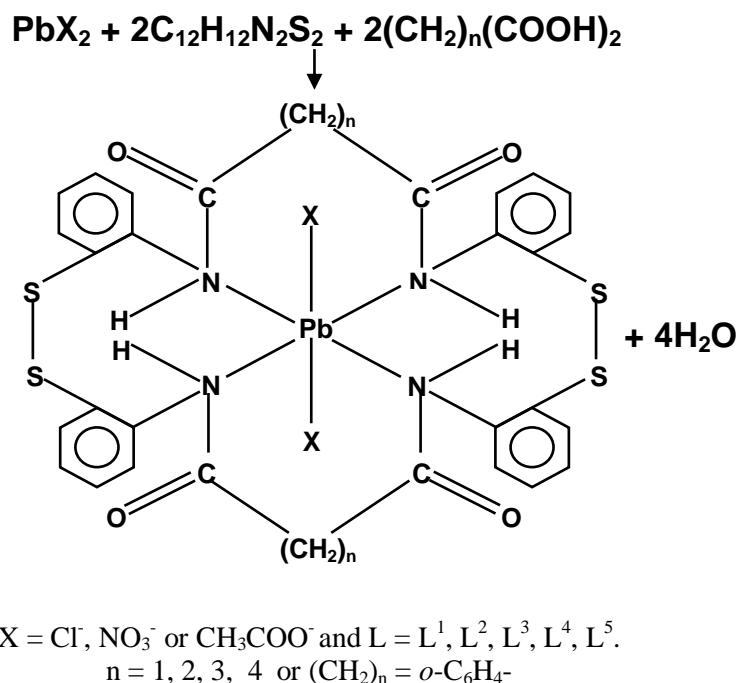
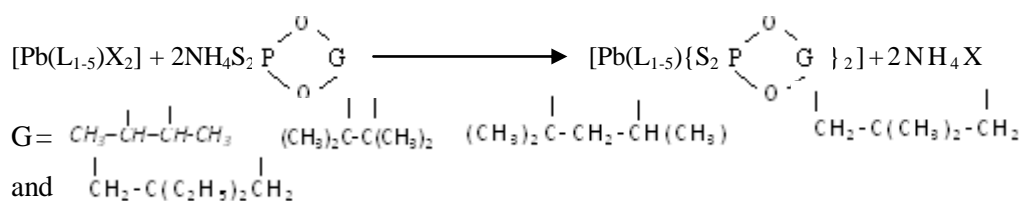


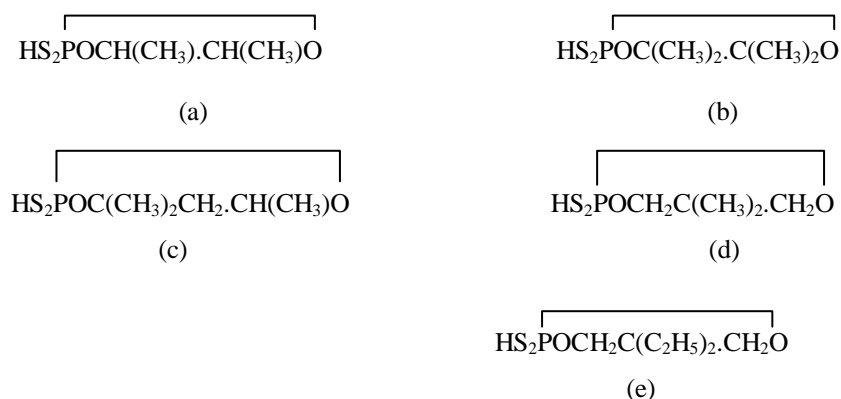
Figure 1. Tentative Structure of Macrocyclic Complexes of Pb(II)

- $\text{L}^1 =$ Macrocyclic ligand derived from *bis*-(2-aminophenyl)disulfide and malonic acid ($n=1$), 22-membered ring;
 {Tetrabenz[2,3,9,10,13,14,20,21][4,8,15,19]tetraaza[1,11,12,22]tetrathiacyclodiicosane[5,7,16,18]tetraone}.
- $\text{L}^2 =$ Macrocyclic ligand derived from *bis*-(2-aminophenyl)disulfide and succinic acid ($n=2$), 24-membered ring;
 {Tetrabenz[2,3,10,11,14,15,22,23][4,9,16,21]tetraaza[1,12,13,24]tetrathiacyclotetraicosane[5,7,17,20]tetraone}.
- $\text{L}^3 =$ Macrocyclic ligand derived from *bis*-(2-aminophenyl)disulfide and glutaric acid ($n=3$), 26-membered ring;
 {Tetrabenz[2,3,11,12,15,16,24,25][4,10,17,23]tetraaza[1,13,14,26]tetrathiacyclohexaicosane[5,9,18,22]tetraone}.
- $\text{L}^4 =$ Macrocyclic ligand derived from *bis*-(2-aminophenyl)disulfide and adipic acid ($n=4$), 28-membered ring;
 {Tetrabenz[2,3,12,13,16,17,26,27][4,11,18,25]tetraaza[1,14,15,28]tetrathiacyclooctaicosane[5,10,19,24]tetraone}.
- $\text{L}^5 =$ Macrocyclic ligand derived from *bis*-(2-aminophenyl)disulfide and phthalic acid ($(\text{CH}_2)_n = o\text{-C}_6\text{H}_4\text{-}$), 24-membered ring;
 {Hexabenz[2,3,6,7,10,11,14,15,18,19,22,23][4,9,16,21]tetraaza[1,12,13,24]tetrathiacyclotetraicosane[5,8,17,20]tetraone}.

The above macrocyclic complexes of Pb^{II} in the THF were reacted with a methanolic solution of ammonium alkylene dithiophosphates in 1:2 molar ratios to afford the alkylene dithiophosphates derivatives of the macrocyclic Pb^{II} complexes in the following manner :



IUPAC names have been mentioned in parenthesis in bold letters. The symbols of the alkylene dithiophosphate anions, of their ammonium salts, used for the synthesis of mixed ligand macrocyclic complexes have been depicted by a-e through the script.



Except THF and DMSO, these derivatives are insoluble in common organic solvents. All derivatives are yellow or light yellow in colour. The molar conductance of 10^{-3} M Solution in DMSO lie in the range $3.0-6.0 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ showing that these complexes are non-electrolyte. The molecular weight determinations indicate their monomeric nature.

Infrared Spectra : In the macrocyclic complexes, the four bands in the regions $1638-1680(\text{s})$, $1516-1582(\text{m})$, $1240-1272(\text{s})$ and $648-690(\text{w}) \text{cm}^{-1}$ have been ascribed to the amide I, amide II, amide III and amide IV in-plane deformation vibrations, respectively[32]. A broad band in the region $3104-3189 \text{cm}^{-1}$ has been assigned to the $\nu(\text{N-H})$ vibration of the secondary amino group. These bands do not show any significant change from their parent macrocyclic complexes. Two bands present in the regions $1040-1072$ and $888-840\text{cm}^{-1}$ may be assigned to (P)-O-C and P-O-(C) stretching vibrations, respectively[33]. The band present between $999-954 \text{cm}^{-1}$ may be attributed to the ring vibrations of dioxaphospholanes and dioxaphosphorinanes respectively, which are probably coupled with C-C stretching vibrations[34,35]. A weak band present in the region $570-538 \text{cm}^{-1}$ has been attributed to P-S symmetric and asymmetric vibrations. A strong band present in the region $728-680\text{cm}^{-1}$, which also appears in ammonium alkylene dithiophosphates at around the same region, is attributed to the P=S moiety. This indicates the unidentate behaviour of the dithiophosphate moieties. The presence of sharp and weak bands in the region $483-418 \text{cm}^{-1}$ and $364-320 \text{cm}^{-1}$ have been assigned to $\nu(\text{Pb-N})$ and $\nu(\text{Pb-S})$ vibrations, respectively[7,8,36].

^1H NMR Spectral Data : The structure of alkylene dithiophosphate derivatives of macrocyclic complexes of Pb(II) have been further confirmed by recording the ^1H NMR using DMSO- d_6 as a solvent and TMS as an internal standard. In addition to the protons appear in the parent macrocyclic complexes, the additional protons of alkylene dithiophosphates moieties appear in the spectra. The methyl protons of tetramethylethylene moiety, butylene dithiophosphate moiety and neo-pentylene dithiophosphate moiety appeared in the range δ 1.36 to 1.59 ppm. The protons of methylene and methine moieties appear in the range δ 3.8 to 4.9 ppm. The broad singlet observed between δ 8.09 to 8.36 ppm has been assigned to the proton of -C(O)NH- group. The protons of -CH₂- group of malonic acid appear as a singlet in the range, δ 3.09 to 3.42 ppm. The methylene protons of -CH₂-CH₂- group of succinic acid appear as a singlet in the

range of δ 3.04 to 3.26 ppm. The protons of α -C atoms of glutaric acid moiety were observed as a multiplet between δ 1.78 to 1.81 ppm. The protons of β -C atoms of the above moiety appeared as a multiplet at δ 1.95 ppm. The protons of α -C atoms of adipic acid moiety appeared at δ 1.81 ppm. The protons of β -C atoms appear in the range δ 1.70 to 1.82 ppm. Aromatic protons of *bis*-(2-aminophenyl)disulfide moiety were observed as a multiplet in the range δ 7.14 to 7.60 ppm. The values are in the expected region[37,38].

^{13}C NMR Spectral Data: In addition to the carbons of parent macrocyclic complexes, the additional carbons of alkylene dithiophosphate moieties appear in the spectra. The carbons of $-\text{CH}_3$ - group of tetramethylene, butylene and neopentylene dithiophosphate moieties appear in the range δ 12.14 to 14.12 ppm. The carbons of methylene and mithine moieties appear in the range δ 38.64 to 43.16 ppm. The carbon of $-\text{CH}_2$ - group of malonic acid moiety lie in the range δ 30.86 to 34.29 ppm. The carbons of $-\text{CH}_2\text{-CH}_2$ - moiety appear in the range δ 27.52 to 31.64 ppm. The α -carbon of glutaric acid moiety were observed in the range δ 29.76 to 30.14 ppm and the β carbons of the above moiety appear in the range δ 24.90 to 27.20 ppm respectively. Signals observed at δ 170.08 to 174.62 ppm have been assigned to the carbons of $>\text{C}=\text{O}$ group. The signals of the carbons of $-\text{C}(\text{O})\text{NH}$ - group appear in the range δ 80.09 to 83.48 ppm. The carbons of phenyl group of *bis*-(2-aminophenyl)disulfide moiety appeared in the range δ 70.49 to 74.86 ppm. The values are in the expected range[37,38].

^{31}P NMR Spectra: ^{31}P NMR spectra of a few compounds were recorded on a 270 MHz spectrometer using $\text{DMSO} - d_6$ as a solvent and H_3PO_4 as an external standard. ^{31}P NMR spectra of few representative compounds could be recorded. The chemical shift values do not show any significant change from their respective ammonium Alkylene dithiophosphate salts. This indicates again the monodentate nature of alkylene dithiophosphate moieties attached to the central lead ion[39,40]. The values of chemical shift of the newly synthesized compounds are depicted in table 1.

Table 1. Analytical and Physico-chemical Data of Alkylene Dithiophosphate Derivatives of Macrocyclic Complexes Pb^{II} containing tetra oxotetra thiotetra aza ligands (1-15)

Sr. No	Compound	Analysis % Found (Calcd.)					Conductivity Λ_M^0 ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)	M.P. (decomp.) $^{\circ}\text{C}$	Mol.wt. Found (Calcd.)	^{31}P NMR Chemical shift (δ)	
		C	H	N	P	S					Pb
1	$[\text{Pb}(\text{L}^1)\{\text{S}_2\text{POCH}(\text{CH}_3)_2\text{CH}(\text{CH}_3)\text{O}\}_2]$ ($\text{C}_{38}\text{H}_{40}\text{N}_4\text{O}_8\text{P}_2\text{S}_8\text{Pb}$)	37.31 (37.84)	3.27 (3.32)	4.58 (4.65)	5.07 (5.14)	20.94 (21.24)	16.93 (17.18)	04	224	1222 (1205)	93.12
2	$[\text{Pb}(\text{L}^1)\{\text{S}_2\text{POC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$ ($\text{C}_{42}\text{H}_{48}\text{N}_4\text{O}_8\text{P}_2\text{S}_8\text{Pb}$)	40.45 (39.96)	3.85 (3.80)	4.49 (4.44)	4.97 (4.91)	20.54 (20.30)	16.61 (16.41)	03	216	1246 (1261)	96.72
3	$[\text{Pb}(\text{L}^1)\{\text{S}_2\text{POC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$ ($\text{C}_{42}\text{H}_{48}\text{N}_4\text{O}_8\text{P}_2\text{S}_8\text{Pb}$)	40.29 (39.96)	3.84 (3.80)	4.48 (4.44)	4.96 (4.91)	20.46 (20.30)	16.55 (16.41)	05	238	1255 (1261)	74.38
4	$[\text{Pb}(\text{L}^2)\{\text{S}_2\text{POCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}\}_2]$ ($\text{C}_{42}\text{H}_{48}\text{N}_4\text{O}_8\text{P}_2\text{S}_8\text{Pb}$)	40.29 (39.96)	3.84 (3.80)	4.48 (4.44)	4.96 (4.91)	20.46 (20.30)	16.55 (16.41)	04	218	1251 (1261)	75.14
5	$[\text{Pb}(\text{L}^2)\{\text{S}_2\text{POCH}_2\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{O}\}_2]$ ($\text{C}_{46}\text{H}_{56}\text{N}_4\text{O}_8\text{P}_2\text{S}_8\text{Pb}$)	41.50 (41.91)	4.21 (4.25)	4.21 (4.25)	4.66 (4.70)	19.25 (19.43)	15.56 (15.72)	06	220	1330 (1317)	94.62
6	$[\text{Pb}(\text{L}^2)\{\text{S}_2\text{POC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$ ($\text{C}_{44}\text{H}_{52}\text{N}_4\text{O}_8\text{P}_2\text{S}_8\text{Pb}$)	41.44 (40.96)	4.82 (4.03)	4.39 (4.34)	4.86 (4.81)	20.09 (19.86)	16.25 (16.05)	05	224	1274 (1289)	91.80

7	$[\text{Pb}(\text{L}^3)\{\text{S}_2\text{POC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$ (C ₄₆ H ₅₆ N ₄ O ₈ P ₂ S ₈ Pb)	42.40 (41.91)	4.30 (4.25)	4.30 (4.25)	4.76 (4.71)	19.66 (19.44)	15.90 (15.72)	03	228	1302 (1317)	93.62
8	$[\text{Pb}(\text{L}^3)\{\text{S}_2\text{POC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$ (C ₄₆ H ₅₆ N ₄ O ₈ P ₂ S ₈ Pb)	41.44 (41.91)	4.20 (4.25)	4.20 (4.25)	4.65 (4.71)	19.22 (19.44)	15.90 (15.72)	04	230	1332 (1317)	76.84
9	$[\text{Pb}(\text{L}^3)\{\text{S}_2\text{POCH}_2\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{O}\}_2]$ (C ₄₈ H ₆₀ N ₄ O ₈ P ₂ S ₈ Pb)	43.37 (42.82)	4.52 (4.46)	4.21 (4.16)	4.67 (4.61)	19.28 (19.03)	15.59 (15.39)	04	234	1328 (1345)	95.72
10	$[\text{Pb}(\text{L}^4)\{\text{S}_2\text{POCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{O}\}_2]$ (C ₄₄ H ₅₂ N ₄ O ₈ P ₂ S ₈ Pb)	40.65 (40.96)	4.00 (4.03)	4.31 (4.34)	4.77 (4.81)	19.71 (19.86)	15.93 (16.05)	03	236	1299 (1289)	96.04
11	$[\text{Pb}(\text{L}^4)\{\text{S}_2\text{POC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$ (C ₄₈ H ₆₀ N ₄ O ₈ P ₂ S ₈ Pb)	43.18 (42.82)	4.49 (4.46)	4.20 (4.16)	4.65 (4.61)	19.19 (19.03)	15.52 (15.39)	06	226	1334 (1345)	76.44
12	$[\text{Pb}(\text{L}^4)\{\text{S}_2\text{POCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}\}_2]$ (C ₄₆ H ₅₆ N ₄ O ₈ P ₂ S ₈ Pb)	41.69 (41.91)	4.23 (4.25)	4.23 (4.25)	4.68 (4.71)	19.33 (19.44)	15.63 (15.72)	04	222	1324 (1317)	78.04
13	$[\text{Pb}(\text{L}^5)\{\text{S}_2\text{POC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$ (C ₅₂ H ₅₂ N ₄ O ₈ P ₂ S ₈ Pb)	45.51 (45.05)	3.79 (3.75)	4.08 (4.04)	4.52 (4.48)	18.67 (18.48)	15.10 (14.95)	03	224	1371 (1385)	96.52
14	$[\text{Pb}(\text{L}^5)\{\text{S}_2\text{POCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{O}\}_2]$ (C ₄₈ H ₄₄ N ₄ O ₈ P ₂ S ₈ Pb)	42.85 (43.34)	3.27 (3.71)	4.16 (4.21)	4.61 (4.66)	19.05 (19.26)	15.40 (15.58)	03	232	1344 (1329)	99.54
15	$[\text{Pb}(\text{L}^5)\{\text{S}_2\text{POC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$ (C ₅₂ H ₅₂ N ₄ O ₈ P ₂ S ₈ Pb)	45.48 (45.05)	3.79 (3.75)	4.08 (4.04)	4.52 (4.48)	18.66 (18.48)	15.09 (14.95)	04	218	1372 (1385)	98.74

Analytical and physico-chemical data of precursor macrocyclic complexes.

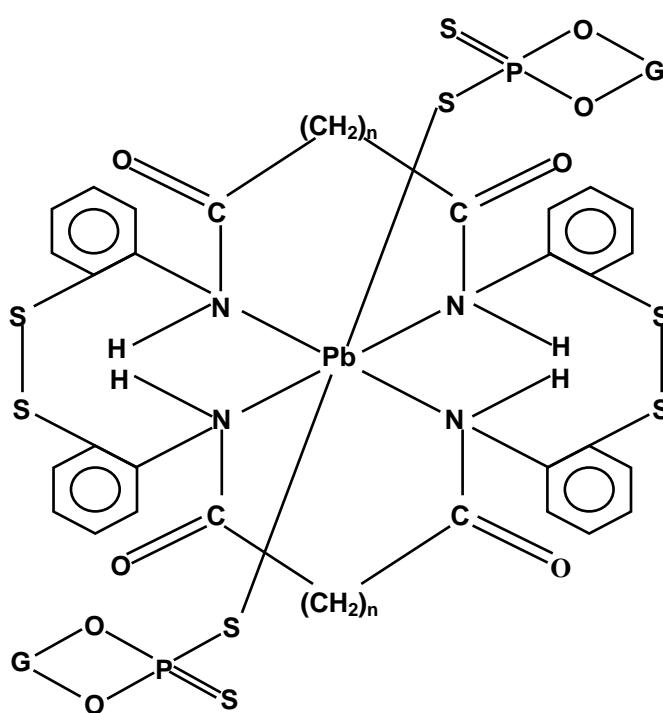
APPLICATIONS

Antimicrobial Activity : The antimicrobial activity of *bis*-(2-aminophenyl)disulfide, dicarboxylic acids, lead salts and the precursor macrocyclic complexes (L¹ to L⁵) has been reported in our earlier communication[15]. Like their precursor macrocyclic complexes, the antifungal activity of alkylene dithiophosphate derivatives has been tested against three fungi, namely *Aspergillus flavus*, *Fusarium oxysporum* and *Alternaria alternata*. The screening data for the average percentage inhibition of the fungi at 100, 125 and 200 ppm concentrations. The values obtained suggest that the alkylene dithiophosphate derivatives of macrocyclic complexes are more fungitoxic than their precursor macrocyclic complexes as well as the alkylene dithiophosphoric acids. Further, the data also indicate that with the increase in the concentration, the fungitoxicity also increases.

The antibacterial activity against two bacteria namely *Salmonella typhi* and *Bacillus subtili* were tested by the inhibition zone technique[15,16]. The values suggest that the alkylene dithiophosphate derivatives of the macrocyclic complexes are more antibacterial than their precursor macrocyclic complexes (PbL¹–PbL⁵).

CONCLUSIONS

The following conclusions have been drawn from the above spectral data. The presence of four characteristic peaks for amide group in the IR spectra indicates the formation of stable macrocycles having amido group. The chemical shift values in ^1H & ^{13}C NMR in the expected range, in all 22-28 membered rings, accordingly, confirms the formation of stable 22-28 membered rings. A strong band observed in the region $670\text{-}700\text{ cm}^{-1}$ and which also appears in ammonium alkylene dithiophosphates, and has been attributed to free $\text{P}=\text{S}$ moiety, indicate the monodentate nature of alkylene dithiophosphate moieties. As the absorption in ^{31}P NMR doesn't show much shift from their parent alkylene dithiophosphate moieties, this also indicates the monodentate nature of the dithiophosphate ligands. Considering the above spectral data the following octahedral geometry has been assigned for these derivatives in which four nitrogen atoms of the macrocyclic ring coordinate to the central lead ion in the square planar form and each dithiophosphate moiety occupy the axial positions binding the central lead ion in unidentate manner through strong electrostatic attraction.



$$n = 1, 2, 3, 4 \text{ or } (\text{CH}_2)_n = o\text{-C}_6\text{H}_4\text{-}$$

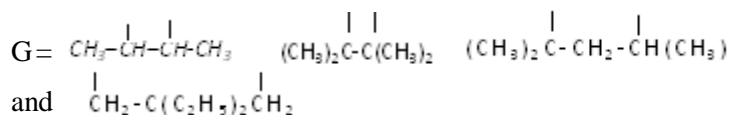


Fig.2. Tentative structure of the Alkylene dithiophosphate derivatives of macrocyclic complexes of Pb^{II} (1-15).

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