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Research Article

MICROWAVE ASSISTED SYNTHESIS AND CHARACTERIZATION OF O-ALKYL OR O-ARYL TRITHIOPHOSPHATE DERIVATIVES OF IRON

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ABSTRACT

Reactions of iron (III) chloride and dipotassium salts of O-alky or O-aryl trithiophosphates have been carried out in 1:3 molar ratio to form $Fe[SSK(S)POR]_3$ and where (R= Me, Et, Pr^i, Bu^i, Ph, CH_2Ph), respectively. These compounds have been synthesized by using solvent free microwave assisted procedure and conventional method also. Microwave assisted procedure have certain benefits over conventional methods like energy consumption is minimum, product yield is high and minimum use of solvent. The newly synthesized complexes have been characterised by IR, NMR (^1H, ^{13}C, ^{31}P), molecular wieght measurement and elemental analysis (C, H, S). With the help of Physico-chemical spectroscopic studies it is found that compounds show octahedral geometry and monomeric in nature. Newly synthesized compounds also show antibacterial activity against gram positive and gram negative bacteria. The antibacterial activity has carried out by paper disk method. A comparative study of antibacterial effect has also been made with standard drugs like Imipenem and Linezolid.

INTRODUCTION

In last few decades[1-5] chemists are taking interest in the chemistry of mettalic and organometallic complexes of phosphate, dithiophosphate. These compounds are widely used as pesticides[6], insecticides[7-8], bacteriosides[9] etc. So it was interested to extend the investigation to trithiophosphate ligand. In the recent years synthesizing and screening the antibacterial activity of various metal derivatives of trithiophosphates ligand have been done[10-14]. Although a few O-alky/O-aryl trithiophosphate derivatives of the tin[15-16], arsenic[17], boron[18] aluminium[19] and acetyl, benzyl and benzoyl chloride[20] have been prepared and studied in our laboratory but the iron derivatives of this ligand have not been synthesized as yet.

The science in which microwave irradiation is applying to chemical reactions is known as microwave chemistry[21-23]. Microwave irradiation method have certain benefits over conventional methods like energy consumption is minimum, product yeild is high, minimum use of solvent and accelerates the rate of the reaction.

In the view of this it was considered to synthesize O-alkyl / O-aryl trithiophosphate derivatives of iron by microwave assisted method and study their chemical bonding, modes, and their antibacterial activity and compare their antibacterial activities with standard drugs like Imipenem and Linezolid.

RESULTS AND DISCUSSION

Reactions of iron (III) chloride and dipotassium salts of O-alkyl / O-aryl trithiophosphates have been carried out in 1:3 molar ratio in methanol. The KCl formed during the reaction is removed by filtration.

$$FeCl_3 + 3K_2S_3POR \xrightarrow[\text{solvent free atm.}]{\text{Microwave irradiation}} Fe[SKS(S)POR]_3 + 3KCl$$

(where R = Me, Et, Pr^i, Bu^i, Ph, CH_2Ph)

Newly synthesized complexes are coloured crystalline solid, non-volatile and monomeric in nature.

Spectral Analysis

IR spectra:- IR spectra were recorded in 4000-200 cm^{-1} region and following bands have been recorded.

1. Presence of absorption band in the region 1050-950 cm^{-1} and 960-827 cm^{-1} indicate the presence of υ(P)-O-C and υP-O-(C) group respectively.

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2. The absorption band at 810-674 cm^{-1} and 510-710 cm^{-1} have been attributed to υP=S and υP-S linkage respectively which shows M←S=P bond is present in the compound.
3. The band present in the region 2379-2351 cm^{-1} indicates the formation of an S-H band which was absent in present ligand.
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. Due to strong chelation of υP-S group with central iron atom, the absorption bands shifted towards lower frequency (30-40 cm^{-1}) from parent trithiophosphate.
6. The appearance of weak intensity absorption band in the region 370-440 cm^{-1} represents the new υFe-S bond.

Table 1 IR spectra data of $Fe[SSK(S)POR]_3$

S.No.	COMPOUND	υ(P)-O-C	υP-O-(C)	υP=S	υP-S	υFe-S
1.	$[CH_3OP(S)SSK]_3Fe$	1048.53vs	923.18s	802.30w	512.39vs	350w
2.	$[C_2H_5OP(S)SSK]_3Fe$	1031.84vs	836.89s	792.00s	710.25w	487.38s
3.	$[^iC_3H_7OP(S)SSK]_3Fe$	965.52vs	891.80s	799.66s	633.99s	452.15s
4.	$[^iC_4H_9OP(S)SSK]_3Fe$	1017.19vs	857.07s	807.38w	593.12w	413.01w
5.	$[C_6H_5OP(S)SSK]_3Fe$	958.20vs	845.56w	689.86w	581.47w	484.82vs
6.	$[o\text{-}CH_3C_6H_4OP(S)SSK]_3Fe$	1044.11vs	951.17s	803.08s	706.98w	489.60s
7.	$[m\text{-}CH_3C_6H_4OP(S)SSK]_3Fe$	998.68vs	890.25s	762.80s	621.12w	471.14s
8.	$[p\text{-}CH_3C_6H_4OP(S)SSK]_3Fe$	1037.30vs	906.12vs	789.91s	527.50w	492.36s

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

NMR spectra

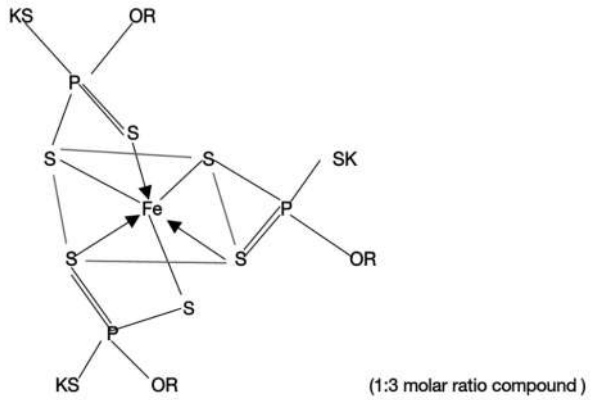
^{1}H NMR spectra:- The ^{1}H NMR spectra of these complexes were recorded in 0-10 ppm region. Charateristics signals of these complexes are summarized in Table -3. These complexes show characteristics resonance signals due to OCH_3, OC_2H_5, OC_3H_7, OC_6H_5, $OC_6H_4CH_3$ protons which are present in expected region[24-26].

^{31}P NMR spectra:- A single resonance signal for these complexes were recorded in the region of 68-110 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.

at 100 ug/ml concentration in DMF solvent. Imipenem and linezolid were used as a standard drugs for comparative studies.

CONCLUSION

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



(1:3 molar ratio compound)

Experimental

During the experimental manipulations moisture was carefully excluded. All the chemicals which we used during the investigation were of reagent grade. Carbon and hydrogen were estimated by colemen C, H and N analyzer. Sulpher and iron were estimated by idometric method and Messenger's method[27], respectively. Molecular weights were determined by knauer vapour pressure osmometer in $CHCl_3$. FT IR spectra were recorded on perkin eimer spectrum version 10.400 spectrophotometer in the range of 4000-200 cm^{-1}. ^{1}H NMR spectra were recorded in $CDCl_3$ and ^{31}PNMR spectra were recorded in $CDCl_3$ on DELTA NMR 400 MHz spectrophotometer using TMS (for ^{1}H).

Synthesis of $[CH_3OP(S)SSK]_3Fe$:- Dipotassium salt of O-methyltrithiophosphate 2.0011g [8.4738 mmol] and iron trichloride 0.4584g [2.8261 mmol] in 1:3 molar ratio were taken in R.B.F. Put this mixture into microwave for 2 minutes. Light green coloured powdery solid product was obtained. It has been washed three-four times by acetone and recrystallize it by recrystallization method.

Table 2 ^{1}H NMR spectra and ^{31}P NMR spectra of $Fe[SSK(S)POR]_3$

S. No.	Compound	^{1}H chemical shift ($-ppm)	^{31}P Chemical shift ($-ppm)
1.	$[CH_3OP(S)SSK]_3Fe$	2.25, s, 3H (OCH_3)	101.19
2.	$[C_2H_5OP(S)SSK]_3Fe$	1.71, t, 3H (CH_3) 2.98, q, 2H (OCH_2)	99.27
3.	$[^iC_3H_7OP(S)SSK]_3Fe$	1.07, d, 6H (CH_3) 2.89-3.11, m (OCH)	94.83
4.	$[^iC_4H_9OP(S)SSK]_3Fe$	1.11, d, 6H (CH_3) 2.29-2.42, m, 1H (CH) 3.26, d, 2H (OCH_2)	86.32
5.	$[C_6H_5OP(S)SSK]_3Fe$	6.41-6.85, m, 5H (OC_6H_5)	106.19
6.	$[o\text{-}CH_3C_6H_4OP(S)SSK]_3Fe$	6.51-6.93, m, 12H (C_6H_4) 1.81, s, 3H (CH_3)	98.42
7.	$[m\text{-}CH_3C_6H_4OP(S)SSK]_3Fe$	6.11-6.36, m, 12H (C_6H_4) 1.77, s, 3H (CH_3)	91.73
8.	$[p\text{-}CH_3C_6H_4OP(S)SSK]_3Fe$	6.03-6.18, m, 12H (C_6H_4) 1.59, s, 3H (CH_3)	89.65

Antibacterial activity

Newly synthesized compounds also show antibacterial activity against gram positive and gram negative bacteria. The antibacterial activity was carried out by paper disc method and inhibition zone is measured in mm. The compounds are tested

Table 3 Synthetic and Analytic Data of $Fe[SSK(S)POR]_3$

S. No.	Reactant .....g....(mmol)		Product		Analysis % found (calcd.)				Molecular Weight found (calcd.)
	$FeCl_3$	$ROPS_3K_2$ R = ……..	....g…	...%..	C	H	S	Fe	
1.	0.4584 [2.8261]	CH_3 2.0011 [8.4738]	$[CH_3OP(S)SSK]_3Fe$ 4.2636	77.76	5.45 (5.56)	1.31 (1.39)	43.45 (44.51)	8.03 (8.63)	632.27 (647.02)
2.	0.4924 [2.6638]	C_2H_5 2.0006 [7.9976]	$[C_2H_5OP(S)SSK]_3Fe$ 4.2067	76.89	9.89 (10.52)	2.04 (2.19)	40.18 (42.10)	7.35 (8.16)	
3.	0.4094 [2.5240]	$^{i}C_3H_7$ 2.0002 [7.5722]	$[^{i}C_3H_7OP(S)SSK]_3Fe$ 4.1361	74.72	13.45 (14.77)	2.42 (2.87)	38.94 (39.39)	6.87 (7.63)	705.86 (731.02)
4.	0.3894 [2.4007]	$^{i}C_4H_9$ 2.0034 [7.2025]	$[^{i}C_4H_9OP(S)SSK]_3Fe$ 4.2507	76.34	17.96 (18.62)	3.31 (3.49)	36.67 (37.25)	6.98 (7.22)	728.07 (773.02)
5.	0.3630 [2.2379]	C_6H_5 2.0021 [6.7150]	$[C_6H_5OP(S)SSK]_3Fe$ 4.4217	79.04	24.48 (25.92)	1.58 (1.80)	33.98 (34.57)	6.16 (6.70)	
6.	0.3465 [2.1362]	o-$CH_3C_6H_4$ 2.0009 [6.4100]	$[o\text{-}CH_3C_6H_4OP(S)SSK]_3Fe$ 4.3229	77.07	27.19 (28.79)	2.17 (2.40)	31.75 (32.91)	5.98 (6.38)	801.11 (875.02)
7.	0.3464 [2.1356]	m-$CH_3C_6H_4$ 2.0001 [6.4074]	$[m\text{-}CH_3C_6H_4OP(S)SSK]_3Fe$ 4.5153	80.53	27.56 (28.79)	2.26 (2.40)	31.67 (32.91)	5.79 (6.38)	
8.	0.3471 [2.1399]	p-$CH_3C_6H_4$ 2.0042 [6.4206]	$[p\text{-}CH_3C_6H_4OP(S)SSK]_3Fe$ 4.4273	78.80	27.70 (28.79)	2.19 (2.40)	31.83 (32.91)	5.59 (6.38)	

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