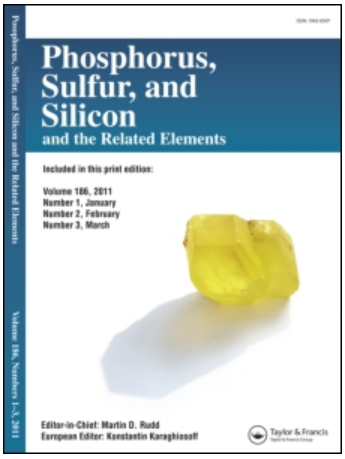

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Synthesis and Characterization of Hg(II) Complexes with 2-Subsituted Benzothiazole Thiophosphates

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Synthesis and Characterization of Hg(II) Complexes with 2-Subsituted Benzothiazole Thiophosphates

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Some complexes of 3-methyl-2-benzothiazolylidenamido thiophosphoryl dichloride (L_1), (3-methyl-2-benzothiazolylidenamido)–bis-(diethylamido) thiophosphate (L_2), 3-benzyl-2-benzothiazolylidenamido thiophosphoryl dichloride (L_3), and (3-benzyl-2-benzothiazolylidenamido)–bis-(diethylamido) thiophosphate (L_4) have been synthesized by a reaction with mercuric chloride in a 1:1 ratio. The complexes have been characterized by elemental analysis, electrical conductivity, and mass and IR spectral studies. The stability constants of these complexes have also been determined by a spectrophotometric technique and compared with zinc complexes of the previously discussed ligands.

Keywords Benzothiazole; mercuric complexes; stability constants; thiophosphate derivatives

INTRODUCTION

Organophosphorus compounds containing heterocyclic rings are used in the field of agrochemistry and pharmaceuticals.[1,2] Functionalized dichlorophosphines serve as useful precursors for organophosphorus compounds,[3,4] and these organophosphorus derivatives can serve as ligands for a number of complexes using different metals.[5,6]

L_1, L_2, L_3, and L_4 are organothiophosphates synthesized by Kabra et al.[7,8,9] using 3-alkyl-2-aminocycloiminium halides as starting materials. In continuation on the synthesis and characterization of complexes of these ligands with Zn(II),[10] we hereby report the synthesis and characterization of Hg(II) complexes.

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RESULTS AND DISCUSSION

Elemental Analysis

On the basis of elemental analyses, mercuric complexes have been assigned a composition involving 1:1 metal:ligand stoichiometry, which is found to be in agreement with the proposed molecular formulae.

Conductometric Titrations

In Figure 1, all graphs have a break at a particular volume of ligand solution added. From the ratio of the amount of metal ion in a 20-mL solution to the amount of ligand in a particular volume added, the possible molar ratio of the complexes were determined, and it was found to be approximately 1:1 metal:ligand for all complexes. Thus, the results of conductometric measurements shown in the Figure 1 support the stoichiometries suggested on the basis of elemental analysis.

Spectrophotometric Titrations

In Figure 2, maxima appeared at $X = 0.5$ for metal complexes of Hg(II) for L_1, L_2, L_3, and L_4 at λ_{max} 590 nm, confirming the formation of complexes in a 1:1 ratio. The results of spectrophotometric titrations that are shown in Figure 2 are also in good accordance with those obtained from the conductometric titration method (Figure 1).

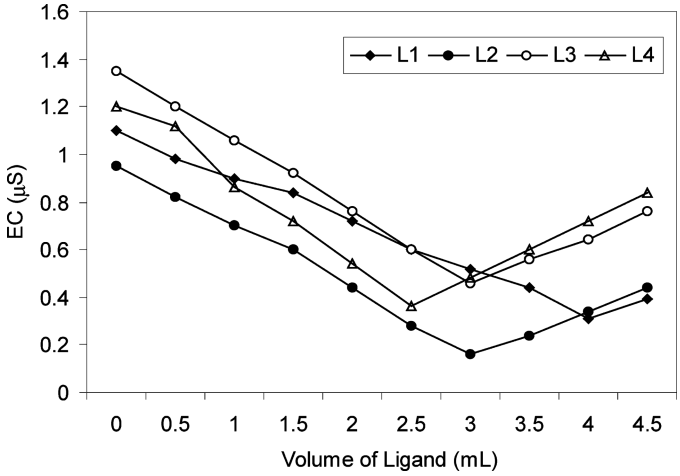


FIGURE 1 The conductometric titration of 20 mL (1×10^{-3} M) $HgCl_2$ with L_1, L_2, L_3, and L_4.

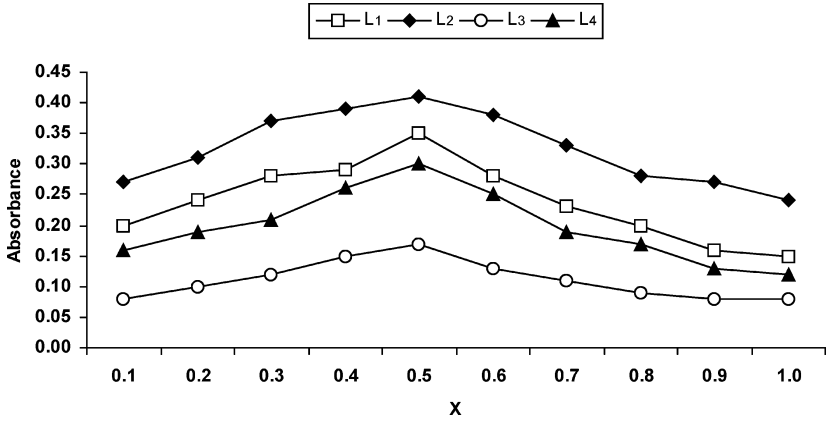


FIGURE 2 Job's continuous variation curves for metal chelates between Hg(II) and L_1, L_2, L_3, and L_4, at λ_{max} 590 nm.

Stability Constants

Numbers of experimental and computational techniques have been developed for determining stability constants of complexes. Stability constants of mercury complexes were calculated by using the results of spectrophotometric methods[11] and are shown in Table I. It is observed from Table I that Hg(II) complexes are more stable than Zn(II)[10] complexes involving the same ligands.

Infrared Spectra

The major IR spectral bands of the ligands and their mercuric complexes are given in Table II.

TABLE I Stability Constants for the Formation of Hg(II)-L and Zn(II)-L Complexes in Solution

Metal Ion (M)	Ligands (L)	M:L Ratio	Stability Constant K_f
Hg(II)	L_1	1:1	8.6×10^4
Zn(II)	L_1	1:1	8.31×10^2
Hg(II)	L_2	1:1	2.95×10^5
Zn(II)	L_2	1:1	7.5×10^3
Hg(II)	L_3	1:1	9.42×10^3
Zn(II)	L_3	1:1	4.0×10^3
Hg(II)	L_4	1:1	5.1×10^4
Zn(II)	L_4	1:1	1.84×10^4

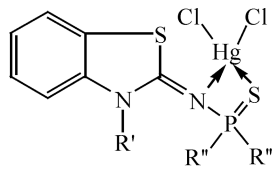
TABLE II Assignment of Main IR Bands (cm^{-1}) of Ligands and Their Hg(II) Complexes

Compound	ν (C═N)	ν (P─N─C)	ν (P═S)	ν (P─Cl)	Other bands
L_1	1595	1085	785(I)	500 (sym.)	—
		745	702(II)	610 (asym.)	—
C_1	1575	1012	763(I)	500 (sym.)	581ν (Hg─N)
		735	622(II)	610 (asym.)	358 ν (Hg─S)
L_2	1603	1063	775(I)	—	—
		685	605(II)	—	—
C_2	1570	1050	755(I)	—	617 ν (Hg─N)
		680	585(II)	—	370 ν (Hg─S)
L_3	1610	1105	800(I)	515 (sym.)	—
		760	717(II)	625 (asym.)	—
C_3	1590	1025	780(I)	515 (sym.)	509 ν (Hg─N)
		6857	697(II)	625 (asym.)	335 ν (Hg─S)
L_4	1620	1080	790(I)	—	—
		700	620(II)	—	—
C_4	1595	1060	770(I)	—	545ν (Hg─N)
		690	660(II)	—	345 ν (Hg─S)

The ligands exhibit a medium strong sharp band in the region 1620–1595 cm^{-1} due to the ν (C═N)[12]. The stretching absorption bands of ν (P─N)[13] and ν (C─N)[13] appeared at 760–685 cm^{-1} and 1105–1063 cm^{-1}, respectively. Two absorption bands of ν (P═S)[14] are observed in the region 800–775 cm^{-1} (I) and 717–605 cm^{-1} (II). In L_1 and L_3, ν (P─Cl) absorption bands appear at 515–500 cm^{-1} and 625–610 cm^{-1} for symmetric and asymmetric stretching vibrations, respectively, which are in good agreement as reported in literature.[15]

In Hg(II) complexes of these ligands, the band due to ν (C═N) exhibits a negative shift of 25–30 cm^{-1} and appears in the region 1590–1570 cm^{-1}. The ν (P─Cl) stretching (symmetric and asymmetric) and ν (P─N) stretching bands remain almost unchanged on the coordination of the ligands to the metal ion. Both absorption bands of ν (P═S) are also shifted to a lower wave number and appear at 780–755 cm^{-1} (I) and 697–585 cm^{-1} (II), respectively. All complexes display some new bands at 617–509 cm^{-1} and 370–335 cm^{-1} assigned to ν (Hg─N)[16,17] and ν (Hg─S)[17] modes, respectively.

The appearance of ν (Hg─N) and ν (Hg─S) absorption bands indicates coordination of a ligand through N and S, which further indicates that the ligands act as bidentate ligands. As reported previously[10] that the exocyclic N and S atoms of the ligands are more electronegative than the endocyclic N and S atoms, which in turn reduces the possibility of complexation through the heterocyclic N and S atoms. The negative



	C_1	C_2	C_3	C_4
R'	CH_3	CH_3	$CH_2C_6H_5$	$CH_2C_6H_5$
R''	Cl	$N(C_2H_5)_2$	Cl	$N(C_2H_5)_2$

FIGURE 3 The suggested structure of the Hg(II) complexes.

shift of ν (C=N) and ν (P=S) bands also eliminates the possibility of a coordination through the heterocyclic N and S atoms and thus confirms the complexation through the exocyclic N and S atoms. Conclusively, the Hg(II) complexes synthesized using these novel organothiophosphates as a ligand can be designated as complexes with tetrahedral geometry. These complexes may be assigned the following structures (Figure 3).

Mass Spectra

For determining the molecular mass of the chelates, mass spectra were recorded. The splitting pattern of the mass spectrum of C_4 is represented in Figure 4.

The appearance of a molecular ion peak at m/z 717.7 confirms the formation of mercuric complex in a 1:1 ratio. The relative abundance of different fragments with their m/z values are represented in Table III.

From the previous discussion, we arrive to the conclusion that Hg(II) complexes of L_1, L_2, L_3, and L_4 are four coordinated tetrahedral complexes involving a fourmembered chelate ring as reported earlier for Zn(II) complexes.[10] However, Hg(II) complexes are more stable than Zn(II)[10] complexes as evident from the stability constant data. It is also

TABLE III Mass Spectral Data of C_4 (Relative Abundance is Given in Parentheses)

Compound	m/z (%)
C_4	717.7(M^+, 30.7), 684.7(30.7), 641.7(16.4), 609.7(16.4), 537.5(10.7), 435.3(16.4), 234.7(67.9), 91.0(100), 65.0(71.5)

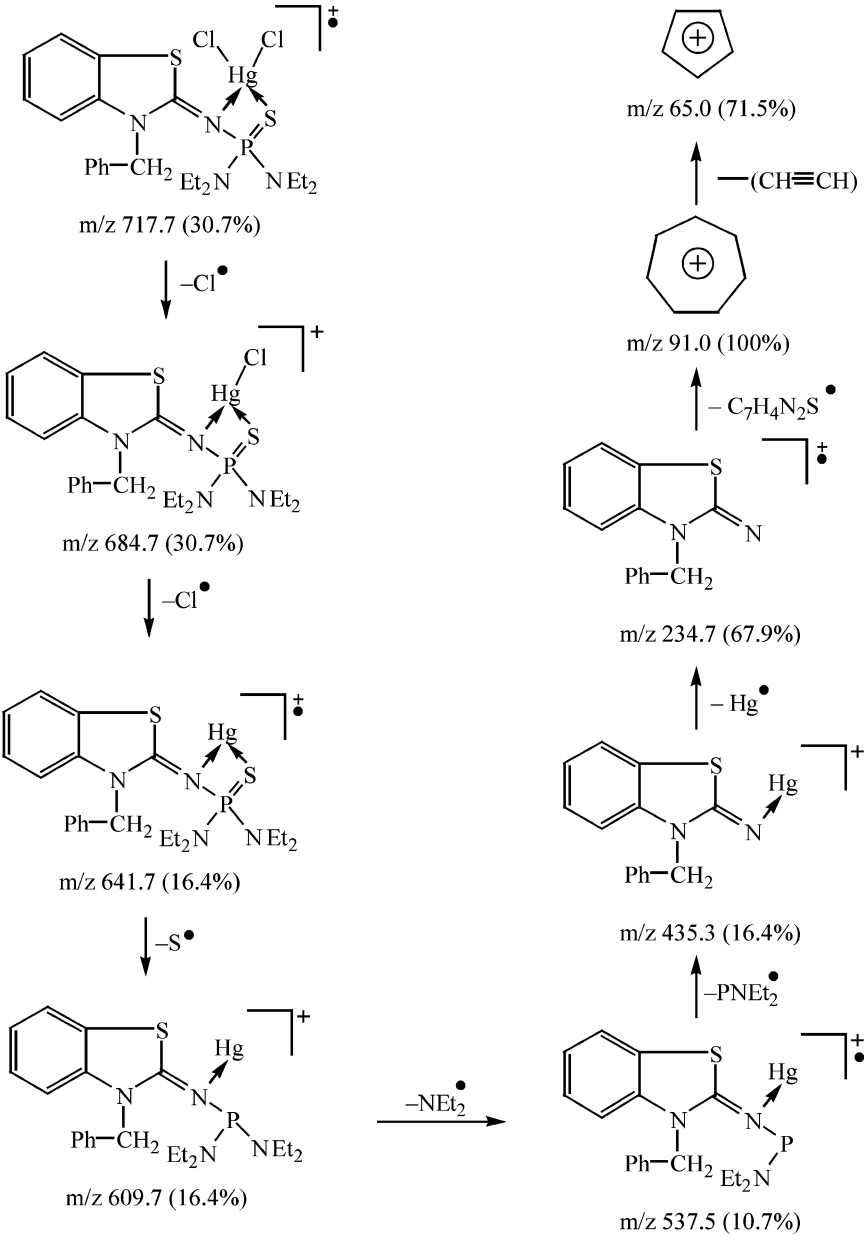


FIGURE 4 The suggested structure of C_4 and the splitting pattern of its mass spectrum.

observed from physical properties that Hg(II) complexes are colored, whereas Zn(II) complexes were white or light colored, which is in accordance to the literature.[18]

EXPERIMENTAL

All solvents and chemicals were purified, dried, and distilled before use by standard methods,[19] and moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes.

Synthesis of Ligands

The structure, synthesis, physical properties, and analytical data of ligands L_1, L_2, L_3, and L_4 were reported previously.[7,8,10]

Conductometric Titrations

Conductometric titrations were carried out between ligands and metal salt to determine the possible molar ratio of complexes. For conductivity measurements, stock solutions of the ligands and mercuric chloride were prepared in methylene chloride. The concentration of the ligands in the solution was kept approximately five times of that the metal solution in order to satisfy the maximum coordination number of the metal ion.

Data of conductometric titrations are summarized in Table IV. From these data, the graphs between the volume of the ligand solution added (mL) and the electrolytic conductance (μS) were plotted, which are shown in Figure 1.

Spectrophotometric Titrations

Spectrophotometric titrations were also carried out to determine the composition of the complexes in DMF solution using a spectrophotometric molar ratio and the continuous variation method[20,21] at λ_{max} of each complex. The job's continuous variation experiment was performed with solutions containing an equimolar solution of Hg(II) ion and lignads (L_1–L_4) in different proportions. The absorbance of these solutions containing a different molar ratio of the metal to ligand were measured at λ_{max}, i.e., 590 nm. The composition of solutions, used in continuous variation experiments and their absorbances with L_1–L_4, are shown in Table V.

TABLE IV Data of Conductometric Titration at 25°C ± 0.1°C. Molarity of $HgCl_2$ Solution: 1×10^{-3} M. Molarity of Ligands Solution: 5×10^{-3} M. Vol. of $HgCl_2$ Solution Taken Initially: 20 mL

Volume of Ligands (mL) Added	Electrolytic Conductance (μS)			
	L_1	L_2	L_3	L_4
0.0	1.10	.95	1.35	1.20
0.5	.98	.82	1.20	1.12
1.0	.90	.70	1.06	.86
1.5	.84	.60	.92	.72
2.0	.72	.44	.76	.54
2.5	.60	.28	.60	.36
3.0	.52	.16	.46	.48
3.5	.44	.24	.56	.60
4.0	.31	.34	.64	.72
4.5	.39	.44	.76	.84

Ligands: L_1, L_2, L_3, and L_4

The continuous variation curves were obtained by plotting the absorbance as a function of molar fraction of the ligands (X) as shown in Figure 2, where $X = \frac{[\text{Ligand}]}{[\text{Ligand}]+[\text{Hg(II)ion}]}$.

Synthesis of Hg(II) Complexes

Mercuric chloride dissolved in methylene chloride was added slowly to the equimolar solution of ligands (L_1–L_4) in methylene chloride and was

TABLE V The Composition of Solutions Used in Continuous Variation Experiments and Their Absorbances with L_1–L_4

S. No.	Solution of Hg(II) Ion (mL)	Solution of Ligands (mL)	$X = \frac{[\text{Ligand}]}{[\text{Ligand}] + [\text{Hg(II)ion}]}$	Absorbance			
				L_1	L_2	L_3	L_4
1	0.9	0.1	0.1	.20	0.27	.08	.16
2	0.8	0.2	0.2	.24	.31	.10	.19
3	0.7	0.3	0.3	.28	.37	.12	.21
4	0.6	0.4	0.4	.29	.39	.15	.26
5	0.5	0.5	0.5	.35	.41	.17	.30
6	0.4	0.6	0.6	.28	.38	.13	.25
7	0.3	0.7	0.7	.23	.33	.11	.19
8	0.2	0.8	0.8	.20	.28	.09	.17
9	0.1	0.9	0.9	.16	.27	.08	.13
10	0.0	1.0	1.0	.15	.24	.08	.12

TABLE VI Physical Properties and Analytical Data of Hg(II) Complexes

	Proposed Molecular Formula of Complex	Color and State	Yield (%)	MP °C	Analysis, % (Calcd.) Found							Mol. Wt. (Calcd.) Found
					C	H	N	S	P	Cl	Hg	
C_1	$C_8H_7N_2PS_2HgCl_4$	Brown solid	66	278	(16.88) 16.75	(1.24) 1.07	(4.92) 4.75	(11.27) 11.12	(5.44) 5.41	(24.91) 24.75	(35.24) 35.19	(569.2) 564.3
C_2	$C_{16}H_{27}N_4S_2PHgCl_2$	Yellow solid	84	250	(29.93) 29.84	(4.24) 4.22	(8.73) 8.64	(9.99) 9.97	(4.82) 4.79	(11.04) 10.93	(31.25) 31.16	(642.0) 639.1
C_3	$C_{14}H_{11}N_2PS_2HgCl_4$	Grey solid	55	265	(26.08) 26.07	(1.72) 1.70	(4.34) 4.20	(9.95) 9.85	(4.80) 4.78	(21.99) 21.85	(31.11) 31.01	(644.8) 641.4
C_4	$C_{22}H_{31}N_4S_2PHgCl_2$	Brown solid	74	245	(36.82) 36.69	(4.35) 4.24	(7.81) 7.73	(8.94) 8.81	(4.32) 4.30	(9.88) 9.77	(27.95) 27.87	(717.7) 713.5

refluxed for 10–12 h. The solids, which separated out, were filtered and washed with methylene chloride and dried in vacuo. Complexes were purified by recrystallization from absolute alcohol and were analyzed. Their physical properties and analytical data are given in Table VI, in which C_1, C_2, C_3, and C_4 are the Hg(II) complexes of L_1, L_2, L_3, and L_4, respectively.

The conductance measurements were carried out on a Conductivity Bridge model 1160E at $25^\circ C \pm 0.1^\circ C$. Absorption spectra of metal chelates in solution were recorded with a digital spectrophotometer Model 301E. IR spectra of ligands as well as complexes were recorded on a Perkin Elmer RXI IR spectrophotometer in the region 4000–200 cm^{-1}, and mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer.

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