Synthesis, Characterization And Antibacterial Activity Of O-Alkyl Or O-Aryl Trithiophosphate Of Mn(II)

Suman Bhatti and Alok Chaturvedi

Synthetic and Surface Science Laboratory, Department Of Chemistry,

S. P. C. Govt. College, Ajmer 305001, Rajasthan, India.

Abstract# Complexes of type $[\{KS_3POR\}_2Mn(NC_5H_5)_2]$ (where R = Me, Et , Pr ^{i}, Bu^i, Ph, Ph-CH_3) have been synthesized by reaction of $MnCl_2.4H_2O$ with dipotassium salt of O-alkyl/O-aryl trithiophosphates and pyridine in 1:2:2 molar ratio, respectively and refluxed in methanol. These newly synthesized derivatives have been characterized by elemental analysis, molecular weight measurement and spectroscopic studies (IR , ^{1}H , ^{13}C, ^{31}P, NMR). On the basis of physico chemical and spectroscopic studies octahedral geometry has been proposed for these derivatives. The newly synthesized derivatives are found to be monomeric in nature and show good antibacterial activity against gram-positive and gram negative bacteria.

Keywords:O-alkyl/O-aryl trithiophosphates, octahedral geometry, monomeric, antibacterial activity, gram-positive and gram negative bacteria.

I. INTRODUCTION

The organic derivatives of transition metal with sulphur and phosphorus containing ligands have important role in metallo-organic chemistry.The synthesis and spectral aspects of partial esters of phosphoric acid and thiophosphoric acid of metallic and organometallic compound have been recently reviewed[1-6]. The interest in the chemistry of derivatives arises from their utility as pesticides[7],insecticides[8],bactereocides[9] lubricant oil[10]etc. Aliphatic monothiophosphates, dithiophosphates and trithiophosphates are used in defoliation, improvement in crop value and indirect control of pest invfestation.Organic trithiophosphate esters have been used as defoliants[11],insecticides[12], nematodicides and inhibitor in steel corrosion [13].

Due to unexceptional bonding modes (monodentate, bidentate, chelating or bridging) of metal complexes with sulphur and phosphorus containing ligands and a wide range of biological and industrial applications , their interpretation possess challenges.

In the recent years synthesizing and screening the antibacterial activity of various metal derivatives of trithiophosphates ligand have been done[14-18]. Although a few O-alky/O-aryl trithiophosphate derivatives of the tin[19-20], arsenic[21], boron[22] aluminium[23] and acetyl, benzyl and benzoyl chloride[24] have been prepared and studied in our laboratory but the manganese derivatives of this ligand have not been synthesized as yet.

Due to interesting structural features and wide range of applications of the ligands containing both sulphur and phosphorus,it was thought worthwhile to synthesize new complexes of O-alkyl/O-aryl trithiophosphate of Mn.

II. RESULT AND DISCUSSION

The reactions of Manganese (II) chloride tetrahydrate, $MnCl_2.4H_2O$ with dipotassium salt of O-alkyl(O-aryl) trithiophosphate and pyridine base in 1:2:2 molar ratio have been carried out by refluxing in dry and distilled methanol.

$$MnCl_2.4H_2O + 2K_2S_3POR + 2NC_5H_5 \longrightarrow [\{KS_3POR\}_2Mn(NC_5H_5)_2] + 2KCl$$

(where R = Me, Et , Pr ^{i}, Bu^i, Ph, Ph-CH_3)

The products obtained from above reactions are light pink solids. Potassium chloride was removed by filtration. The newly synthesized complexes have been purified by washing them 3-4 times with acetone and recrystallized. These complexes were insoluble in common organic solvents but soluble in co-ordinated solvents like DMSO, DMF etc.

III. SPECTRAL ANALYSIS

IR spectra:- IR spectra were recorded in 4000-200 cm$^-$ region and following characteristic bands were observed.

1) The υ(P)-O-C and υP-O-(C) stretching modes have been observed in region 1044-1090 cm^{-1}, respectively.
2) The strong and medium intensity bands for υP=S and υP-Swere observed in the region 873-995 cm^{-1} and 702-800 cm^{-1}, respectively. In comparison to parent trithiophosphate ligand these bands were found in lower frequency region,which shows the bidentate modes of binding by the trithiophosphate ligand.
3) The S-H vibration expected in the region 2400-2500 cm^{-1} could not be observed in the spectra of these compounds.
4) There is no absorption band found in the region 1200-1100 cm^{-1} which indicates that υP=O linkage is absent in these complexes.
5) Formation of Mn-N bond cause new absorption band for υMn-N in the region 478-442 cm^{-1} due to coordinated pyridine base.
6) Strong intensity absorption band in the region 507-547 cm^{-1} represents the new υMn-S bond.

Table - 1
IR spectra data of $Mn[SSK(S)POR]_2(NC_5H_5)_2$

S.No.	COMPOUND	υ(P)-O-C	υP-O-(C)	υP=S	υP-S	υMn-S
1.	$[CH_3OP(S)SSK]_2 Mn(NC_5H_5)_2$	1079.18vs	1025.13s	994.01w	702.48vs	546.81w
2.	$[C_2H_5OP(S)SSK]_2 Mn(NC_5H_5)_2$	1078.67vs	1024.38s	902.67s	798.20w	515.04s
3.	$[^iC_3H_7OP(S)SSK]_2Mn(NC_5H_5)_2$	1077.97vs	1028.4s	905.41s	732.05S	540.45s
4.	$[^iC_4H_9OP(S)SSK]_2 Mn(NC_5H_5)_2$	1065.28vs	1019.81s	971.60w	799.07w	519.93w
5.	$[C_6H_5OP(S)SSK]_2 Mn(NC_5H_5)_2$	1044.15vs	1008.23w	901.10w	732.21w	507.26vs
6.	$[o\text{-}CH_3C_6H_4OP(S)SSK]_2 Mn(NC_5H_5)_2$	1073.33vs	1022.86s	935.29s	742.95w	541.42s
7.	$[m\text{-}CH_3C_6H_4OP(S)SSK]_2 Mn(NC_5H_5)_2$	1056.89vs	1032.10s	913.44s	738.99w	553.26s
8.	$[p\text{-}CH_3C_6H_4OP(S)SSK]_2 Mn(NC_5H_5)_2$	1089.33vs	1034.65vs	873.11s	711.42w	545.71s

vs = very strong, s = strong, w = weak

NMR Spectra

^{1}H NMR spectra :- The ^{1}H NMR spectra of these complexes have been recorded in deuterated DMSO in 0-10 ppm region. Spectral data of these complexes are summarized in Table-2. These complexes show characteristics resonance signals due to OCH_3, OC_2H_5, OC_3H_7, OC_6H_5, $OC_6H_4CH_3$ protons which are present in expected region[25].

^{31}P NMR spectra :- The ^{31}P NMR spectra of these complexes shows only one resonance signal in the range 87.43-105.27 ppm. Signals shift towards downfield by 20-30 ppm from its original position in parent trithiophosphate ligand due to formation of strong metal- sulphur bond.

Table - 2
^{1}H NMR spectra and ^{31}P NMR spectra of $Mn[SSK(S)POR]_2(NC_5H_5)_2$

Sr. No.	Compound	^{1}H chemical shift ($-ppm)	^{31}P Chemical shift ($-ppm)
1.	$[CH_3OP(S)SSK]_2Mn(NC_5H_5)_2$	2.35, s, 3H (OCH_3) 7.65,s,5H(NC_5H_5)	100.6
2.	$[C_2H_5OP(S)SSK]_2Mn(NC_5H_5)_2$	1.71, t, 3H (CH_3) 2.98, q, 2H (OCH_2) 7.73,s,5H(NC_5H_5)	99.21
3.	$[^iC_3H_7OP(S)SSK]_2Mn(NC_5H_5)_2$	1.07, d, 6H (CH_3) 2.89-3.11, m (OCH) 7.89,s,5H(NC_5H_5)	95.38
4.	$[^iC_4H_9OP(S)SSK]_2Mn(NC_5H_5)_2$	1.11, d, 6H (CH_3) 2.29-2.42, m, 1H (CH) 3.26, d, 2H (OCH_2) 7.95,s,5H(NC_5H_5)	87.43
5.	$[C_6H_5OP(S)SSK]_2Mn(NC_5H_5)_2$	6.41-6.85, m, 5H (OC_6H_5) 8.12,s,5H(NC_5H_5)	105.27
6.	$[o\text{-}CH_3C_6H_4OP(S)SSK]_2Mn(NC_5H_5)_2$	6.51-6.93, m, 12H (C_6H_4) 1.81, s, 3H (CH_3) 7.75,s,5H(NC_5H_5)	99.95
7.	$[m\text{-}CH_3C_6H_4OP(S)SSK]_2 Mn(NC_5H_5)_2$	6.11-6.36, m, 12H (C_6H_4) 1.77, s, 3H (CH_3) 7.66,s,5H(NC_5H_5)	92.70
8.	$[p\text{-}CH_3C_6H_4OP(S)SSK]_2 Mn(NC_5H_5)_2$	6.03-6.18, m, 12H (C_6H_4) 1.59, s, 3H (CH_3) 7.57,s,5H(NC_5H_5)	88.65

Antibacterial activity :-

All newly synthesized derivatives were screened for their antibacterial activity against gram-negative and gram-positive bacteria. The activity was carried out by using paper disc method. The diameter of zone of inhibition is measured in mm. The complex $[\{K_2S_3PO^iC_3H_7\}Mn(NC_5H_5)_2]$ show greater value of diameter of zone of inhibition i.e. higher effectiveness against gram-positive bacteria and complex

$[\{KS_3POC_6H_5(CH_3)\}Mn(NC_5H_5)_2]$ against gram - negative bacteria.

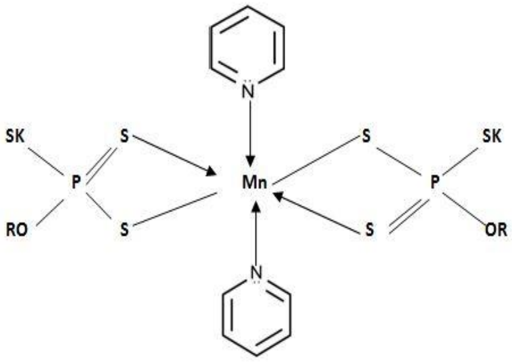
These complexes are more effective as compare to standard drugs like Imipenem and Linezolid.

Table-3
Antibacterial activity of manganese(II) derivatives of the type $Mn[SSK(S)POR]_2(NC_5H_5)_2$

Sr. No.	Compound	Gram positive bacteria zone of inhibition in mm	Gram negative bacteria zone of inhibition in mm
1.	Solvent	0	0
2.	$CH_3OPS(S)(SK)_2$	9	6
3.	$C_2H_5OPS(S)(SK)_2$	8	5
4.	$^iPrOP(S)(SK)_2$	10	3
5.	$^iBuOP(S)(SK)_2$	5	8
6.	$PhOP(S)(SK)_2$	10	12
7.	o-CH_3 $PhOP(S)(SK)_2$	12	14
8.	m-CH_3 $PhOP(S)(SK)_2$	11	13
9.	p-CH_3 $PhOP(S)(SK)_2$	9	10
10.	$[CH_3OP(S)SSK]_2Mn(NC_5H_5)_2$	27	19
11.	$[C_2H_5OP(S)SSK]_2Mn(NC_5H_5)_2$	29	17
12.	$[^iC_3H_7OP(S)SSK]_2Mn(NC_5H_5)_2$	36	22
13.	$[^iC_4H_9OP(S)SSK]_2Mn(NC_5H_5)_2$	26	23
14.	$[C_6H_5OP(S)SSK]_2Mn(NC_5H_5)_2$	20	32
15.	[o-$CH_3C_6H_4OP(S)SSK]_2Mn(NC_5H_5)_2$	24	31
16.	[m-$CH_3C_6H_4OP(S)SSK]_2Mn(NC_5H_5)_2$	20	29
17.	[p-$CH_3C_6H_4OP(S)SSK]_2Mn(NC_5H_5)_2$	19	25
18.	Impinemen	12	30
19.	Linezolid	18	10

IV. CONCLUSION

With the help of physico-chemical spectroscopic studies the structure of these complexes may be as follow :-



It shows that trithiophosphate moiety is attached with bidentate. Two pyridine molecules form coordinate bond with central metal atom. A manganese complex is octahedral with coordination number 6.

V. EXPERIMENTAL

Moisture was carefully excluded during the experimental manipulations. Manganese dichloride, phosphorus pentasulphide and all the alcohols were procured from Sigma Aldrich and were used as received. Manganese was estimated gravimetrically as $Mn_2P_2O_7$[25]. Carbon and hydrogen were estimated by colemen C, H and N analyser. Messenger's method[26] was used for estimation of sulphur. Molecular weight were determined by Knauer vapour pressure osmometer in $CHCl_3$. IR spectra were recorded as KBr pallets in spectral range 4000-200cm^{-1}.

Synthesis of $[CH_3OP(S)SSK]_2Mn(NC_5H_5)$:- To an methanolic 25mL solution of $MnCl_2.4H_2O$ (0.4192g, 2.1171mmol) ,an methanolic solution of $K_2S_3POCH_3$ (1.0150g, 4.2406mmol) was added with constant stirring followed by addition of pyridine (0.3395g, 4.2968mmol). A light pink colour precipitate was formed immediately. The mixture was refluxed for 3-4 hours then the precipitate was separated by filtration. It has been washed three-four times by acetone and recrystallize it by recrystallization method. Other complexes are formed by same method.

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Table - 4
Synthetic and Analytic Data of $Mn[SSK(S)POR]_2(NC_5H_5)_2$

S. No.	Reactant .....g....(mmol			Product ....g... ...%..	Analysis % found (calcd.)				Molecular Weight found (calcd.)
	$MnCl_2$	$ROPS_3K$ R=……..	Pyridine		C	H	S	Mn	
1.	0.4192 [2.1171]	CH_3 1.0150 [4.2406]	0.3395 [4.2968]	1.1923 92.7	22.43 (23.72)	2.49 (2.63)	30.88 (31.63)	8.75 (9.06)	590.27 (607.02)
2.	0.3992 [2.0160]	C_2H_5 1.0080 [4.0287]	0.3182 [4.0280]	1.1575 89.8	25.75 (26.45)	2.99 (3.15)	29.30 (30.24)	7.78 (8.66)	
3.	0.3778 [1.9081]	$^{i}C_3H_7$ 1.0075 [3.8163]	0.3012 [3.8129]	1.2008 94.9	27.65 (28.95)	3.15 (3.62)	27.25 (28.95)	7.65 (8.29)	635.86 (663.02)
4.	0.3650 [1.8435]	$^{i}C_4H_9$ 1.0250 [3.6870]	0.2910 [3.6842]	1.1687 91.7	30.99 (31.26)	3.55 (4.05)	26.09 (27.78)	7.17 (7.96)	649.07 (691.02)
5.	0.3304 [1.680]	C_6H_5 1.0025 [3.3642]	0.2656 [3.3623]	1.1253 92.2	35.28 (36.11)	2.01 (2.73)	25.25 (26.26)	6.85 (7.52)	
6.	0.3178 [1.6054]	o-$CH_3C_6H_4$ 1.0050 [3.2108]	0.2529 [3.2010]	1.1450 93.7	36.48 (37.84)	3.20 (3.41)	23.57 (25.23)	6.89 (7.23)	731.11 (761.02)
7.	0.3183 [1.6078]	m-$CH_3C_6H_4$ 1.0065 [3.2156]	0.2533 [3.2067]	1.1183 91.4	36.94 (37.84)	2.88 (3.41)	24.39 (25.23)	6.73 (7.23)	
8.	0.3192 [1.6123]	p-$CH_3C_6H_4$ 1.0093 [3.2246]	0.2540 [3.2153]	1.0955 89.3	35.98 (37.84)	2.79 (3.41)	24.08 (25.23)	6.57 (7.23)	

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