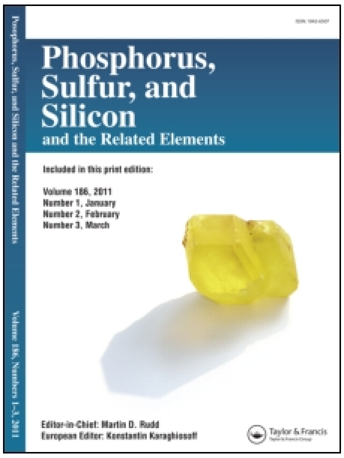


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Characterization of Some New Zinc(II) Complexes Incorporating Heterocyclic Thiophosphates as a Ligand

Gita Seth[a]; Vijaya Kabra[a]; Jasvinder Kaur[a]; Ritu Mathur[a]; Priti Kaushik[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

To cite this Article Seth, Gita , Kabra, Vijaya , Kaur, Jasvinder , Mathur, Ritu and Kaushik, Priti(2006) 'Synthesis and Characterization of Some New Zinc(II) Complexes Incorporating Heterocyclic Thiophosphates as a Ligand', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 5, 1001 — 1010

To link to this Article: DOI: 10.1080/10426500500272251

URL: http://dx.doi.org/10.1080/10426500500272251

Phosphorus, Sulfur, and Silicon, 181:1001–1010, 2006

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500500272251

Synthesis and Characterization of Some New Zinc(II) Complexes Incorporating Heterocyclic Thiophosphates as a Ligand

Gita Seth
Vijaya Kabra
Jasvinder Kaur
Ritu Mathur
Priti Kaushik
Department of Chemistry, University of Rajasthan, Jaipur, India

New tetracoordinated complexes of Zn (II) have been synthesized by the reaction between zinc chloride and 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-(diethyl-amido) thiophosphate (L_4) in a 1:1 ratio. The complexes have been isolated and characterized by elemental analysis, electrical conductivity, and mass and IR spectral studies. The stability constants of these complexes also have been determined in aqueous solution by spectrophotometric methods.

Keywords Benzothiazole; four-membered chelates; organophosphorus ligands; zinc complexes

INTRODUCTION

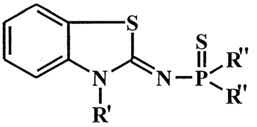
The organophosphorus compounds containing a heterocyclic moiety and their coordination compounds with a metal ion have drawn much attention due to their importance in biological and medicinal chemistry.[1–4]

L_1, L_2, L_3, and L_4 are novel organothiophosphates prepared by Kabra and colleagues[5,6] using 3-alkyl-2-aminocycloiminium halides as starting materials. It has been observed on the basis of semiemperical computational calculations of these ligands using a MOPAC[7] package that the exocyclic atoms N and S have almost the same electronegativity and are found to be more electronegative in comparison to the endocyclic

Received January 24, 2005; accepted April 22, 2005.

We are thankful to Central Research Drug Institute, Lucknow for extending IR and mass spectral facilities.

Address correspondence to Gita Seth, University of Rajasthan, Department of Chemistry, Jaipur 302004, India. E-mail: gita27@sify.com



	L_1	L_2	L_3	L_4
R'	CH_3	CH_3	CH_2C_6H	$CH_2C_6H_5$
R''	Cl	$N(C_2H_5)_2$	Cl	$N(C_2H_5)_2$

FIGURE 1 Structure of the ligands.

S. Hence, it was considered worthwhile to explore these compounds as ligands in the metal complex formation. The structure of the ligands is shown in Figure 1.

The complexes of L_1, L_2, L_3 and L_4 were prepared in order to investigate the coordination behaviour of these ligands towards zinc (II) ion.

EXPERIMENTAL

All chemicals and solvents used in this study were dried and purified by standard methods.

The ligands L_1, L_2, L_3, and L_4 were synthesized according to the method previously reported.[5,6] Their elemental analysis and physical properties are given in Table I.

To ascertain the possible molar ratio of the complexes, conductometric titrations were carried out between ligands and metal salt. It is evident from these titrations that complexes are formed in a 1:1 ratio (Figure 2).

Stock solutions of the ligands and zinc chloride were prepared by dissolving the requisite amount in methylene chloride for conductivity measurements. The concentration of the ligands in the solution was kept approximately five times that of metal solution, in order to satisfy the maximum coordination number of metal ion. The conductance measurements were carried out on a Conductivity Bridge Model 1160 E at 25°C ± 0.1°C.

Synthesis of Zn(II) Complexes

The complexes were formed by refluxing ligands with zinc chloride in a 1:1 ratio in methylene chloride for 10–12 h. The solid chelates, which

TABLE I Physical Properties and Analytical Data of Ligands

Ligand	Color and state	Yield (%)	M.P.°C	Analysis, % (calcd.) found					Mol. WT. (calcd.) found
				C	H	N	S	P	
L_1 3-methyl-2-benzothiazolylidenamido-thiophosphoryl dichloride $C_8H_7N_2PS_2Cl_2$	Cadmium yellow solid	63	95–97	(32.30) 32.15	(2.37) 2.20	(9.42) 9.25	(21.54) 21.39	(10.40) 10.23	(297.7) 294.8
L_2 (3-methyl-2-benzothiazolylidenamido)-bis-(diethylamido) thiophosphate $C_{16}H_{27}N_4S_2P$	White solid	79	60–61	(51.87) 51.78	(7.34) 7.37	(15.12) 15.06	(17.31) 17.02	(8.36) 8.24	(370.5) 369.8
L_3 3-benzyl-2-benzothiazolylidenamido-thiophosphoryl dichloride $C_{14}H_{11}N_2PS_2Cl_2$	Lemon yellow solid	52	82–85	(45.04) 45.02	(2.97) 2.83	(7.50) 7.30	(17.18) 17.08	(8.30) 8.16	(373.3) 371.7
L_4 (3-benzyl)-2-benzothiazolylidenamido)- bis-(diethylamido) thiophosphate $C_{22}H_{31}N_4S_2P$	Yellow solid	69	55–57	(59.16) 59.03	(6.99) 6.88	(12.54) 12.42	(14.37) 14.24	(6.94) 6.83	(446.2) 444.5

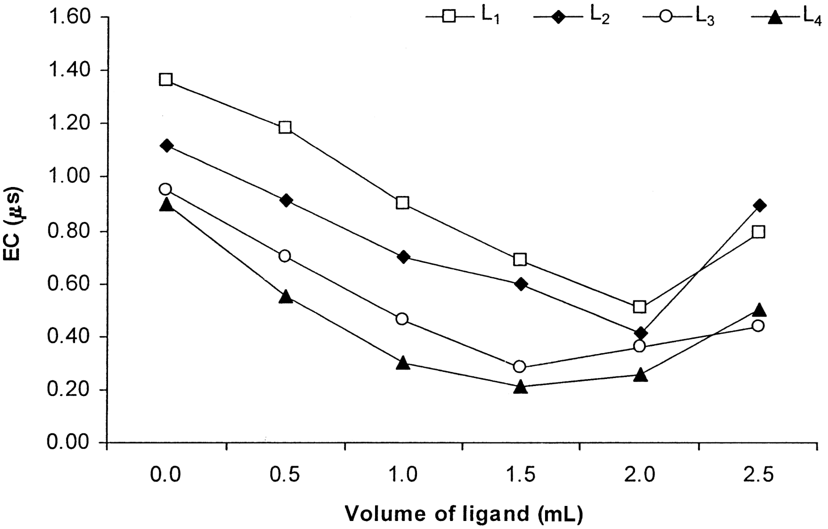


FIGURE 2 Conductometric titration of 20 mL (1×10^{-3} M) $ZnCl_2$ with L_1, L_2, L_3, and L_4.

precipitated out, were filtered and washed with methylene chloride to remove the excess of ligands and dried in vacuo. The chelates were purified by recrystallization from absolute alcohol. The complexes were analyzed and their elemental analysis is given in Table II.

The absorption spectra of metal chelates in solution were taken with a digital spectrophotometer model 301E. The IR spectra were recorded on a Perkin Elmer RXI IR spectrophotometer in the region of 4000–200 cm^{-1}, and mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer.

RESULTS AND DISCUSSION

Elemental Analysis

Results of elemental analyses reveal that the reaction of ligands and $ZnCl_2$ gives a four-coordinated structure for these complexes.

Conductometric Titrations

Results of conductometric titrations of 20 mL of a 1×10^{-3} M metal ion solution against 5×10^{-3} M of each ligand solution shown in

TABLE II Physical Properties and Analytical Data of Zn (II) Complexes

Emperical formula of complex	Color and state	Yield (%)	M.P.°C	Analysis, % (calcd.) found							Mol. Wt. (calcd.) found
				C	H	N	S	P	Cl	Zn	
C_1											
$C_8H_7N_2PS_2ZnCl_4$	Yellow	70	260	(22.14)	(1.64)	(6.45)	(14.77)	(7.14)	(32.67)	(15.07)	(434.0)
	solid			22.01	1.47	6.28	14.62	7.11	32.51	15.02	429.7
C_2											
$C_{16}H_{27}N_4S_2PZnCl_2$	White	86	225	(37.92)	(5.37)	(1.10)	(12.65)	(0.61)	(13.99)	(12.90)	(506.8)
	solid			37.83	5.35	1.01	12.63	0.58	13.88	12.81	426.2
C_3											
$C_{14}H_{11}N_2PS_2ZnCl_4$	Cream	59	247	(33.01)	(2.18)	(0.55)	(12.58)	(0.61)	(27.83)	(12.83)	(509.6)
	solid			33.00	2.16	0.41	12.48	0.59	27.69	12.73	453.8
C_4											
$C_{22}H_{31}N_4S_2PZnCl_2$	Creamish	76	220	(45.36)	(5.36)	(0.96)	(11.00)	(0.53)	(12.17)	(11.23)	(582.5)
	solid			45.23	5.25	0.88	10.87	0.51	12.06	11.15	500.7

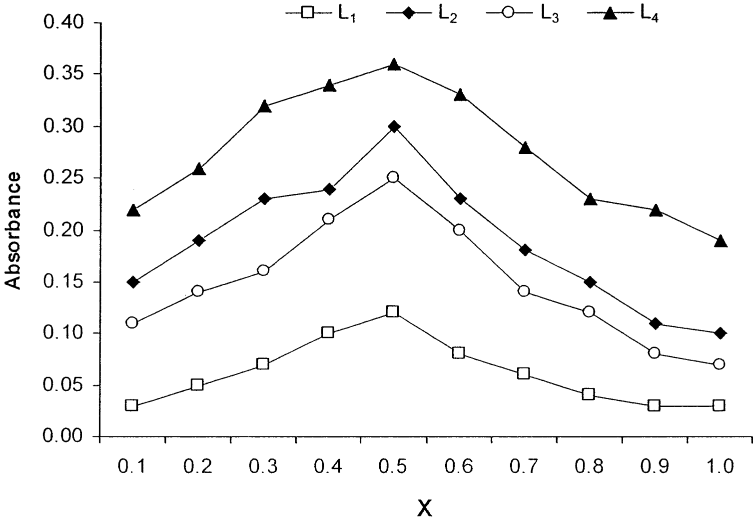


FIGURE 3 Job's continuous variation curves for metal chelates between Zn(II) and L_1, L_2, L_3, and L_4 at λ_{max} 620 nm.

Figure 2 support the stoichiometries suggested on the basis of elemental analysis.

Spectrophotometric Titrations

The composition of the complexes in N,N′-dimethylformamide (DMF) solution were also calculated from a spectrophotometric molar ratio and a continuous variation method[8,9] at λ_{max} of each complex. The representative results shown in Figure 3 are in good accordance with those obtained from the conductometric titration method (Figure 2).

Stability Constants

The results of spectrophotometric methods can also be utilized for calculation of the apparent stability of the metal chelates.[10] Table III shows that the stability runs in the following order:

$$L_4 > L_2 > L_3 > L_1$$

The relatively lower values of stability constants for these chelates can be attributed to the formation of a less stable four-membered chelate ring through the exocyclic sulphur and nitrogen atoms from the ligands.

TABLE III The Stability Constants for the Formation of Zn(II)-L Complexes in an Aqueous Medium

Metal ion (M)	Ligands (L)	M:L Ratio	Stability constant K_f
Zn(II)	L_1	1:1	8.31×10^2
Zn(II)	L_2	1:1	7.5×10^3
Zn(II)	L_3	1:1	4.0×10^3
Zn(II)	L_4	1:1	1.84×10^4

Infrared Spectra

Definite evidence for the structure and coordination sites of ligands under investigation is obtained from the IR data summarized in Table IV.

The ligands exhibit a medium strong sharp band in the region 1620–1595 cm^{-1} due to the ν (C=N).[11] The stretching absorption bands of ν (P—N)[12] and ν (C—N)[12] appeared at 760–685 cm^{-1} and 1105–1063 cm^{-1}, respectively. Two absorption bands of ν (P=S)[13] are observed in the region 800–775 cm^{-1} (I) and 717–605 cm^{-1} (II). In L_1 and $L_3 \nu$ (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 the literature.[14]

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

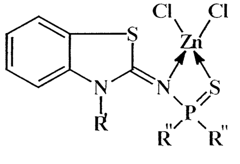
Compound	ν (C=N)	ν (P—N—C)	ν (P=S)	ν (P—Cl)	Other bands
L_1	1595	1085 745	785 (I) 702 (II)	500 (sym.) 610 (asym.)	—
C_1	1580	1015 740	775 (I) 692 (II)	500 (sym.) 610 (asym.)	465 ν (Zn-N) 345 ν (Zn-S)
L_2	1603	1063 685	775 (I) 605 (II)	—	—
C_2	1585	1052 682	765 (I) 595 (II)	—	475 ν (Zn-N) 325 ν (Zn-S)
L_3	1610	1105 760	800 (I) 717 (II)	515 (sym.) 625 (asym.)	—
C_3	1595	1035 759	790 (I) 707 (II)	515 (sym.) 625 (asym.)	480 ν (Zn-N) 360 ν (Zn-S)
L_4	1620	1080 700	790 (I) 620 (II)	—	—
C_4	1600	1065 695	780 (I) 610 (II)	—	490 ν (Zn-N) 340 ν (Zn-S)

The Zn(II) complexes of these ligands exhibit a negative shift in the ν (C=N) stretching band, and it appears in the region 1600–1580 cm^{-1}. The ν (P—Cl) stretching (symmetric and asymmetric) and ν (P—N) stretching bands remain almost unchanged. Both absorption bands of ν (P=S) are also shifted to a lower wave number by the negative shift of 5–15 cm^{-1} and appear at 790–765 cm^{-1} (I) and 707–595 cm^{-1} (II), respectively. Two new medium, weak, and sharp bands appear at 490–465 cm^{-1} and 360–325 cm^{-1}, which appear at the same position as reported in literature for ν (Zn—N)[15,16] and ν (Zn—S)[16] vibrations, respectively. The shifting of ν (C=N) and ν (P=S) absorption bands and the appearance of ν (Zn—N) and ν (Zn—S) absorption bands indicate the coordination of a ligand through N and S outside the benzothiazol ring, which further indicates that the ligands act as bidentate ligands with an (NS) donor set. On the basis of the elemental analysis and spectral studies, the four coordinated structure may be suggested for the complex (Figure 4).

Mass Spectra

Mass spectra were recorded for determining the molecular mass of the chelates. The splitting pattern of the mass spectrum of C_2 is represented in Figure 5.

The molecular ion peak appears at m/z 506.8, thus confirming the formation of a metal complex in a 1:1 ratio. This peak after the removal of two chlorine radicals in the subsequent steps generates the ions at m/z 473.8 and m/z 430.8, respectively. It may further lose a sulphur radical to form the ion at m/z 398.8, which splits off a diethylamido moiety, producing an ion at m/z 326.6, this diethylamido moiety also appears



	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 4 Suggested structure of the Zn (II) complexes.

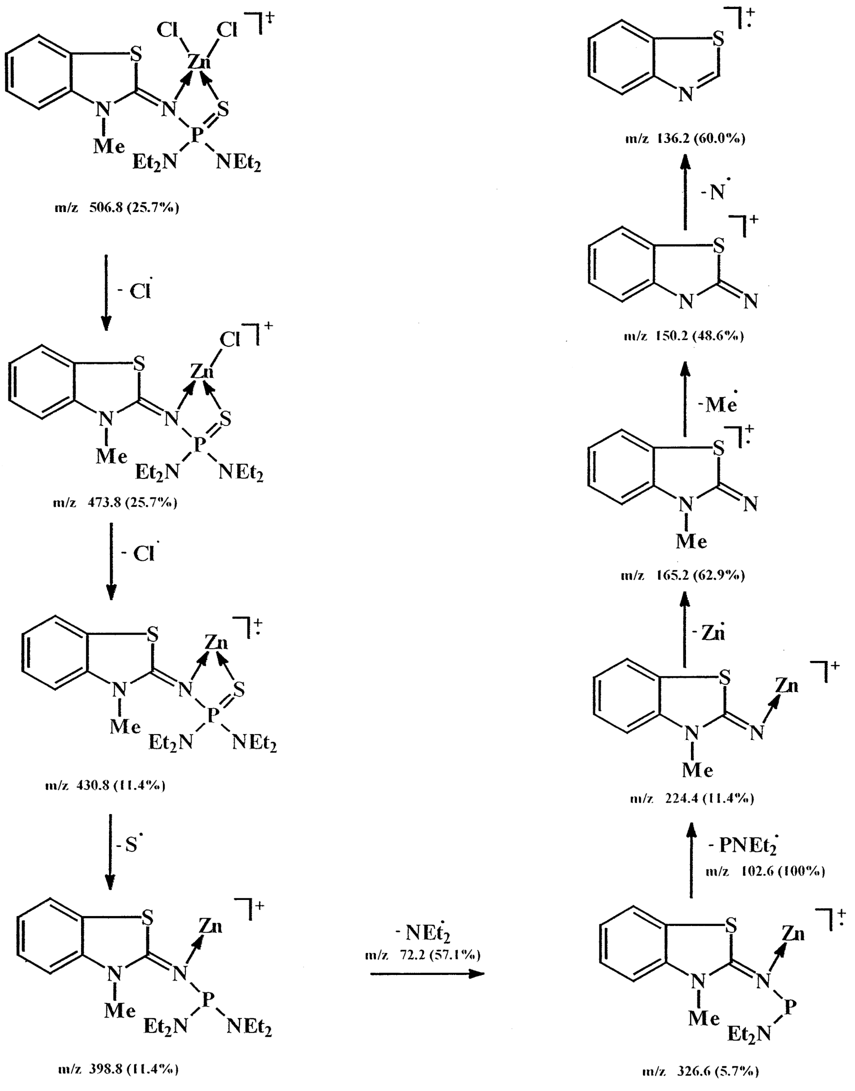


FIGURE 5 Suggested structure of C_2 and the splitting pattern of its mass spectrum.

at m/z 72.2. The $PNEt_2$ radical is lost to form an ion at m/z 224.4, and itself appears as the base peak at m/z 102.6. Further fragmentation involves the removal of the Zn radical and the formation of a peak at m/z 165.2. Splitting off a $-CH_3$ radical leads to a peak at m/z 150.2. After the removal of a nitrogen radical, a peak appears at m/z 136.2 in

TABLE V Mass Spectral Data of C_2 (Relative abundance is given in Parentheses)

Compound	m/z %
C_2	506.8 (M^+, 25.7), 473.8 (25.7), 430.8 (11.4), 398.8 (11.4), 326.6 (5.7), 224.4 (11.4), 165.2 (62.9), 150.2 (48.6), 136.2 (60.0) 102.6 (100), 72.2 (57.1)

the mass spectrum. Relative abundance of these ions are represented in Table V.

REFERENCES

[1] J. Reucroft and P. G. Sammes, *Quar. Rev. Chem. Soc.*, **25,** 135 (1971).
[2] H. G. Khorana, In Some Recent Development in Chemistry of Phosphate Esters of Biological Interest (John Wiley and Sons, New York, 1961).
[3] A. V. Podgornyi, A. A. Tolmachev, A. S. Shtepanek, A. A. Kudryavtsev, and A. M. Pinchuk, *Zh. Obshch. Khim.*, **60,** 2440 (1990).
[4] D. C. Cupertino, R. W. Keyte, A. M. Z. Slawin, and D. Woollins, *Polyhedron,* **17,** 4219 (1998).
[5] V. Kabra, N. Gupta, and R. Mathur, *J. Indian Chem. Soc.*, **81,** 338 (2004).
[6] V. Kabra, N. Gupta, S. Jain, and V. Saxena, *Heteroatom Chemistry,* **14,** 498 (2003).
[7] J. J. P. Stewart, MOPAC 6.0, QCPE, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO (1990).
[8] P. Jop, *Ann. Chim. Phys.*, **9,** 113 (1928).
[9] P. A. Yoe and A. L. Jones, *Ind Eng. Chem. (Anal. Edit)*, **16,** 111 (1944).
[10] I. M. Issa, R. M. Issa, and M. K. Hassan, *Egypt. J. Chem.*, **16,** 19 (1973).
[11] N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nucl. Chem.*, **33,** 2451 (1971).
[12] D. E. Corbridge, *J. Appl. Chem.*, **6,** 456 (1956). In The IR Spectra of Organophosphorus Compounds in Topics in Phosphorus Chemistry (John Wiley and Sons, London, 1969).
[13] R. A. Nyquist, W. W. Mueider, and M. N. Wass, *Spectrochim. Acta,* **26A,** 769 (1970).
[14] M. Backe-Goehring, L. Leichner, and B. Scharf, *Z. Anorg. Allgem. Chem.*, **343,** 154 (1966).
[15] A. G. Fabretti, G. C. Franchino, and G. Peyronel, *Spectrochim. Acta*, **36A,** 517 (1980).
[16] D. K. Breitinger and C. E. Zybill, *Organomet. Inorg. Chem.*, **5,** 109 (1999).