

Microwave Assisted Synthesis and Characterization of O-Alkyl or O-Aryl Trithiophosphate Derivatives of Ruthenium

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ABSTRACT :-An environ-economic route is used for the synthesis of ruthenium (III) derivatives of O-alkyl or O-aryl trithiophosphate in 1:3 molar ratio to form $Ru[SSK(S)POR]_3$ where (R= Me, Et, Prⁱ, Buⁱ, Ph, CH₂Ph) respectively.

These compounds have been synthesized by solvent free microwave assisted condition resulting from the reaction between ruthenium trichloride and potassium salt of O-alkyl or O-aryl trithiophosphate.

In comparison between conventional and microwave assisted method, conventional method involving tedious work, excess use of solvent and extra labour work for separation and purification of compounds but in microwave method the reaction time is shorter, higher yield of product, eco-friendly, less requirement of energy so this method is useful alternative for the preparation of compounds.

These compounds are dark brown or black coloured powdery solids, monomer in nature and soluble in common organic solvents.

These newly synthesized compounds have been characterized by elemental analysis, molecular weight determination and spectroscopic (IR, NMR) studies.

The antibacterial activity has also been investigated by paper disc method and compared with standard drugs.

KEYWORDS: - Ruthenium (III) chloride, O-alkyl /O-aryl trithiophosphate, octahedral geometry, antibacterial activity, gram positive and gram negative bacteria.

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I. Introduction

The science in which chemical reactions are carried out in presence of microwave irradiation is known as microwave chemistry^{1,4}. This method is very beneficial because reaction time is shorter, product yield is high, minimum use of solvent, energy consumption is minimum and eco-friendliness. On the other hand in conventional method excess use of solvents with tedious work is involved.

For synthesis of organic compounds solvent free microwave assisted method provide green chemical alternative route⁵⁻⁸. In the recent years chemists are taking interest in the metal, organometallic complexes and organic derivatives of phosphate and dithiophosphate ester⁹⁻¹² and trithiophosphate compounds¹³⁻¹⁶.

These organometallic complexes are used as defoliant¹⁷, insecticides¹⁸⁻¹⁹, nematocides, pesticides²⁰, bacteriocides²¹ and inhibitor of steel corrosion²².

The survey of literature reveals that synthesizing and screening the antibacterial activity of some metal derivatives of trithiophosphate ligands have been proved²³⁻²⁴.

Although a few O-alkyl / O-aryl trithiophosphate derivatives of tin²⁵⁻²⁶, arsenic²⁷, boron²⁸, aluminium²⁹, antimony³⁰ and acetyl, benzyl and benzoyl chloride³¹ have been prepared and studied as antibacterial agents in our laboratory but the ruthenium derivatives of this ligands have not been synthesized and studied for their antibacterial activity as yet.

Ruthenium compounds can be used in solar cells. Ruthenium is one of the most effective hardeners for Platinum and Palladium and is alloyed with these metals to make electrical contacts for severe wear resistance. Ruthenium compounds are used to color ceramics and glass. Some ruthenium complexes absorb light throughout the visible spectrum and are being actively researched in various, potential, solar energy technologies.

In view of this it was considered to synthesis O-alkyl / O-aryl trithiophosphate complexes of ruthenium (III) by microwave assisted method and studied their chemical bonding modes and their antibacterial activity and also compare their antibacterial activities with standard drugs like Imipenem and Linezolid.

II. Experimental

During the experimental manipulations moisture was carefully excluded. Dipotassium salts of O-alkyl/O-aryl trithiophosphates have been synthesized by the methods reported in the literature³². 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. Sulphur was estimated by Idometric method³³ and Messenger's method³³, respectively. Molecular weights were determined by Knauer vapour pressure osmometer in CHCl₃. FT IR spectra were recorded on Perkin Elmer spectrum version 10.400 spectrophotometer in the range of 4000-200 cm⁻¹. ¹H NMR spectra were recorded in DMSO and ³¹P NMR spectra were recorded in DMSO on DELTA NMR 400 MHz spectrophotometer using TMS (for ¹H).

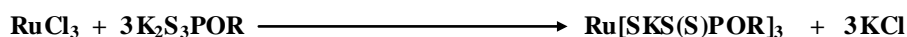
Synthesis of [CH₃CH₂OP(S)SSK]₃Ru :- Dipotassium salt of O-ethyltrithiophosphate 1.0013gm [4.0027 mmol] and ruthenium trichloride 0.2767gm [1.3339 mmol] in 1:3 molar ratio were taken in R.B.F. and add some amount of distilled water then put this mixture into microwave oven model no. EM21ES80BK for 2 minutes at 50 Hz frequency and 230V voltage which rated input is 1300W and rated output is 800W and its microwave frequency is 2450 MHz. Dark brown/black coloured powdery solid product was obtained. It has been washed three-four times by acetone and recrystallize and purify it by recrystallization method(Table-1).

Table – 1 Synthetic and Analytic Data of Ru[SSK(S)POR]₃

S. No.	Reactantsg....(mmol)		Productg ...%	Analysis % found (calcd.)				Molecular Weight found (calcd.)
	RuCl ₃	ROPS ₃ K ₂ R = ..		C	H	S	Ru	
1.	0.2930 [1.4125]	CH ₃ 1.0008 [4 2379]	[CH ₃ OP(S)SSK] ₃ Ru 2.6979 92	5.05 (5.20)	1.28 (1.30)	40.17 (41.61)	14.33 (14.60)	676.44 (691.98)
2.	0.2767 [1.3339]	C ₂ H ₅ 1.0013 [4.0027]	[C ₂ H ₅ OP(S)SSK] ₃ Ru 2.7910 95	9.67 (9.80)	2.01 (2.04)	38.74 (39.23)	12.97 (13.77)	
3.	0.2618 [1.2621]	ⁱ C ₃ H ₇ 1.0005 [3.7876]	[ⁱ C ₃ H ₇ OP(S)SSK] ₃ Ru 2.6157 89	12.52 (13.91)	1.99 (2.07)	36.86 (37.11)	12.76 (13.02)	
4.	0.2491 [1.2008]	ⁱ C ₄ H ₉ 1.0024 [3.6038]	[ⁱ C ₄ H ₉ OP(S)SSK] ₃ Ru 2.6824 91	16.73 (17.60)	3.15 (3.30)	34.94 (35.20)	12.04 (12.35)	795.86 (817.98)
5.	0.2321 [1.1189]	C ₆ H ₅ 1.0011 [3.3577]	[C ₆ H ₅ OP(S)SSK] ₃ Ru 2.7710 94	23.59 (24.60)	1.53 (1.70)	31.45 (32.20)	11.21 (11.51)	837.29 (877.98)
6.	0.2216 [1.0683]	o-CH ₃ C ₆ H ₄ 1.0008 [3.2061]	[o-CH ₃ C ₆ H ₄ OP(S)SSK] ₃ Ru 2.7135 92	26.19 (27.39)	2.09 (2.28)	30.23 (31.30)	9.79 (10.98)	
7.	0.2217 [1.0687]	m-CH ₃ C ₆ H ₄ 1.0012 [3.2074]	[m-CH ₃ C ₆ H ₄ OP(S)SSK] ₃ Ru 2.5966 88	26.96 (27.39)	2.11 (2.28)	30.67 (31.30)	9.58 (10.98)	
8.	0.2219 [1.0697]	p-CH ₃ C ₆ H ₄ 1.0022 [3.2106]	[p-CH ₃ C ₆ H ₄ OP(S)SSK] ₃ Ru 2.7469 93	26.83 (27.39)	2.13 (2.28)	30.53 (31.30)	9.87 (10.98)	897.55 (919.98)

III. Results And Discussion :-

Reactions of ruthenium (III) chloride and dipotassium salts of O-alkyl / O-aryl trithiophosphates have been carried out in 1:3 molar ratio by using solvent free microwave assisted method which leads high yield of product. The KCl formed during the reaction is removed by filtration.



(where R = Me, Et, Prⁱ, Buⁱ, Ph, CH₂Ph)

Newly synthesized derivatives are coloured crystalline solid, non-volatile and monomeric in nature, insoluble in common organic solvents but soluble in coordinated solvents like DMSO, DMF etc.

IV. Spectral Analysis :-

IR spectra :- IR spectra were recorded in 4000-200 cm⁻¹ region and following bands have been recorded.(Table-2)

1. Presence of absorption band in the region 1637.05-1606.02 cm⁻¹ and 1165.11-1081.86 cm⁻¹ indicate the presence of ν(P)-O-C and νP-O-(C) group respectively.
2. The absorption band at 1036.04-956.28 cm⁻¹ and 875.86-606.50 cm⁻¹ have been attributed to νP=S and νP-S linkage respectively which shows M←S=P bond is present in the compound.
3. The S-H band which arises in the region 2379-2351 cm⁻¹ was absent in these complexes.
4. There is no absorption band found in the region 1200-1100 cm⁻¹ which indicates that νP=O linkage is absent in these complexes.
5. Due to strong chelation of νP-S group with central ruthenium 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 $580.06-472.80\text{ cm}^{-1}$ represents the new $\nu_{\text{Ru-S}}$ bond.

Table – 2 IR Spectra Data of $\text{Ru}[\text{SSK}(\text{S})\text{POR}]_3$

S.No.	COMPOUND	$\nu(\text{P})-\text{O}-\text{C}$	$\nu\text{P}-\text{O}-(\text{C})$	$\nu\text{P}=\text{S}$	$\nu\text{P}-\text{S}$	$\nu_{\text{Ru-S}}$
1.	$[\text{CH}_3\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	1625.65	1165.11	1024.52	875.86	580.06
2.	$[\text{C}_2\text{H}_5\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	1629.90	1107.6	1036.04	605.32	507.03
3.	$[\text{C}_3\text{H}_7\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	1623.61	1152.38	993.23	851.38	563.67
4.	$[\text{C}_4\text{H}_9\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	1615.75	1140.19	998.01	865.29	572.59
5.	$[\text{C}_6\text{H}_5\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	1637.05	1151.66	995.18	852.23	563.75
6.	$[\text{o}-\text{CH}_3\text{C}_6\text{H}_4\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	1627.16	1125.41	973.26	775.68	552.65
7.	$[\text{m}-\text{CH}_3\text{C}_6\text{H}_4\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	1606.02	1081.86	956.28	606.50	472.80
8.	$[\text{p}-\text{CH}_3\text{C}_6\text{H}_4\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	1612.17	1095.69	968.18	615.33	485.68

ν_s = very strong, ν_s = strong, ν_w = weak

NMR spectra :-

^1H NMR spectra :- The ^1H NMR spectra of these complexes were recorded in 0-10 ppm region. Characteristics 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 , $\text{OC}_6\text{H}_4\text{CH}_3$ protons which are present in expected region³⁴⁻³⁶.

^{31}P NMR spectra :- A single resonance signal for these complexes were recorded in the region of 89.21-102.04 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 - 3 ^1H NMR spectra and ^{31}P NMR spectra of $\text{Ru}[\text{SSK}(\text{S})\text{POR}]_3$

S. No.	Compound	^1H chemical shift (-ppm)	^{31}P Chemical shift (-ppm)
1.	$[\text{CH}_3\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	2.15, s, 3H (OCH_3)	99.69
2.	$[\text{C}_2\text{H}_5\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	1.82, t, 3H (CH_3) 2.95, q, 2H (OCH_2)	97.43
3.	$[\text{C}_3\text{H}_7\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	1.09, d, 6H (CH_3) 2.91-3.11, m (OCH)	95.65
4.	$[\text{C}_4\text{H}_9\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	1.34, d, 6H (CH_3) 2.24-2.39, m, 1H (CH) 3.22, d, 2H (OCH_2)	89.21
5.	$[\text{C}_6\text{H}_5\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	6.36-6.81, m, 5H (OC_6H_5)	102.04
6.	$[\text{o}-\text{CH}_3\text{C}_6\text{H}_4\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	6.71-6.96, m, 12H (C_6H_4) 1.83, s, 3H (CH_3)	98.78
7.	$[\text{m}-\text{CH}_3\text{C}_6\text{H}_4\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	6.15-6.39, m, 12H (C_6H_4) 1.79, s, 3H (CH_3)	96.81
8.	$[\text{p}-\text{CH}_3\text{C}_6\text{H}_4\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	6.09-6.21, m, 12H (C_6H_4) 1.64, s, 3H (CH_3)	92.27

Antibacterial activity :- Newly synthesized compounds also show antibacterial activity against gram positive and gram negative bacteria (Table-4). The antibacterial activity was carried out by paper disc method and inhibition zone is measured in mm. The compounds are tested at $100\text{ }\mu\text{g/mL}$ concentration in DMF solvent. Imipenem and linezolid were used as a standard drugs for comparative studies.

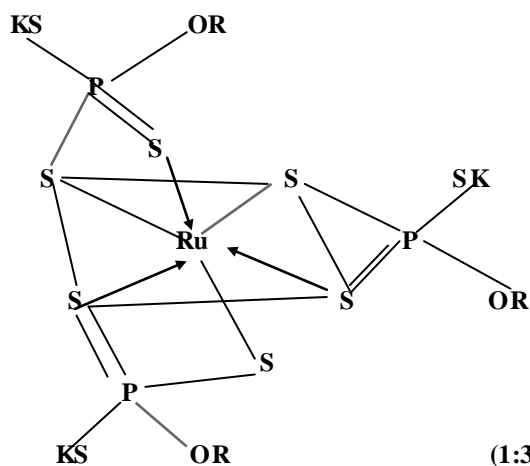
Table-4 Antibacterial Activity of $\text{Ru}[\text{SSK}(\text{S})\text{POR}]_3$

S. No.	Compounds	Gram Positive Bacteria Zone of inhibition in mm	Gram Negative Bacteria Zone of inhibition in mm
1.	$[\text{CH}_3\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	13	15
2.	$[\text{C}_2\text{H}_5\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	9	17
3.	$[\text{C}_3\text{H}_7\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	19	16
4.	$[\text{C}_4\text{H}_9\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	21	18
5.	$[\text{C}_6\text{H}_5\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	17	23
6.	$[\text{o}-\text{CH}_3\text{C}_6\text{H}_4\text{OP}(\text{S})\text{SSK}]_3\text{Ru}$	20	31

7.	$[m\text{-CH}_3\text{C}_6\text{H}_4\text{OP(S)SSK}]_3\text{Ru}$	24	28
8.	$[p\text{-CH}_3\text{C}_6\text{H}_4\text{OP(S)SSK}]_3\text{Ru}$	22	32
9.	Imipenem	12	30
10.	Linezo lid	18	10

V. Conclusion

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



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