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Dialkyldithiophosphate Derivatives of Some Macrocyclic Complexes of Sr(II) And Ba(II) Having N_4S_4 Potential Donors in 22-28 Membered rings

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ABSTRACT

Dialkyldithiophosphate derivatives of macrocyclic complexes of Sr(II) and Ba(II), having N_4S_4 potential donors, of the general formula, $[M(L)\{S_2P(OR)_2\}_2]$ where M= Sr(II) and Ba(II), L=macrocyclic ligands L^1, L^2, L^3, L^4 and L^5; R= C_2H_5-, $C_3H_7^n$ or $C_3H_7^i$ have been synthesized from the reaction of $[M(L)X_2]$(where M = Sr(II) and Ba(II), X= Cl^-, NO_3^- or CH3CHOO$^-$) with sodium dialkyldithiophosphate in 1:2 molar ratios in THF. These complexes have been characterized by elemental analysis, molar conductance, molecular weight determinations, IR, ^1H, ^{13}C & ^{31}P NMR. Molecular weight determinations of these complexes indicate their monomeric nature. Octahedral structures have been proposed on the basis of IR, ^1H, ^{13}C & ^{31}P NMR, in which four nitrogen atoms of the macrocyclic ring coordinate to the central metal (M = Sr(II) and Ba(II)), ion square-planar geometry and each dithiophosphate moiety occupies the axial positions binding the central metal (M= Sr(II) and Ba(II),) ion in a unidentate manner. The antimicrobial activities of these derivatives have been studied by screening them Aspergillus flavus, Fusarium oxysporum, Alternaria alternata and bacteria like Salmonella typhi and Bacillus subtili. Dialkyldithiophosphate derivatives were found to be more fungitoxic and antibacterial than their corresponding macrocyclic complexes.

Keywords: Macrocyclic complexes, *bis*-(2-aminophenyl)disulphide, Sr(II) and Ba(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 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]. Inspite of vast innovation in macrocyclic chemistry and tremendous interest in mixed ligand complexes, no mixed ligand macrocyclic complex was reported till our publications. Dialkyldithiophosphate 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 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 N_2S_2 potential donors in 14 to 20 membered rings[15-32]. We have also reported the macrocyclic complexes of Ni(II), Sn(II) and Pb(II) with dialkyl- and alkylene dithiophosphate having N_4S_4 potential donors in 22-28

membered rings[17,24,29-32]. In continuation to the above work we hereby report the synthesis, characterization and antimicrobial studies of dialkyldithiophosphate derivatives of macrocyclic complexes of Sr(II) and Ba(II), having N_4S_4 potential donors in 22 to 28 membered rings.

MATERIALS AND METHODS

All the strontium and barium 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) disulphide was synthesized by the dimerization of the *o*-aminothiophenol by H_2O_2 as reported in the literature[33]. Dialkyldithiophosphoric acids were prepared by the reactions of various alcohols C_2H_5OH, $C_3H_7{}^nOH$, $C_3H_7{}^iOH$ with phosphorus pentasulphide. Phosphorus pentasulphide was added slowly in about 2 h to the anhydrous alcohol heated on a water bath. After complete addition of phosphorus pentasulphide, reactants were warmed till the evolution of hydrogen sulphide gas ceased. Solvents were removed under reduced pressure and the dialkyldithiophosphoric acid thus obtained was purified by distillation under reduced pressure.

Sodium salts of dialkyldithiophosphoric acids were prepared by the reaction of dialkyldithiophosphoric acids with corresponding sodium alkoxide in equimolar ratio. To the sodium alkoxide (prepared by dissolution of sodium metal in excess of parent alcohol) was added drop by drop, the benzene solution of dialkyldithiophosphoric acid in 1:1 molar ratio. The reaction was exothermic; however, for the sake of completion of reaction the contents were warmed for about 1 h. Solvent was removed under reduced pressure and the white solid thus obtained was washed with benzene and finally dried under reduced pressure, yielding a white crystalline solid.

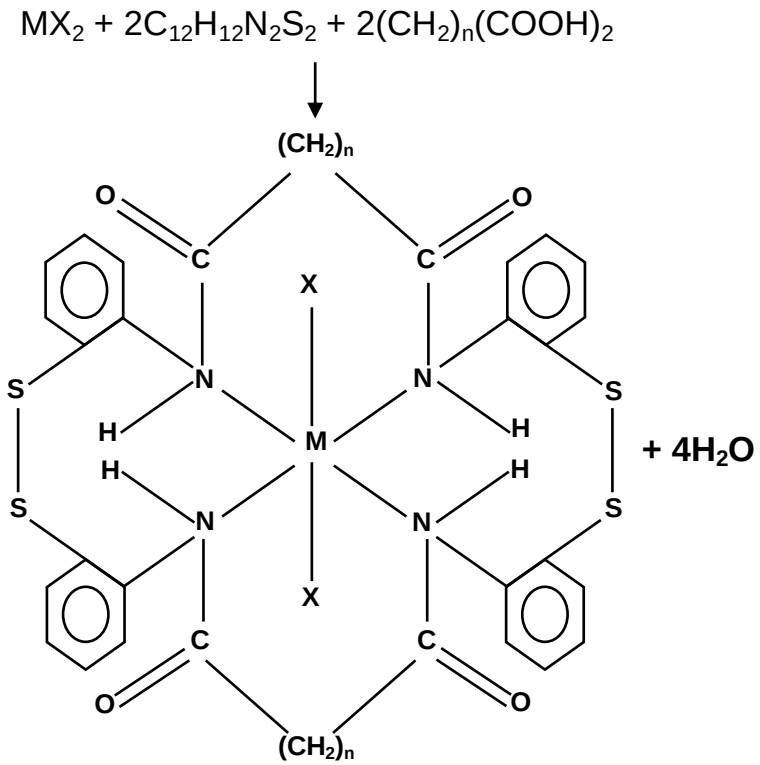
Microanalyses for carbon, hydrogen, nitrogen and sulphur were determined from SICART, Vallabh Vidyanagar. Strontium, barium and phosphorus were estimated by standard method[34]. The molecular weights were determined by Rast Camphor method. Infrared data were recorded on a Perkin-Elmer FT-IR spectrophotometer as KBr pellets. ^1H and ^{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 spectra were recorded on the same instrument using DMSO-d_6 as a solvent and H_3PO_4 as an external standard.

Synthesis of precursor macrocyclic complexes {Tetra benzo [2,3,9, 10,13, 14,20, 21] [4,8,15, 19] tetra aza [1,11,12,22]tetrathiacyclodiicosane [5, 7,16,18] tetraone}: A solution of strontium chloride (2.506 g, 0.009 mol) in methanol was reacted with *bis*-(2-aminophenyl)disulphide (4.630 g, 0.018 mol) dissolved in methanol. This was followed by the addition of a methanolic solution of malonic acid (1.940 g, 0.018 mol). Reaction mixture was refluxed for 6 h. The white precipitate obtained was filtered, washed with methanol and dried under vacuum. (Found : C,44.32; H,2.95; N,6.89; Cl,7.74; S,15.75; Sr,10.72%). Calc. for $C_{30}H_{24}N_4S_4O_4Cl_2{\cdot}Sr$(fw 790.62) : C,45.33; H,3.03; N,7.08; Cl,8.98; S,16.18; Sr,11.08%) m.p.204^o C; yield 5.50g(74%). The complexes of barium were prepared by the same method.

Synthesis of dialkyldithiophosphate derivative of macrocyclic complexes: Macrocyclic complex mentioned above (1.325g, 0.0016mol) was dissolved in THF and was reacted with methanolic solution of sodium diethyldithiophosphate (0.675g, 0.0032mol) in 1:2 molar ratio. Reaction mixture was refluxed for ~3 hours. On cooling the white crystals of dithiophosphate derivative were 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 sodium chloride ions formed during the reaction. Product was dried under vacuo and was crystallized with THF / C_2H_5OH mixture. The complexes of barium were prepared by the same method.

RESULTS AND DISCUSSION

Reaction of strontium and barium salts with *bis*-(2-aminophenyl) disulphide and various dicarboxylic acids in 1:2:2 molar ratio in methanol takes place in the following manner :



n = 1, 2, 3, 4 or $(CH_2)_n$ = *o*-C_6H_4- ; M = Sr(II) and Ba(II), X=Cl^-,NO_3^-,CH_3CHOO^-

Figure 1. General Structure of Macrocyclic Complexes of Sr(II) and Ba(II),

The above macrocyclic complexes of Sr(II) and Ba(II), in THF react with a methanolic solution of sodium dialkyldithiophosphate in 1:2 molar rations to afford the dialkyldithiophosphate derivatives of the macrocyclic Sr(II) and Ba(II), complexes in the following manner :

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

R= C_2H_5-, $C_3H_7^n$ or $C_3H_7^i$

L = Macrocyclic ligands L^1,L^2,L^3,L^4 and L^5

L^1= Macrocyclic ligand derived from *bis*-(2-aminophenyl)disulphide and malonic acid (n=1), **22-membered ring;**

{Tetrabenzo[2,3,9,10,13,14,20,21][4,8,15,19]tetraaza [1,11,12,22]tetrathiacyclodiicosane[5,7,16,18] tetraone}.

L^2= Macrocyclic ligand derived from *bis*-(2-aminophenyl)disulphide and succinic acid (n=2), **24-membered ring;**

{Tetrabenzo[2,3,10,11,14,15,22,23][4,9,16,21]tetraaza [1,12,13,24]tetrathiacyclotetraicosane[5,7,17,20]tetraon}.

L^3= Macrocyclic ligand derived from *bis*-(2-aminophenyl) disulphide and glutaric acid (n=3), **26-membered ring;**

{Tetrabenzo[2,3,11,12,15,16,24,25][4,10,17,23]tetraaza [1,13,14,26]tetrathiacyclohexaicosane[5,9,18,22]tetraone}.

L^4 = Macrocyclic ligand derived from *bis*-(2-aminophenyl) disulphide and adipic acid(n=4), **28-membered ring.**

{Tetrabenzo[2,3,12,13,16,17,26,27][4,11,18,25]tetraaza [1,14,15,28]tetrathiacyclooctaicosane[5,10,19,24]tetraone}.

L^5 = Macrocyclic ligand derived from *bis*-(2-aminophenyl) disulphide and phthalic acid ($(CH_2)_n$ = *o*-C_6H_4-), **24- membered ring;**

{Hexabenzo[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}.

Table 1.

Sr. No.	Ligand	Yield %	Physical State	B.P. °C mm Hg	Analysis % Sulphur Found (Calcd.)
1	$(C_2H_5O)_2PS_2H$	82	Colorless viscous liquid	76/2.0	34.57 (34.40)
2	$(C_3H_7{}^nO)_2PS_2H$	81	Colorless viscous liquid	78/2.0	29.82 (29.90)
3	$(C_3H_7{}^iO)_2PS_2H$	71	Colorless viscous liquid	84/2.0	29.97 (29.90)

The derivatives of macrocyclic complexes of the following dialkyl dithiophosphoric acids have been synthesized. Physical Properties and Analysis of Dialkyldithiophosphoric Acids has been given in table 1.

The reaction mixture was refluxed for ca. 3 h. On cooling the crystals of the dithiophosphate derivatives separated out. Except THF and DMSO, these derivatives are insoluble in almost all organic solvents. The physical data of these derivatives are given in table 1. All derivatives are white or off white in colour, which melts with decomposition at high temperature (224-244 ^oC). The molar conductance of 10^{-3} M solution in DMSO lie in the range 04-07 $ohm^{-1}cm^2mol^{-1}$ showing that these complexes are non-electrolyte. The molecular weight determinations indicate their monomeric nature (Table 2).

Table 2. Analytical Data of Dialkyldithiophosphate Derivatives of Macrocyclic Complexes of Sr(II) and Ba(II),

Sr. No.	Compound	Analysis % Found (Calcd.)						Molecular Wight Found (Calcd.)	Conductivity ^M $^{-1}$ ^{2} $^{-1}$ Ohm Cm Mol	M.P. (decomp.) ^{0}C	^{31}P NMR Chemical shift (δ)
		C	H	N	S	P	Sr(II) or Ba(II)				
1	$[Sr(L^1)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{38}H_{44}N_4SrO_8P_2S_8)$	40.47 (41.84)	3.95 (4.03)	5.03 (5.13)	23.00 (23.49)	5.57 (5.69)	7.87 (8.04)	1112.82 (1089.62)	04	226	96.20
2	$[Ba(L^1)\{S_2P(OC_3H_7{}^n)_2\}_2]$ $(C_{42}H_{52}N_4BaO_8P_2S_8)$	42.65 (42.16)	4.40 (4.35)	4.73 (4.68)	21.66 (21.41)	5.24 (5.18)	11.62 (11.48)	1181.64 (1195.33)	06	228	98.14
3	$[Ba(L^1)\{S_2P(OC_3H_7{}^i)_2\}_2]$ $(C_{42}H_{52}N_4BaO_8P_2S_8)$	42.91 (42.16)	4.42 (4.35)	4.76 (4.68)	21.79 (21.41)	5.27 (5.18)	11.69 (11.48)	1174.52 (1195.33)	07	232	-
4	$[Ba(L^1)\{S_2P(OC_3H_7{}^n)_2\}_2]$ $(C_{42}H_{52}N_4BaO_8P_2S_8)$	42.59 (42.94)	4.36 (4.29)	5.12 (5.01)	22.52 (22.90)	5.63 (5.54)	8.02 (8.83)	1139.43 (1117.62)	04	229	96.19
5	$[Sr(L^2)\{S_2P(OC_3H_7{}^n)_2\}_2]$ $(C_{44}H_{56}N_4SrO_8P_2S_8)$	44.28 (44.98)	4.69 (4.77)	4.69 (4.77)	21.47 (21.81)	5.19 (5.28)	7.34 (7.46)	1192.36 (1173.62)	05	241	-
6	$[Ba(L^2)\{S_2P(OC_3H_7{}^i)_2\}_2]$ $(C_{44}H_{56}N_4BaO_8P_2S_8)$	43.84 (43.16)	4.65 (4.57)	4.65 (4.65)	21.25 (21.925)	5.14 (5.06)	11.40 (11.22)	1204.29 (1223.33)	06	239	99.19
7	$[Sr(L^3)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{42}H_{52}N_4SrO_8P_2S_8)$	44.58 (43.99)	5.59 (5.53)	4.95 (4.88)	22.64 (22.34)	5.48 (5.41)	7.75 (7.64)	1130.52 (1145.62)	04	224	90.80
8	$[Ba(L^3)\{S_2P(OC_3H_7{}^n)_2\}_2]$ $(C_{46}H_{60}N_4BaO_8P_2S_8)$	43.51 (44.11)	4.73 (4.79)	4.41 (4.47)	20.18 (20.45)	4.88 (4.95)	10.82 (10.97)	1268.44 (1251.33)	06	236	92.44
9	$[Sr(L^3)\{S_2P(OC_3H_7{}^i)_2\}_2]$ $(C_{46}H_{60}N_4SrO_8P_2S_8)$	45.58 (45.94)	4.87 (4.99)	4.71 (4.66)	21.12 (21.30)	5.19 (5.15)	7.21 (7.29)	1213.42 (1201.62)	05	238	-
10	$[Ba(L^4)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{44}H_{56}N_4BaO_8P_2S_8)$	43.61 (43.16)	4.62 (4.57)	4.62 (4.57)	21.14 (20.92)	5.12 (5.06)	11.34 (11.22)	1210.63 (1223.33)	06	239	96.89
11	$[Sr(L^4)\{S_2P(OC_3H_7{}^n)_2\}_2]$ $(C_{48}H_{64}N_4SrO_8P_2S_8)$	46.31 (46.84)	5.14 (5.20)	4.50 (4.55)	20.58 (20.81)	4.98 (5.04)	7.04 (7.12)	1243.73 (1229.62)	04	242	-

12	$[Ba(L^4)\{S_2P(OC_3H_7^i)_2\}_2]$	45.77	5.08	4.45	20.34	4.92	10.91	1258.24	07	235	92.62
	$(C_{48}H_{64}N_4BaO_8P_2S_8)$	(45.02)	(5.00)	(4.37)	(20.01)	(4.84)	(10.73)	(1279.33)			
13	$[Sr(L^5)\{S_2P(OC_2H_5)_2\}_2]$	46.99	3.91	4.56	20.88	5.05	7.14	1225.58	05	244	94.76
	$(C_{48}H_{48}N_4SrO_8P_2S_8)$	(47.46)	(3.95)	(4.61)	(20.09)	(5.10)	(7.21)	(1213.62)			
14	$[Ba(L^5)\{S_2P(OC_3H_7^n)_2\}_2]$	47.90	4.29	4.29	19.65	4.75	10.54	1302.64	04	231	91.30
	$(C_{52}H_{56}N_4BaO_8P_2S_8)$	(47.29)	(4.24)	(4.24)	(19.40)	(4.69)	(10.40)	(1319.33)			
15	$[Sr(L^5)\{S_2P(OC_3H_7^i)_2\}_2]$	49.42	4.36	4.35	20.32	4.93	6.82	1252.23	05	229	-
	$(C_{52}H_{56}N_4SrO_8P_2S_8)$	(49.14)	(4.41)	(4.41)	(20.16)	(4.88)	(6.90)	(1269.62)			

[a]Analytical and physico-chemical data of precursor macrocyclic complexes.

Infrared spectra : As observed in the macrocyclic complexes, the four bands in the region 1684-1644(s), 1600-1542(m), 1294-1240(s) and 690-640(w) cm^{-1} have been ascribed to amide I, amide II, amide III and amide IV in plane deformation vibrations, respectively[35]. A broad band present in the region 3238–3068 cm^{-1} has been assigned to ν(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 region 1084-1040 and 894-850 cm^{-1} may be assigned to (P)–O–C and P–O–(C) stretching vibrations respectively[36]. A weak band present in the region 584-544 cm^{-1} has been attributed to P–S symmetric and asymmetric vibrations. A strong band observed in the region 770-690 cm^{-1}, which also appears in sodium dialkyl-dithiophosphates around the same region, is attributed to free P=S moiety. This indicates the unidentate behaviour of dithiophosphate moieties. The presence of sharp bands in the region 490-440 cm^{-1} and 368-329 cm^{-1} have been assigned to ν(Sr-N) or ν(Ba-N) and ν(Sr-S) or ν(Ba-S) vibrations, respectively[7,8,37].

^{1}H NMR Spectral Data: The structure of dialkylenedithiophosphate derivatives of macrocyclic complexes of Sr(II) and Ba(II) have been further confirmed by recording the 1H NMR using DMSO-d6 as a solvent and TMS as an internal standard. In addition to the protons appear in the parent macrocyclic complexes, the additional protons of dialkyldithiophosphate moieties appears in the spectra. The protons of CH3- group of diethyldithiophosphate moieties appeared as a triplet in the range δ 1.40 to 1.72 ppm. Protons of CH3- group of iso-propyl moiety appeared as a doublet in the range δ 1.46 to 1.62 ppm and the protons of CH3- 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 3.8 to 4.4 ppm. The broad singlet observed between δ 7.90 to 8.30 ppm has been assigned the proton of –C(O)NH- group. The protons of -CH2- group of malonic acid appear as a singlet in the range, δ 3.20 to 3.68 ppm. The methylene protons of -CH2- CH2- group of succinic acid appear as a singlet in the range of δ 3.14 to 3.26 ppm. The protons of α - C atoms of glutaric acid moiety were observed as a multiplate δ 3.46 ppm. The protons of β-C atoms of the above moiety appeared as a multiplet δ 2.09 ppm. The protons of α-C atoms of adipic acid moiety appeared between δ 3.46 to 3.64 ppm. The protons of β-C atoms appear in the δ 1.81 to 1.99 ppm. Aromatic protons of bis-(2-aminophenyl)disulphide moiety were observed as a multiplet in the range δ 7.17 to 7.96 ppm. The values are in the expected region[38,39].

^{13}C NMR Spectral Data: The ^{13}C NMR spectral data of a few complexes could be recorded 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 alkylenedithiophosphate moieties appear in the spectra. The carbons of CH_3- group of diethyl, di *n*-propyl and di *iso*-propyl dithiophosphates appear in the region δ 13.09 to 14.72 ppm. The carbon of CH3- group of diethyl, di *n*-propyl and di *iso*-propyl lie in the δ 40.08 to 42.06 ppm. The carbon of -CH_2- group of malonic acid moiety lie in the range δ 30.42 to 34.89 ppm. The carbons of –CH_2-CH_2- moiety appear in the range δ 26.14 to 27.19 ppm. The α-carbon of glutaric acid moiety were observed in the range δ 31.99 to 34.89 ppm and the β- carbons of the above moiety appear in the range δ 27.19 to 28.82 ppm respectively. The α carbons of adipic acid moiety appeared at δ 34.89 ppm and β-carbon at δ 29.10 ppm. The carbon of phthalic acid moiety observed at δ 74.09 ppm. Signals observed at δ 182.20 to 194.09 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 81.26 to 86.24 ppm. The carbons of phenyl group of *bis*-(2-aminophenyl) disulphide moiety appeared in the range δ 70.46 to 74.52 ppm. The values are in the expected range[38,39].

^{31}P NMR: ^{31}P NMR spectra of a few representative compounds could be recorded. The spectra were recorded on a Jeol 270 MHz spectrometer using DMSO-d_6 as a solvent and H_3PO_4 as an external standard. The chemical shift values do not show any significant change from their parent dialkyldithiophosphoric acids. This indicates again the monodentate nature of dialkyldithiophosphate moieties attached to the central metal (M= Sr(II) and Ba(II)ion[40,41].

APPLICATIONS

Antimicrobial Activity: The antimicrobial activity of *bis*-(2-aminophenyl)disulfide, dicarboxylic acids, metal salts and parent macrocyclic complexes (ML^1-ML^5) has been reported in our earlier communication[15]. Like their precursor macrocyclic complexes, the antifungal activity of dialkyldithiophosphate derivatives has been tested against three fungi, *Aspergillus flavus*, *Fusarium oxysporum* and *Alternaria alternata*. The screening data for the average percentage inhibition of the fungi at 100, 125 and 200 ppm concentration, are given in Table-III. The values obtained suggest that the dialkyldithiophosphate derivatives of macrocyclic complexes are more fungitoxic than their precursor macrocyclic complexes.

The antibacterial activity against two bacteria, namely *Salmonella* typhi and *Bacillus* subtili, were tested by the inhibition zone technique[15,16]. The data obtained are presented in Table-III. The values suggest that the dialkyldithiophosphate derivatives of macrocyclic complexes are more antibacterial than their precursor macrocyclic complexes (ML^1-ML^5).

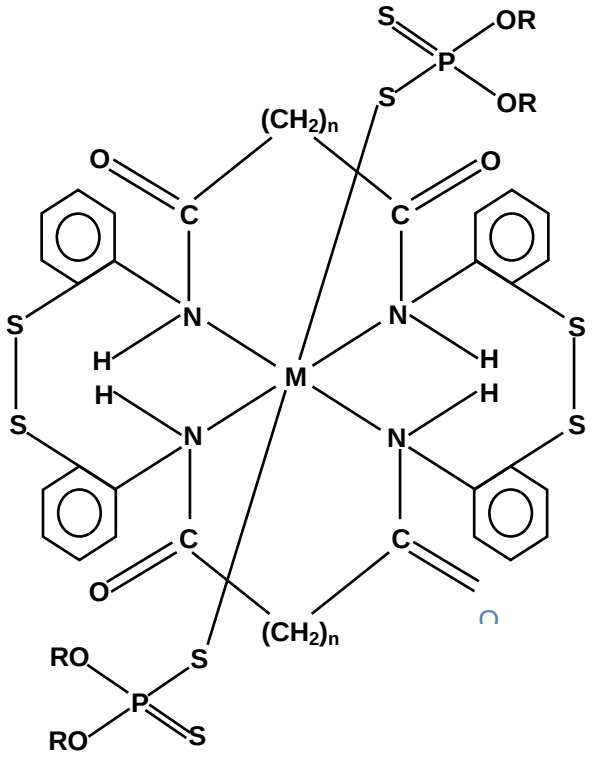
Table 3 Antifungal Activity And Antibacterial Activity of Dialkyldithiophosphate Derivatives of Macrocyclic Complexes of Sr(II) and Ba(II)

S.No	Compound	Average % of Inhibition after 72 h at 30± 2°C									**percentage growth inhibition after** 24 hours at 30 ± 2°C (conc. in ppm)			
		Aspergillus flavus			***Fusarium oxysporum***			***Alternaria alternata***			***Bacillus Subtili***		***Salmonella typhi***	
		100	125	200	100	125	200	100	125	200	500	1000	500	1000
A	Bavestin (standard)	92	96	99	90	94	98	94	97	99	97	99	96	99
B	*Bis*-(2-aminophenyl)disiulphide	30	34	40	31	35	39	32	37	41	11	13	10	12
C	$BaCl_2.2H_2O$	21	24	27	23	31	40	22	35	40	10	12	12	14
D	$Sr(NO_3)_2$	24	32	39	23	38	42	21	36	44	12	14	11	13

E	$Ba(CH_3COO)_2$	22	34	42	21	36	44	24	34	41	09	11	11	13
F	$HOOC\text{-}CH_2\text{-}COOH$	23	32	40	19	34	42	22	32	39	08	09	08	09
G	$HOOC\text{-}(CH_2)_2\text{-}COOH$	22	31	42	20	30	39	23	31	40	07	10	09	10
H	$HOOC\text{-}(CH_2)_3\text{-}COOH$	22	26	30	23	29	23	26	27	31	07	09	06	08
I	$HOOC\text{-}(CH_2)_4\text{-}COOH$	23	24	29	24	30	33	24	29	32	08	10	09	11
J	$HOOC\text{-}C_6H_4\text{-}COOH$	20	23	29	21	26	30	20	26	30	08	06	09	08
K	$(C_2H_5O)_2P(S)SH$	61	65	66	70	72	74	75	68	70	27	31	28	34
L	$(C_3H_7O^n)_2P(S)SH$	62	64	65	66	72	73	75	66	72	29	32	28	36
M	$(C_3H_7O^i)_2P(S)SH$	72	74	68	65	70	72	74	71	73	31	34	30	32
1	$[Sr(L^1)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{38}H_{44}N_4SrO_8P_2S_8)$	66	69	72	75	74	68	65	61	62	32	36	31	36
2	$[Ba(L^1)\{S_2P(OC_3H_7{}^n)_2\}_2]$ $(C_{42}H_{52}N_4BaO_8P_2\ S_8)$	61	60	70	72	74	78	65	69	70	33	37	34	38
3	$[Ba(L^1)\{S_2P(OC_3H_7{}^i)_2\}_2]$ $(C_{42}H_{52}N_4BaO_8P_2S_8)$	71	74	75	65	69	72	70	73	74	31	38	32	39
4	$[Sr(L^2)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{40}H_{48}N_4SrO_8P_2S_8)$	65	69	70	72	74	78	80	79	65	29	37	30	38
5	$[Sr(L^2)\{S_2P(OC_3H_7{}^n)_2\}_2]$ $(C_{44}H_{56}N_4SrO_8P_2S_8)$	69	71	73	75	65	69	70	71	72	30	36	32	40
6	$[Ba(L^2)\{S_2P(OC_3H_7{}^i)_2\}_2]$ $(C_{44}H_{56}N_4BaO_8P_2S_8)$	72	74	75	65	69	68	78	75	73	31	39	32	41
7	$[Sr(L^3)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{42}H_{52}N_4SrO_8P_2S_8)$	65	66	69	70	72	75	66	69	70	33	36	34	39
8	$[Ba(L^3)\{S_2P(OC_3H_7{}^n)_2\}_2]$ $(C_{46}H_{60}N_4BaO_8P_2S_8)$	72	75	73	65	66	69	71	73	75	29	38	30	42
9	$[Sr(L^3)\{S_2P(OC_3H_7{}^i)_2\}_2]$ $(C_{46}H_{60}N_4SrO_8P_2S_8)$	68	66	65	70	73	74	69	73	76	32	38	33	43
10	$[Ba(L^4)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{44}H_{56}N_4BaO_8P_2S_8)$	76	65	66	63	70	72	75	73	65	33	40	34	41
11	$[Sr(L^4)\{S_2P(OC_3H_7{}^n)_2\}_2]$ $(C_{48}H_{64}N_4SrO_8P_2S_8)$	71	73	68	71	73	75	66	65	78	34	38	39	44
12	$[Ba(L^4)\{S_2P(OC_3H_7{}^i)_2\}_2]$ $(C_{48}H_{64}N_4BaO_8P_2S_8)$	71	73	76	69	66	74	76	77	65	33	36	35	42
13	$[Sr(L^5)\{S_2P(OC_2H_5)_2\}_2]$ $(C_{48}H_{48}N_4SrO_8P_2S_8)$	66	70	73	75	76	65	69	70	72	39	43	40	45
14	$[Ba(L^5)\{S_2P(OC_3H_7{}^n)_2\}_2]$ $(C_{52}H_{56}N_4BaO_8P_2S_8)$	74	76	65	69	70	73	75	76	68	40	44	41	47
15	$[Sr(L^5)\{S_2P(OC_3H_7{}^i)_2\}_2]$ $(C_{52}H_{56}N_4SrO_8P_2S_8)$	68	65	75	73	69	68	65	63	70	32	42	34	41

CONCLUSIONS

The above spectral data indicate the following octahedral geometry **(Fig. 2)** for the above derivatives in which four nitrogen atoms of the macrocyclic ring coordinate to the central metal (M=Sr(II) and Ba(II)) ion in the square-planar form and each dithiophosphate moiety occupies the axial position binding the central metal (M=Sr(II) and Ba(II)) ion in unidentate manner through strong electrostatic attraction.



Where, M = Sr(II) and Ba(II); R=C_2H_5-, $C_3H_7{}^{i}$- or $C_3H_7{}^{n}$-;
n = 1, 2, 3, 4 or $(CH_2)_n$ = *o*-C_6H_4- &
L = Macrocyclic ligands L^1, L^2, L^3, L^4 and L^5

Fig.2. Tentative structure of the dialkyldithiophosphate derivatives of macrocyclic complexes of Sr(II) and Ba(II)

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