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

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## ABSTRACT

Nickel (II) O-alkyl or O-aryl trithiophosphate of type $Ni[SSK(S)POR]_2$ (where R= Me, Et, $Pr^i$, $Bu^i$, Ph, o-$CH_3C_6H_4$, m-$CH_3C_6H_4$, p-$CH_3C_6H_4$) have been synthesized by solvent free microwave assisted method from the reaction of Nickel (II) chloride hexahydrate with dipotassium salts of O-alkyl or O-aryl trithiophosphate ligand in 1:2 molar ratio, respectively. Newly synthesized compounds are black colored powdery solids and soluble in common organic solvents like DMSO, $CHCl_3$, $CCl_4$, alcohol etc. These compounds have been characterized by elemental analysis, molecular weight determination and spectroscopic (IR, $^1H$ NMR and $^{31}P$ NMR) studies. With the help of them octahedral geometry has been proposed for these compounds. These derivatives also show good antibacterial activity against gram positive and gram negative bacteria and comparative study of antibacterial effect has also been made with standard drugs like Imipenem and Linezolid.

**Keywords:** Nickel (II) chloride hexahydrate, O-alkyl /O-aryl trithiophosphate, Octahedral geometry, Antibacterial activity

## 1. INTRODUCTION

Microwave chemistry is the science in which microwave irradiation is applying to reactant in chemical reactions [1-4]. This method leads to reduce the reaction time, higher yields of product, minimum use of solvent, cleaner reaction profiles eco-friendliness. It also provides green chemical route for synthesis of organic compounds [5-8]. On the other side in conventional method toxic solvents are used which are hazardous for health and cause severe health problem.

In the recent years considerable interest have been evinced by chemist in the chemistry of metallic, organometallics complexes of monothiophosphate, dithiophosphate ester [9-12]. These organometallic compounds are widely used as defoliants [13], insecticides [14-15], nematodicides, pesticides [16], bacteriocides [17] and inhibitor of steel corrosion [18]. So it was interested to extend the investigation of trithiophosphate ligand [19-22]. Dipotassium salts of trithiophosphate exist in two isomeric form $[(RO)P(S)S_2]$ (thiono) and $[(RS)P(O)S_2]$ (thiolo) [23].

The survey of literature reveals that synthesizing and screening the antibacterial activity of some metal derivatives of trithiophosphates ligand have been done [24-28].

Although a few O-alkyl or O-aryl trithiophosphate derivatives of tin [29-30], arsenic [31], boron [32], aluminium [33], antimony [34] some transition metals like V [35], Fe [36], Cr [37], Zn [38], Mn [39] and acetyl, benzyl and benzoyl chloride [40] have been studied as antibacterial agents in our laboratory but nickel derivatives of trithiophosphates have not been synthesized and studied yet.

$NiCl_2$ and its hydrate form are useful in organic synthesis. It use as a mild Lewis acid e.g. for the regioselective isomerization of dienols. As a precursor to form nickel boride, as a catalyst for making dialkyl/ arylphosphonates from phosphates and aryl iodide. Solution of nickel chloride is also used for electroplating nickel onto other metal items. On the basis of these uses dithiophosphate compounds of nickel has been already prepared. So it was considered to synthesize O-alkyl/O-aryl trithiophosphate compounds of nickel (II) by microwave assisted method and studied their chemical bonding modes and their antibacterial activity and also compare their antibacterial activities with standard drugs.

## 2. EXPERIMENTAL

Dipotassium salts of O-alkyl / O-aryl trithiophosphates had been prepared by the methods reported in the

literature [41]. The chemicals used in the investigation were of reagent grade. Carbon, hydrogen and nitrogen were estimated by Colemen C, H and N analyzer. Nickel was estimated by gravimetrically as nickel dimethylglyoxime. Sulphur was estimated by Messenger's method [42]. Molecular weights were determined by Knauer vapour pressure osmometer in $CHCl_3$. FT IR spectra were recorded on Perkin Elmer spectrum version 10.400 spectrophotometer in 4000-200 $cm^{-1}$range. $^1H$ NMR spectra were recorded in $CDCl_3$ and $^{31}P$ NMR spectra were recorded in $CDCl_3$ on DELTA NMR 400 MHz spectrophotometer using TMS (for $^1H$ ).

### 2.1.Synthesis of $[CH_3OP(S)SSK]_2Ni$

Nickel (II) chloride hexahydrate; 1.0073g [4.2375 mmol] and dipotassium salt of O-methyltrithiophosphate; 2.0014g [8.4751 mmol] in 1:2 molar ratio were taken in R.B.F. and some amount of distilled water was added. The mixture was put into microwave for 2-3 minutes at 50 Hz frequency. Product obtained as black colored powdery solids, washed 3-4 times by acetone and recrystallized by recrystallization method (Table1).

**Table 1: Synthetic and Analytic Data of $Ni[ROP(S)SSK]_2$**

| Reactant …….g……(mmol) | | Product | | Analysis % found (calcd.) | | | | Molecular Weight found (calcd.) |
|---|---|---|---|---|---|---|---|---|
| $NiCl_2.H_2O$ | $ROPS_3K_2$ R = ……. | ….g… | …%.. | C | H | S | Ni | |
| 1.0073 | $CH_3$ | $[CH_3OP(S)SSK]_2Ni$ | | 5.18 | 1.13 | 41.78 | 12.33 | 432.24 |
| [4.2375] | 2.0014 [8.4751] | 3.6058 | 94 | (5.30) | (1.32) | (42.41) | (12.96) | (452.63) |
| 0.9515 | $C_2H_5$ | $[C_2H_5OP(S)SSK]_2Ni$ | | 9.43 | 2.03 | 39.24 | 12.06 | - |
| [4.0027] | 2.0026 [8.0055] | 3.5714 | 91 | (9.98) | (2.08) | (39.94) | (12.21) | |
| 0.9002 | $^iC_3H_7$ | $[^iC_3H_7OP(S)SSK]_2Ni$ | | 13.92 | 2.39 | 36.99 | 11.13 | - |
| [3.7869] | 2.0008 [7.5744] | 3.5829 | 93 | (14.15) | (2.75) | (37.74) | (11.53) | |
| 0.8554 | $^iC_4H_9$ | $[^iC_4H_9OP(S)SSK]_2Ni$ | | 17.07 | 3.16 | 34.89 | 10.19 | 504.96 |
| [3.5985] | 2.0020 [9.1975] | 3.4761 | 90 | (17.88) | (3.35) | (35.77) | (10.93) | (536.63) |
| 0.7977 | $C_6H_5$ | $[C_6H_5OP(S)SSK]_2Ni$ | | 24.53 | 1.27 | 32.93 | 9.80 | 513.39 |
| [3.3557] | 2.0012 [6.7120] | 3.6380 | 94 | (24.97) | (1.73) | (33.29) | (10.17 | (576.63) |
| 0.7625 | o-$CH_3C_6H_4$ | o-$[CH_3C_6H_4OP(S)SSK]_2Ni$ | | 27.14 | 2.07 | 30.79 | 9.05 | - |
| [3.2076] | 2.0028 [6.4161] | 3.4525 | 89 | (27.78) | (2.31) | (31.75) | (9.70) | |
| 0.7622 | m-$CH_3C_6H_4$ | m-$[CH_3C_6H_4OP(S)SSK]_2Ni$ | | 26.99 | 2.06 | 31.22 | 9.08 | 578.17 |
| [3.2064] | 2.0018 [6.4129] | 3.5672 | 92 | (27.78) | (2.31) | (31.75) | (9.70) | (604.63) |
| 0.7626 | p-$CH_3C_6H_4$ | p-$[CH_3C_6H_4OP(S)SSK]_2Ni$ | | 27.18 | 2.11 | 31.13 | 9.14 | - |
| [3.2081] | 2.0030 [6.4167] | 3.6857 | 95 | (27.78) | (2.31) | (31.75) | (9.70) | |

## 3. RESULTS AND DISCUSSION

Reactions of nickel (II) chloride and dipotassium salts of O-alkyl / O-aryl trithiophosphates had been carried out in 1:2 molar ratio by using solvent free microwave assisted method which leads high yield of product. The KCl formed during the reaction was removed by filtration.

$$NiCl_2.6H_2O + 2K_2S_3POR \longrightarrow Ni[SSK(S)POR]_2 + 2KCl$$

(Where R = Me, Et, $Pr^i$, $Bu^i$, Ph, o-$CH_3C_6H_4$, m-$CH_3C_6H_4$, p-$CH_3C_6H_4$ )

These reactions were completed within 2-3 minutes in microwave. Then reaction mixture was dissolved in minimum amount of distilled water after filtration and dried. Newly synthesized derivatives are black colored crystalline solid, soluble in $CHCl_3$, $CCl_4$ , DMSO, DMF etc.

These compounds were also prepared by conventional method. In this method nickel (II) chloride was taken with dipotassium salts of O-alkyl / O-aryl trithiophosphate in 1:2 molar ratio in 20mL distilled water, respectively. Refluxed the reaction mixture for 5-6 hours. Product formed as precipitates, filtered and washed with acetone 3-4 times and recrystallized by DMSO:acetone mixture (1:3).

It was observed that product yield was more in microwave method than conventional method.

**Table 2: IR Spectra Data of Ni[ROP(S)SSK]$_2$**

| COMPOUND | υ(P)-O-C | υP-O-(C) | υP=S | υP-S | υNi-S |
|---|---|---|---|---|---|
| $[CH_3OP(S)SSK]_2Ni$ | 1095.71s | 1048.85vs | 823.19s | 551.21s | 445.66m |
| $[C_2H_5OP(S)SSK]_2Ni$ | 1090.14vs | 1014.63vs | 796.82s | 500.73m | 427.46w |
| $[^iC_3H_7OP(S)SSK]_2Ni$ | 1092.83vs | 1013.37m | 840.56s | 591.12w | 441.63m |
| $[^iC_4H_9OP(S)SSK]_2Ni$ | 1085.18s | 1013.61s | 795.61m | 513.45w | 437.25m |
| $[C_6H_5OP(S)SSK]_2Ni$ | 1080.24vs | 1011.34vs | 797.95m | 601.60s | 455.49s |
| $[o\text{-}CH_3C_6H_4OP(S)SSK]_2Ni$ | 1075.32s | 1023.21s | 801.01m | 572.52s | 458.23s |
| $[m\text{-}CH_3C_6H_4OP(S)SSK]_2Ni$ | 1093.18vs | 1028.78vs | 798.35s | 565.60m | 451.71m |
| $[p\text{-}CH_3C_6H_4OP(S)SSK]_2Ni$ | 1085.91vs | 1030.69vs | 810.12s | 575.78s | 459.35s |

*vs = very strong, s = strong, w = weak, m = medium*

### 3.1. Spectral Analysis

#### *3.1.1.* IR spectra

1. IR spectra were recorded in the region 4000-200 $cm^{-1}$ (Table-2) and compared the IR spectra with those of the starting material which showed high intensity absorption bands in 1095.71-1075.32$cm^{-1}$ and 1048.85-1011.34$cm^{-1}$ region due to υ(P)-O-C and υP-O-(C) group respectively.
2. A new medium intensity absorption band in the region 459.35-427.46 $cm^{-1}$ represents the υNi-S bond.
3. The absorption band υP=S and υP-S are observed at 840.56-795.61$cm^{-1}$ and 601.60-500.73$cm^{-1}$, respectively.

#### *3.1.2.* NMR spectra

**$^1$H NMR spectra:** The $^1$H NMR spectra were recorded at 0-10 ppm region. $^1$H NMR spectra of these derivatives are summarized in table-3. These derivatives show the characteristics 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 [43-45].

**$^{31}$P NMR spectra:** The $^{31}$P NMR spectra were recorded at 68-72 ppm in parent trithiophosphate ligand. These metal derivatives show only one resonance signal in the region 89.60-107.54 ppm. The signal is shifted towards downfield by 30 ppm from its original position in parent trithiophosphate ligand which shows the formation of strong metal-sulphur bond. (Table-3)

**Table 3: $^1$H NMR spectra and $^{31}$P NMR spectra of Ni[ROP(S)SSK]$_2$**

| COMPOUND | $^1$H Chemical Shift (δ-ppm) | $^{31}$P Chemical Shift (δ-ppm) |
|---|---|---|
| $[CH_3OP(S)SSK]_2Ni$ | 2.41, s, 3H ($OCH_3$) | 102.35 |
| $[C_2H_5OP(S)SSK]_2Ni$ | 1.79, t, 3H ($CH_3$), 2.88, q, 2H ($OCH_2$) | 100.49 |
| $[^iC_3H_7OP(S)SSK]_2Ni$ | 1.13, d, 6H ($CH_3$), 2.93-3.19, m, (OCH) | 96.71 |
| $[^iC_4H_9OP(S)SSK]_2Ni$ | 1.25, d, 6H ($CH_3$), 2.31-2.49, m, 1H (CH), 3.28, d, 2H ($OCH_2$) | 89.60 |
| $[C_6H_5OP(S)SSK]_2Ni$ | 6.99-7.22, m, 10H ($OC_6H_5$) | 107.54 |
| $[o\text{-}CH_3C_6H_4OP(S)SSK]_2Ni$ | 7.19-7.46, m, 8H ($C_6H_4$), 1.93, s, 6H ($CH_3$) | 99.85 |
| $[m\text{-}CH_3C_6H_4OP(S)SSK]_2Ni$ | 6.91-7.11, m, 8H ($C_6H_4$), 1.76, s, 6H ($CH_3$) | 94.29 |
| $[p\text{-}CH_3C_6H_4OP(S)SSK]_2Ni$ | 6.74-6.96, m, 8H ($C_6H_4$), 1.62, s, 6H ($CH_3$) | 91.46 |

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

### 3.2. Antibacterial activity

Antibacterial activity studies of the newly synthesized derivatives have been carried out by paper disc method. The zone of inhibition was measured in mm. The compounds are tested at 100 µg/mL concentration in DMF solvent. The observation show that compounds 10, 12, 14 are more effective against gram positive bacteria and compounds 13, 15, 17 are more effective against gram negative bacteria. For their comparative studies Imipenem and Linezolid were used as standard drugs.

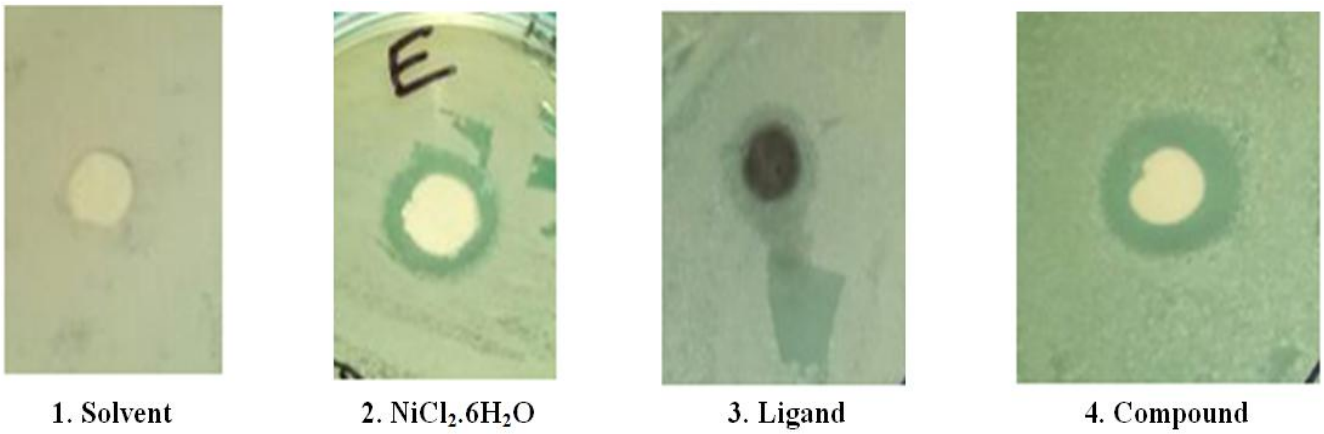



**Fig. 1: Effect of $Ni[C_2H_5OP(S)SSK]_2$ on gram positive bacteria**

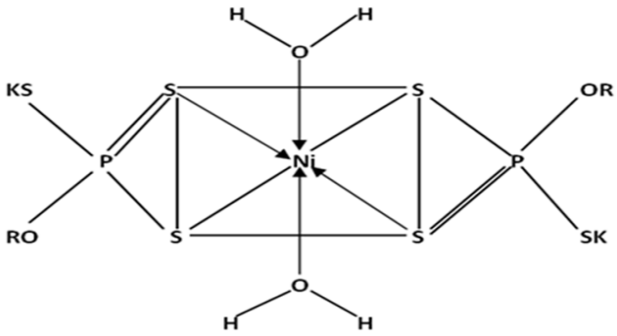
**Table 4: Antibacterial Activity of $Ni[ROP(S)SSK]_2$**

| Compounds | Gram Positive Bacteria Zone of inhibition in mm | Gram Negative Bacteria Zone of inhibition in mm |
|---|---|---|
| Solvent | 0 | 0 |
| $CH_3OP(S)(SK)_2$ | 7 | 6 |
| $C_2H_5OP(S)(SK)_2$ | 8 | 5 |
| $^{i}C_3H_7OP(S)(SK)_2$ | 9 | 3 |
| $^{i}C_4H_9OP(S)(SK)_2$ | 6 | 8 |
| $C_6H_5OP(S)(SK)_2$ | 8 | 9 |
| o-$CH_3C_6H_4OP(S)(SK)_2$ | 10 | 12 |
| m-$CH_3C_6H_4OP(S)(SK)_2$ | 12 | 9 |
| p-$CH_3C_6H_4OP(S)(SK)_2$ | 9 | 10 |
| $[CH_3OP(S)SSK]_2Ni$ | 28 | 19 |
| $[C_2H_5OP(S)SSK]_2Ni$ | 24 | 21 |
| $[^{i}C_3H_7OP(S)SSK]_2Ni$ | 29 | 23 |
| $[^{i}C_4H_9OP(S)SSK]_2Ni$ | 25 | 29 |
| $[C_6H_5OP(S)SSK]_2Ni$ | 30 | 28 |
| [o-$CH_3C_6H_4OP(S)SSK]_2Ni$ | 27 | 33 |
| [m-$CH_3C_6H_4OP(S)SSK]_2Ni$ | 23 | 20 |
| [p-$CH_3C_6H_4OP(S)SSK]_2Ni$ | 26 | 31 |
| Imipenem | 12 | 30 |
| Linezolid | 18 | 10 |

## 4. CONCLUSION

On the basis of physico-chemical spectroscopic studies the structure of these complexes may be as follows:-

Due to non availability of suitable crystals the authentic structure of the complexes, synthesized by us could not be assigned by X-ray crystallography, however on the basis of spectroscopic studies octahedral geometry for these complexes have been suggested.




**(1:2 molar ratio compound)**

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