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Synthesis and Characterization of O-Alkyl or O-Aryl Trithiophosphates of Zinc

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ABSTRACT: O-Alkyl/O-aryl trithiophosphates of zinc have been synthesized by the reaction of $ZnCl_2$ with dipotassium salt of O-alkyl/O-aryl trithiophosphates. Reaction is carried out in 1:2 molar ratio in refluxing methanol. Initially in the presence of triethylamine, mathematical reactions between P_2S_5 and appropriate aliphatic alcohol/aromatic alcohol, are carried out to obtain O-alkyl/O-aryl trithiophosphoric acid. O-alkyl/O-aryl trithiophosphoric acids are obtained in lower layer. They are separated, distilled and react with KOH to form dipotassium salts of O-alkyl/O-aryl trithiophosphate.

The newly synthesized zinc trithiophosphato derivatives are white powdery solid which are insoluble in common organic solvents but are soluble in coordinating solvents like DMSO, DMF, etc. These products are monomeric in nature and have been characterized by elemental analysis, molecular weight measurement and IR and NMR(1H and ^{31}P) spectral studies. On the basis of above chemical parameter and spectral studies, tetra coordinated nature of Zn metal has been established.

KEYWORDS: Zinc chloride, O-alkyl/O-aryl trithiophosphates, monomeric, tetra coordination.

I. INTRODUCTION

During last 3 – 4 decades, organometallic compounds containing metal – sulphur bond has been one of the most active areas of organometallic chemistry¹⁻⁵. These compounds have interesting biological applications⁶⁻⁷ as well as found importance in industries⁸⁻⁹ and agriculture¹⁰⁻¹¹.

A survey of literature indicates that a wide work has done on metal, organometal and organic derivatives of monothio phosphate and dithio phosphates ester¹²⁻¹⁵. It has been considerable interest to evinced the investigation on trithiophosphate ligand¹⁶⁻¹⁷. Complexes of O-alkyl trithiophosphates show interesting structural features in their unusual bonding modes (monodentate, bidentate, ambidentate, chelating, bridging) towards different metals^{15,18-21}.

Aliphatic trithiophosphates are used in improvement of crop value²² and indirect control of pesticides²³. Organic trithiophosphates are used in steel corrosion of defoliant²⁴, insecticides²⁵⁻²⁶, nematocidals²⁶ and inhibitors²⁶.

Although O-alkyl and O-alkylene dithiophosphate of zinc²⁷ have been studied in our laboratory as well as in others, yet the study on trithiophosphates derivatives of zinc have not been carried out as yet.

In view of this it was considered worthwhile to synthesize O-alkyl or O-aryl trithiophosphate derivatives of zinc to study the chemical bonding modes.

II. EXPERIMENTAL

During the experimental work of synthesis of O-alkyl or O-aryl trithiophosphate derivatives of zinc, moisture was carefully excluded. Dipotassium salts of O-alkyl or O-aryl trithiophosphates have been synthesized by the methods reported in the literature²⁸. During present investigation all the solvents were of reagent grade. Carbon and hydrogen were estimated by Coleman C, H and N analyzer. Sulphur was estimated by Messenger's method²⁹ and zinc was estimated by gravimetric method²⁹. Molecular weights were determined by Knauer vapour pressure osmometer in chloroform. FTIR spectra were recorded on a Perkin Elmer 10.4.00 spectrophotometer in the range of $4000 - 200\text{cm}^{-1}$.

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^1H NMR spectra were recorded in CDCl_3 and ^{31}P NMR spectra were recorded in DMSO-D_6 on DELTA 2 NMR 400 MHz spectrophotometer using TMS (for ^1H) and H_3PO_4 (for ^{31}P) as an external reference.

SYNTHESIS OF $\text{Zn}[\text{K}(\text{S})(\text{S}_2)\text{POCH}_3]_2$

Zinc chloride 0.5775g[4.2372 mmol] and dipotassium salt of O-methyltrithiophosphate 2.0000g[8.4745 mmol] in (1:2)molar ratio were dissolved in 40mL methanol in R.B.F. This mixture was refluxed with constant stirring for 8-10h. Then it was kept at $0-5^\circ\text{C}$ in a deep freezer for 24h. A white colour sticky solid was obtained. After adding 20mL of acetone at the same temperature, white powdery solid product was obtained. The solvent was removed by filtration in an alkoxy funnel and excess of solvent was removed under vacuum. The obtained product was washed 3-4 times with acetone for purification. (Table – 1)

Analysis calcd. for $\text{Zn}[\text{K}(\text{S})(\text{S}_2)\text{POCH}_3]_2$

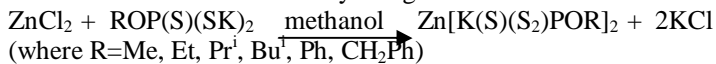
C=4.84; H=2.03; S=38.78; Zn=13.18

Found C=4.52; H=1.89; S=37.94; Zn=13.04

All other derivatives were synthesized and purified by above method.

III. RESULTS AND DISCUSSION

Reaction of zinc chloride with dipotassium salt of O-alkyl or O-aryl trithiophosphates are carried out in 1:2 molar ratio in 40mL methanol as solvent by using conventional method.



Zinc chloride was taken with dipotassium salt of O-alkyl or O-aryl trithiophosphate in 1:2 molar ratio in 40mL methanol, respectively. The reaction mixture was refluxed for 8-10h. It was kept at $0-5^\circ\text{C}$ in a deep freezer for 24h. The obtained derivatives were separated as white sticky solid. Adding 20mL acetone in it, white powdery solid was obtained. Potassium chloride was removed in filterate. These compounds were washed with acetone and recrystallized and excess of solvent was removed under vacuum. These complexes were insoluble in common organic solvents but soluble in DMSO, DMF and other coordinating solvents.

IR Spectra

IR spectra were recorded in the region $4000-200\text{cm}^{-1}$ (Table-2) and following characteristic changes were observed:-

1. The absorption band at $705.5 - 739.2\text{ cm}^{-1}$ and $573.5 - 620.8\text{ cm}^{-1}$ assigned to $\nu\text{P}=\text{S}$ and $\nu\text{P}-\text{S}$ linkage, respectively. Shifting of bands towards lower frequency ($20 - 30\text{ cm}^{-1}$) from parent trithiophosphate indicate strong chelation of thiophosphoryl group to metal atom and also indicates bidentate nature of this group.
2. The $\nu(\text{P})-\text{O}-\text{C}$ and $\nu\text{P}-\text{O}-(\text{C})$ linkage were present in the region $1039.6 - 1099.7\text{ cm}^{-1}$ and $812.4 - 836.8\text{ cm}^{-1}$, respectively.
3. The appearance of a new medium and weak intensity absorption band in the region $448.6 - 491.3\text{ cm}^{-1}$ indicates the formation of zinc-sulphur³⁰ bond.

NMR Spectra

^1H NMR Spectra

The PMR spectra were recorded in 300.13 MHz region. These derivatives show characteristic resonance signals due to alkoxy and phenyl protons (Table-3). The characteristic resonance signals due to OCH_3 , OCH_2 , OCH , OC_6H_5 and OC_6H_4 protons are present in the expected region³¹⁻³².

^{31}P NMR Spectra

^{31}P NMR spectra were recorded in 121.49 MHz region. The spectra was obtained in the region $105.74 - 116.48\text{ ppm}$. The chemical shift was shifted to downfield ($\delta 25 - 35\text{ ppm}$) as compared to the parent trithiophosphate ligand (Table – 3). It indicates bidentate mode of bonding of ligand moiety in newly synthesized compounds.

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Table 1 : Synthetic and Analytical Data of Zn[K(S)(S₂)POR]₂

S.NO	Reactantg..... (mmol)		Molar Ratio	Productg.... %	Found Analysis % (Calcd.)				Molecular Weight Found (Calcd.)
	ZnCl ₂	ROP(S)(SK) ₂ R... or Ar...			C	H	S	Zn	
1	0.5775 [4.2372]	CH ₃ 2.0000 [8.4745]	1:2	Zn[K(S)(S ₂)POCH ₃] ₂ 4.0253 95	4.52 (4.84)	1.89 (2.03)	37.94 (38.78)	13.04 (13.18)	492.86 (495.93)
2	0.5452 [4.0002]	C ₂ H ₅ 2.0000 [8.0000]	1:2	Zn[K(S)(S ₂)POC ₂ H ₅] ₂ 3.9485 94	8.92 (9.16)	2.27 (2.69)	35.96 (36.71)	12.14 (12.47)	-
3	0.5162 [3.7875]	ⁱ C ₃ H ₇ 2.0000 [7.5757]	1:2	Zn[K(S)(S ₂)PO ⁱ C ₃ H ₇] ₂ 3.8946 93	12.76 (13.05)	3.09 (3.28)	34.23 (34.84)	11.56 (11.84)	-
4	0.4902 [3.5967]	ⁱ C ₄ H ₉ 2.0000 [7.1942]	1:2	Zn[K(S)(S ₂)PO ⁱ C ₄ H ₉] ₂ 3.9125 93	15.93 (16.56)	3.45 (3.82)	32.89 (33.16)	10.94 (11.26)	-
5	0.4573 [3.3553]	C ₆ H ₅ 2.0000 [6.7114]	1:2	Zn[K(S)(S ₂)POC ₆ H ₅] ₂ 3.8274 92	22.87 (23.24)	2.02 (2.27)	30.64 (31.02)	10:13 (10.54)	618.14 (620.06)
6	0.4368 [3.2049]	o-CH ₃ -C ₆ H ₄ 2.0000 [6.4102]	1:2	Zn[K(S)(S ₂)POC ₆ H ₄ -CH ₃] ₂ 3.9462 95	25.72 (25.94)	2.53 (2.80)	29.12 (29.67)	9.58 (10.08)	-
7	0.4368 [3.2049]	m-CH ₃ -C ₆ H ₄ 2.0000 [6.4102]	1:2	Zn[K(S)(S ₂)POC ₆ H ₄ -CH ₃] ₂ 3.8742 93	25.72 (25.94)	2.53 (2.80)	29.12 (29.67)	9.58 (10.08)	-
8	0.4368 [3.2049]	p-CH ₃ -C ₆ H ₄ 2.0000 [6.4102]	1:2	Zn[K(S)(S ₂)POC ₆ H ₄ -CH ₃] ₂ 3.9214 94	25.72 (25.94)	2.53 (2.80)	29.12 (29.67)	9.58 (10.08)	-

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Table 2 : IR Spectral Data of Zn[K(S)(S ₂)POR] ₂						
S.No.	Compound	v(P)-0-(C)	vP-0-(C)	vP=S	vP-S	vZn-S
1	Zn[K(S)(S ₂)POCH ₃] ₂	1009.5s	812.4s	705.5s	573.5s	448.6m
2	Zn[K(S)(S ₂)POC ₂ H ₅] ₂	1003.4s	816.7m	718.8s	579.6m	449.4w
3	Zn[K(S)(S ₂)PO ⁱ C ₃ H ₇] ₂	1006.2s	819.9s	721.2m	580.4s	465.3s
4	Zn[K(S)(S ₂)PO ⁱ C ₄ H ₉] ₂	1099.7s	825.6s	730.5s	620.8s	472.5s
5	Zn[K(S)(S ₂)POC ₆ H ₅] ₂	1059.8s	822.2m	719.2m	596.1m	464.6w
6	Zn[K(S)(S ₂)POC ₆ H ₄ -CH ₃] ₂ o-	1054.3s	829.4s	728.3s	597.2s	478.6m
7	Zn[K(S)(S ₂)POC ₆ H ₄ -CH ₃] ₂ m-	1044.5s	832.7s	733.4s	602.3m	482.4s
8	Zn[K(S)(S ₂)POC ₆ H ₄ -CH ₃] ₂ p-	1039.6s	836.8s	739.2vs	605.5m	491.3m

Vs = very strong, s = strong, m = medium, w = weak

Table 3 : ¹ H NMR and ³¹ P NMR Spectral Data of Zn[K(S)(S ₂)POR] ₂			
S.No.	Compound	¹ H Chemical Shift (δ-----PPm)	³¹ P Chemical Shift (δ-----PPm)
1	Zn[K(S)(S ₂)POCH ₃] ₂	3.48, s, 6H(OCH ₃) 4.67, s, 2H	116.48
2	Zn[K(S)(S ₂)POC ₂ H ₅] ₂	1.92, t, 6H(CH ₃) 3.59, q, 4H(OCH ₂)	112.24
3	Zn[K(S)(S ₂)PO ⁱ C ₃ H ₇] ₂	1.15, d, 12H(CH ₃) 3.44-3.41, m, 2H(OCH)	107.99
4	Zn[K(S)(S ₂)PO ⁱ C ₄ H ₉] ₂	1.65, d, 12H(CH ₃) 2.45-2.38, m, 2H(CH) 3.36, d, 4H(OCH ₂)	105.74

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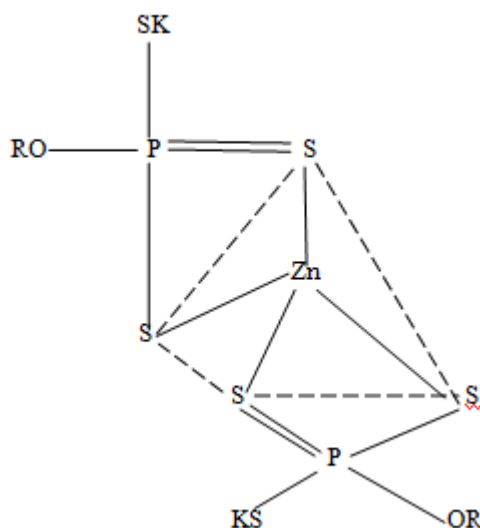
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5	$Zn[K(S)(S_2)POC_6H_5]_2$	6.68-6.66, m, 10H(OC ₆ H ₅)	116.48
6	$Zn[K(S)(S_2)POC_6H_4-CH_3]_2$ o-	3.2, s, 6H(CH ₃) 6.68-6.72, m, 8H(OC ₆ H ₄)	114.32
7	$Zn[K(S)(S_2)POC_6H_4-CH_3]_2$ m-	3.43, s, 6H(CH ₃) 6.98-7.00, m, 8H(OC ₆ H ₄)	112.56
8	$Zn[K(S)(S_2)POC_6H_4-CH_3]_2$ p-	3.47, s, 6H(CH ₃) 7.07-7.09, m, 8H(OC ₆ H ₄)	106.70

s= singlet, d = doublet, t = triplet, q = quartet, m = multiplet

IV. CONCLUSION

On the basis of physico-chemical (elemental analysis, molecular weight determination) and spectroscopic data (IR, ¹H, ³¹P), the structure of the complexes may be as follows.



On the basis of spectroscopic studies, a tetrahedral geometry for these complexes has been suggested.

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