Journal of Current Chemical & Pharmaceutical Sciences

*J. Curr. Chem. Pharm. Sc.: 2(3), 2012, 133-148*
*ISSN 2277-2871*

# SYNTHESIS, STRUCTURAL ELUCIDATION AND ANTIMICROBIAL ACTIVITIES OF SOME ALKYLENE DITHIOPHOSPHATE DERIVATIVES OF MACROCYCLIC COMPLEXES OF Ni (II) HAVING $N_2S_2$ POTENTIAL DONORS IN 18 TO 24 MEMBERED RINGS

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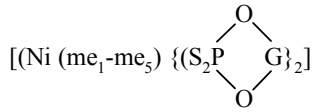
(*Received : 15.05.2012; Revised : 24.05.2012; Accepted : 27.05.2012*)

## ABSTRACT

Alkylene dithiophosphate derivatives of macrocyclic complexes of Nickel (II), having $N_2S_2$ potential donors, of the general formula,



Where mc = macrocyclic ligands and G = $CH_3-\underset{|}{\overset{|}{CH}}-\underset{|}{\overset{|}{CH}}-CH_3$, $(CH_3)_2-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-(CH_3)_2$ and $(CH_3)_2-\underset{|}{\overset{|}{C}}-CH_2-\underset{|}{\overset{|}{CH}}-$ have been synthesized from the reactions of [Ni ($mc_1$–$mc_5$)$X_2$], Where X = $Cl^-$, $NO_3^-$, or $CH_3COO^-$, with ammonium alkylene dithiophosphates in 1 : 2 molar ratios in THF. These complexes have been characterized by elemental analysis, molar conductance, molecular weight determination, IR, $^{31}P$ NMR, electronic spectra, and magnetic measurements. Molecular weight determination of these complexes indicates their monomeric nature. Octahedral structure has been proposed on the basis of $^{31}P$ NMR, electronic spectra, and magnetic measurements. Two sulphur atoms and two nitrogen atoms of the macrocyclic ring coordinate to the central nickel ion in the square planar form, and each dithiophosphate moiety occupies the axial positions binding the central nickel ion in unidentate behavior. Antimicrobial activities of these derivatives have been studied by screening them against fungi, such as *Aspergillus flavus, Fusarium oxysporum, Trichoderma harzianum,* and bacteria, such as *Salmonella typhi* and *Bacillus subtili*. Alkylene dithiophosphate derivatives were found to be more fungitoxic and antibacterial than their corresponding macrocyclic complexes.

**Key words**: Alkylene dithiophosphates, Macrocyclic complexes, Nickel (II).

## INTRODUCTION

Due to importance in biological systems and as a synthetic model for many metalloenzyme reactions[1-3], their novel structural features, and unusual magnetic properties, there has been considerable interest in the transition metal chemistry in the mixed ligand compounds during last few years[4-15]. Recently a number of mixed-ligand complexes involving Ni (II) with sulphur-containing ligand have been reported, and

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their structures have been confirmed by single-crystal X-Ray Crystallography[16-20]. Macrocyclic complexes of both transition and nontransition elements have received considerable interest during the past one and one half decades due to their wide diversity in chemical[21-28] and biological systems[29-31]. Macrocyclic complexes having tetraaza[32-36], dioxotetraaza[37-38], tetraoxotetraaza[39], tetraoxo octaaza[40] and trioxotetraaza[41] are well reported. Recently we have reported synthesis, characterization and biocidal screening of some new thioaza macrocyclic complexes of Ni (II)[42]. Inspite of vast innovations in macrocyclic chemistry and tremendous interest in mixed ligand complexes, no macrocyclic complex having mixed ligand system has been reported so far.

Alkylene dithiophosphates has been our area of research for many years[43-51]. Recently the synthesis, characterization, and antimicrobial aspects of the mixed-ligand macrocyclic complexes of Ni (II) having dialkyldithiophosphate moieties have been reported[42]. In continuation of the above research we hereby report the synthesis characterization and antimicrobial aspects of alkylene dithiophosphate derivatives of macrocyclic complexes of Ni (II), in which two sulphur atoms and two nitrogen atoms of the macrocyclic ring coordinate to the central nickel ion in the square planar form and each dithiophosphate moiety occupy the axial positions binding the central nickel ion in unidentate manner through strong electrostatic attraction.

## EXPERIMENTAL

### Materials and methods

All of the nickel salts and dicarboxylic acids of Analytical Reagent grade were obtained from S.d-fine Chemicals (Mumbai, India) and were used without further purification. *p*-aminothiophenol was used as obtained from Merck (Germany and UK). Solvents were purified and dried by standard methods.

Microanalysis for carbon, hydrogen, nitrogen, and sulphur were determined from Sophisticated Instrumentation Center for Applied Research Testing (SICART), Vallabh Vidyanagar. Nickel and phosphorus were estimated by standard methods[52]. The molecular weights were determined by Rast Camphor method. Infrared data were recorded on a Perkin-Elmer Fourier transform infrared (FTIR) spectrophotometer as KBr pellets. Magnetic data were recorded on Faraday balance. Electronic spectra were recorded on GBC 911 spectrophotometer in the range 380-1000 nm. $^{31}$P NMR spectra were recorded on 270 MHz spectrometer using $CDCl_3$ as a solvent and $H_3PO_4$ as an external standard.

### Synthesis of macrocyclic complexes and its derivatives

Macrocyclic complexes were prepared by the methods as reported earlier[42].

### Macrocyclic complex derived from template condensation of malonic acid and p-aminothiophenol in the presence of nickel chloride

A solution of nickel chloride (0.852 g, 0.0035 mmol) in methanol was reacted with *p*-aminothiophenol (0.896 g, 0.0071 mmol) dissolved in methanol. This was followed by the addition of a methanolic solution of malonic acid (0.745 g, 0.0071 mmol). Reaction mixture was refluxed for 10 h at 80$^{o}$C. The green precipitate obtained on cooling was filtered, washed with methanol, and dried in vacuo.

### Macrocyclic complex derived from template condensation of succinic acid and p-aminothiophenol in the presence of nickel chloride

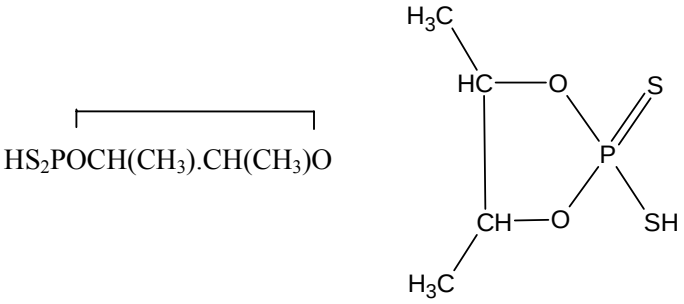
A solution of nickel chloride (1.245 g, 0.0052 mmol) in methanol was reacted with *p*-aminothiophenol (1.309 g, 0.0104 mmol) dissolved in methanol. This was followed by the addition of a

methanolic solution of succinic acid (1.248 g, 0.0105 mmol). Reaction mixture was refluxed for 10 h at 80°C. The green precipitate obtained on cooling was filtered, washed with methanol, and dried in vacuo.

Alkylene dithiophosphoric acids and their ammonium salts were prepared by the methods as reported earlier[44]. The derivatives of macrocyclic complexes of the following alkylene dithiophosphoric acids have been synthesized.

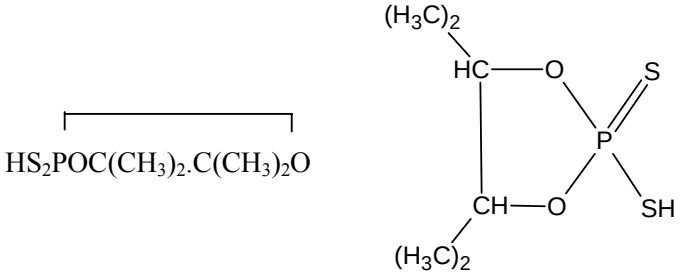
Butylene dithiophosphoric acid.

**(2-Mercapto-2-thiono-4,5 dimethyl 1,2,3-dioxaphospholane)**



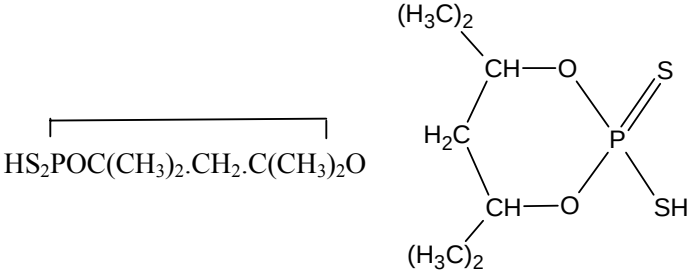

Tetramethylethylene dithiophosphoric acid.

**(2-Mercapto-2-thiono-4,4,5,5-tetremethyl-1,3,2-dioxaphospholane)**




Hexylene dithiophosphoric acid.

**(2-Mercapto-2-thiono-4,4,6-trimethyl-1,3,2-dioxaphosphorinane)**




**Synthesis of butylene dithiophosphate derivative of macrocyclic complex obtained from the reaction of ammonium butylene dithiophosphate with the complex derived by the template condensation of succinic acid and p-aminothiophenol in the presence of nickel chloride**

Macrocyclic complex mentioned above (0.816 g, 0.0015 mmol) was dissolved in tetrahydro furane (THF) and was reacted with methanolic solution of ammonium butylene dithiophosphate (0.636 g, 0.0031 mmol) in 1 : 2 molar ratio. Reaction mixture was refluxed for ~2 h at 90°C. On cooling the green crystals of

dithiophosphate derivative were separated out, which were filtered through G-3 filtering funnel. This crude product was washed several times with methanol by vigrous shaking in filtration funnel to remove the ammonium chloride formed during the reaction. Product was dried in vacuo and was crystallized with THF/$C_2H_5OH$ mixture.

**Synthesis of hexylene dithiophosphate derivative of macrocyclic complex obtained from the reaction of ammonium hexylene dithiophosphate with the complex derived by the template condensation of succinic acid and o-aminothiophenol in the presence of nickel chloride**

Macrocyclic complex mentioned above (0.690 g, 0.0013 mmol) was dissolved in THF and was reacted with methanolic solution of ammonium hexylene dithiophosphate (0.613 g, 0.0026 mmol) in 1 : 2 molar ratio. Reaction mixture was refluxed for ~2h at 90°C. On cooling the green crystals of dithiophosphate derivative were separated out, which were filtered through G-3 filtering funnel. This crude product was washed several times with methanol by vigrous shaking in filtration funnel to remove the ammonium chloride formed during the reaction. Product was dried in vacuo and was crystallized by THF/$C_2H_5OH$ mixture. Relevant data for the similar syntheses are given in Table 1.

## RESULTS AND DISCUSSION

Macrocyclic complexes of Ni (II) in THF react with methanolic solution of ammonium alkylene dithiophosphate in 1 : 2 molar ratios to afford alkylene dithiophosphate derivatives of macrocyclic Ni(II) complexes in the following manner:

$$[Ni(mc_1 - mc_5)X_2] + 2NH_4S_2P\begin{matrix}O\\ \diagup\ \diagdown\\ \ \ G\\ \diagdown\ \diagup\\ O\end{matrix} \rightarrow [Ni(mc_1 - mc_5)\{S_2P\begin{matrix}O\\ \diagup\ \diagdown\\ \ \ G\\ \diagdown\ \diagup\\ O\end{matrix}\}_2] + 2\,NH_4X$$

where $mc_1$ to $mc_5$ are the macrocyclic complexes derived by the template condensation of *p*-aminothiophenol with dicarboxylic acids in the presence of $NiCl_2 \cdot 6H_2O$ in methanol,

G = $CH_3\text{-}\underset{|}{C}H\text{-}\underset{|}{C}H\text{-}CH_3$, $(CH_3)_2\text{-}\underset{|}{C}\text{-}\underset{|}{C}\text{-}(CH_3)_2$, and $(CH_3)_2\text{-}\underset{|}{C}\text{-}CH_2\text{-}\underset{|}{C}H$- and X = $Cl^-$, $NO_3^-$ or $CH_3COO.^-$

Most of the complexes were prepared starting with chloride salts of macrocyclic complexes. For comparison a few representative compounds have been prepared starting with nitrate and acetate salts of macrocyclic complexes. The reaction starts at room temperature, but for completion of reaction the reaction mixture was refluxed for ~2 h. On cooling the crystals of dithiophosphate derivatives were separated out. Except for THF and dimethysulfoxied (DMSO), these derivatives are insoluble in almost all organic solvents. All derivatives are dull, shining, or dark red in colour and melt with decomposition at high temperature. The molar conductance of $10^{-3}$ M solution in DMSO lie in the range 3.48-7.14 $ohm^{-1}$ $cm^2$ $mol^{-1}$, showing that these complexes are nonelectrolyte (Table 2). The molecular weight determinations indicate their monomeric nature (Table 1). The analytical data of these derivatives are given in Table 3.

**Table 1: Reaction of macrocyclic complexes of Ni (II) with ammonium alkylene dithiophosphates.**

| S. No. | Macrocyclic complex [Moleculer formula] (Empirical formula) g (mmol) | Amonium alkylenedithiophosohate g (mmol) | [Product] (Empirical formula) Yield (g)% | M.P. (decomp.)$^{o}$ C | M. Wt. Found (Caled.) |
|---|---|---|---|---|---|
| **1** | $[Ni(mc_1)Cl_2]$ $(C_{18}H_{14}N_2S_2O_4NiCl_2)$ 0.816(0.0015) | $NH_4S_2POCH(CH_3)CH(CH_3)O)$ $(C_4H_8S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_1)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{26}H_{30}N_2P_2S_6O_8Ni)$ 1.00(82%). | 238 | 824.40 (810.7) |
| **2** | $[Ni(mc_1)Cl_2]$ $(C_{18}H_{14}N_2S_2O_4NiCl_2)$ 0.748(0.0014) | $NH_4S_2POC(CH_3)_2C(CH_3)_2O)$ $(C_6H_{12}S_2O_2P.NH_4)$ 0.665(0.0029) | $[Ni(mc_1)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$ 1.08(84%). | 235 | 856.7 (864.7) |
| **3** | $[Ni(mc_1)Cl_2]$ $(C_{18}H_{14}N_2S_2O_4NiCl_2)$ 0.690(0.0013) | $NH_4S_2POC(CH_3)_2CH_2CH(CH_3)O$ $(C_6H_{12}S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_1)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$ 0.960(82%). | 215 | 845.7 (862.7) |
| **4** | $[Ni(mc_2)Cl_2]$ $(C_{20}H_{18}N_2S_2O_4NiCl_2)$ 0.816(0.0015) | $NH_4S_2POCH(CH_3)CH(CH_3)O$ $(C_4H_8S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_2)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{28}H_{34}N_2P_2S_6O_8Ni)$ 1.080(82%). | 222 | 820.5 (834.7) |
| **5** | $[Ni(mc_2)Cl_2]$ $(C_{20}H_{18}N_2S_2O_4NiCl_2)$ 0.768(0.0014) | $NH_4S_2POC(CH_3)_2C(CH_3)_2O$ $(C_4H_8S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_2)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$ 1.060(81%). | 256 | 887.7 (890.7) |
| **6** | $[Ni(mc_2)Cl_2]$ $(C_{20}H_{18}N_2S_2O_4NiCl_2)$ 0.680(0.0013) | $NH_4S_2POC(CH_3)_2CH_2CH(CH_3)O$ $(C_4H_8S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_2)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$ 1.112(84%). | 232 | 862.4 (890.7) |
| **7** | $[Ni(mc_3)Cl_2]$ $(C_{22}H_{22}N_2S_2O_4NiCl_2)$ 0.880(0.0016) | $NH_4S_2POCH(CH_3)CH(CH_3)O$ $(C_4H_8S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_3)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$ 1.50(84%). | 214 | 902.4 (918.7) |

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| S. No. | Macrocyclic complex [Moleculer formula] (Empirical formula) g (mmol) | Amonium alkylenedithiophosohate g (mmol) | [Product] (Empirical formula) Yield (g)% | M.P. (decomp.) $^{o}$C | M. Wt. Found (Caled.) |
|---|---|---|---|---|---|
| **8** | $[Ni(mc_3)Cl_2]$ $(C_{22}H_{22}N_2S_2O_4NiCl_2)$ 0.740(0.0014) | $NH_4S_2POC(CH_3)_2C(CH_3)_2O$ $(C_4H_8S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_3)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8Ni)$ 1.00(82%). | 210 | 943.2 (920.7) |
| **9** | $[Ni(mc_3)Cl_2]$ $(C_{22}H_{22}N_2S_2O_4NiCl_2)$ 0.692(0.0013) | $NH_4S_2POC(CH_3)_2CH_2CH(CH_3)O$ $(C_4H_8S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_3)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8Ni)$ 1.098(84%). | 202 | 912.4 (920.7) |
| **10** | $[Ni(mc_4)Cl_2]$ $(C_{18}H_{14}N_2S_2O_4NiCl_2)$ 0.780(0.0014) | $NH_4S_2POCH(CH_3)CH(CH_3)O$ $(C_4H_8S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_4)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$ 1.180(76%). | 217 | 878.8 (992.7) |
| **11** | $[Ni(mc_4)Cl_2]$ $(C_{18}H_{14}N_2S_2O_4NiCl_2)$ 0.762(0.0014) | $NH_4S_2POC(CH_3)_2C(CH_3)_2O$ $(C_4H_8S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_4)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8Ni)$ 1.970(82%). | 230 | 967.4 (948.7) |
| **12** | $[Ni(mc_4)Cl_2]$ $(C_{18}H_{14}N_2S_2O_4NiCl_2)$ 0.816(0.0015) | $NH_4S_2POC(CH_3)_2CH_2CH(CH_3)O$ $(C_4H_8S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_4)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8Ni)$ 0.980(78%). | 221 | 938.2 (948.7) |
| **13** | $[Ni(mc_5)cl_2]$ $(C_{18}H_{14}N_2S_2O_4NiCl_2)$ 0.690(0.0013) | $NH_4S_2POCH(CH_3)CH(CH_3)O$ $(C_4H_8S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_5)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{36}H_{34}N_2P_2S_6O_8Ni)$ 1.00(83%). | 223 | 920.2 (932.7) |
| **14** | $[Ni(mc_5)Cl_2]$ $(C_{18}H_{14}N_2S_2O_4NiCl_2)$ 0.785(0.0015) | $NH_4S_2POC(CH_3)_2.C(CH_3)_2O$ $(C_4H_8S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_5)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{40}H_{42}N_2P_2S_6O_8Ni)$ 1.080(84%). | 220 | 984.7 (990.3) |
| **15** | $[Ni(mc_5)Cl_2]$ $(C_{18}H_{14}N_2S_2O_4NiCl_2)$ 0.694(0.0013) | $NH_4S_2POC(CH_3)_2CH_2CH(CH_3)O$ $(C_4H_8S_2O_2P.NH_4)$ 0.636(0.0031) | $[Ni(mc_5)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{40}H_{42}N_2P_2S_6O_8Ni)$ 1.044(80%). | 230 | 982.6 (990.3) |

## Infrared spectra

Characteristic IR absorption frequencies of these derivatives are given in Table 4. As observed in the macrocyclic complexes, the four bands in the regions 1690-1650 (s), 1587-1555 (m), 1278-1252 (s), and 690-635 (w) $cm^{-1}$ have been ascribed to amide I, amide II, amide III and amide IV in plane deformation vibrations, respectively[53]. A broad band present in the region 3278-3150 $cm^{-1}$ has been assigned to *v* (NH) vibration of the secondary amino group. These bands do not show any significant change from their parent macrocyclic complexes.[42] Two bands present in the regions 1070-1040 and 890-855 $cm^{-1}$ may be assigned to (P)-O-C and P-O-(C) stretching vibrations, respectively.[54] The bands present between 1000-950 $cm^{-1}$ may be attributed to the ring vibrations of dioxaphospholanes and dioxaphosphorinanes[55,56] respectively, which are probably coupled with C-C stacking vibrations. A weak band present in the region 560-540 $cm^{-1}$ has been attributed to P-S symmetric and asymmetric vibrations. A strong band observed in the region 710-670 $cm^{-1}$, which also appears in ammonium alkylene dithiophosphates around the same region, is attributed to free P = S moiety. This indicates the unidentate behavior of dithiophosphate moieties[57,58]. The presence of sharp bands in the region 460-410 $cm^{-1}$ and 360-315 $cm^{-1}$ have been assigned to *v* (Ni-N) and *v* (Ni-S) vibrations, respectively[46].

## $^{31}$P NMR

Due to paramagnetic nature of Ni (II), in octahedral geometry the $^{1}$H NMR of its complexes can't be observed as easily as can the diamagnetic Ni (II) complexes. We reported the $^{1}$H NMR of some paramagnetic Ni (II) complexes earlier[45,46]. During the present investigations it was not possible to obtain the $^{1}$H NMR spectra. $^{31}$P NMR spectra of a few representative compounds could be recorded. The spectra were recorded on 270 MHz spectrometer using $CDCl_3$ as a solvent and $H_3PO_4$ as an external standard. As we reported earlier[45,46], the position of chemical shift in $^{31}$P is not influenced by the paramagnetic nature of nickel ion. The values of chemical shifts of the newly synthesized compounds are reported in Table 2. The chemical shift values do not show any significant change from their parent alkylene dithiophosphoric acids. This again indicates the monodentate nature of alkylene dithiophosphate moieties attached to the central nickel ion[57,58].

**Table 2: Physico-chemical properties of the alkylene dithiophosphates derivatives of macrocyclic complexes of Ni (II)**

| S. No. | Compound | Magnetic Moment $\mu_{eff}$ (B.M.) | Electronic spectra $\lambda_{max}$ (nm) | | Conductivity | $^{31}$P NMR Chemical Shift (δ) |
|---|---|---|---|---|---|---|
| | | | $\nu_2$ | $\nu_3$ | | |
| **1** | $[Ni(mc_1)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{26}H_{30}N_2P_2S_6O_8Ni)$ | 3.15 | 660 | 425 | 3.47 | 96.80 (95.49) |
| **2** | $[Ni(mc_1)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$ | 3.21 | 665 | 400 | 6.21 | - |
| **3** | $[Ni(mc_1)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$ | 3.20 | 650 | 410 | 4.52 | - |

Cont…

| | | | | | | |
|---|---|---|---|---|---|---|
| **4** | $[Ni(mc_2)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{28}H_{34}N_2P_2S_6O_8Ni)$ | 3.06 | 650 | 415 | 7.15 | - |
| **5** | $[Ni(mc_2)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$ | 3.14 | 660 | 400 | 6.82 | 98.24 (93.07) |
| **6** | $[Ni(mc_2)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$ | 3.08 | 680 | 410 | 6.40 | - |
| **7** | $[Ni(mc_3)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$ | 3.20 | 655 | 400 | 5.75 | - |
| **8** | $[Ni(mc_3)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8Ni)$ | 2.97 | 660 | 410 | 5.15 | - |
| **9** | $[Ni(mc_3)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8Ni)$ | 3.03 | 680 | 400 | 7.42 | 86.12 (73.20) |
| **10** | $[Ni(mc_4)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$ | 3.15 | 680 | 410 | 5.15 | - |
| **11** | $[Ni(mc_4)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8Ni)$ | 3.21 | 665 | 420 | 6.52 | 98.15 (93.07) |
| **12** | $[Ni(mc_4)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8Ni)$ | 3.05 | 670 | 400 | 5.41 | - |
| **13** | $[Ni(mc_5)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{36}H_{34}N_2P_2S_6O_8Ni)$ | 3.20 | 760 | 420 | 4.21 | 98.24 (95.49) |
| **14** | $[Ni(mc_5)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{40}H_{42}N_2P_2S_6O_8Ni)$ | 2.97 | 655 | 415 | 4.32 | - |
| **15** | $[Ni(mc_5)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{40}H_{42}N_2P_2S_6O_8Ni)$ | 2.98 | 670 | 400 | 5.75 | 84.78 (73.20) |

Values of the $^{31}P$ chemical shifts of parent alkylene dithiophosphoric acids are given in parenthesis

**Table 3: Analytical data of the alkylene dithiophosphates derivatives of macrocyclic complexes of Ni (II)**

| S. No. | Compound | Found (calcd.) | | | | | |
|---|---|---|---|---|---|---|---|
| | | C | H | N | P | S | Ni |
| **1** | $[Ni(mc_1)\overline{\{S_2POCH(CH_3)CH(CH_3)O\}_2}]$ $(C_{26}H_{30}N_2P_2S_6O_8Ni)$ | 38.21 (38.48) | 3.22 (3.70) | 3.54 (3.45) | 7.55 (7.76) | 23.66 (23.68) | 7.54 (7.24) |
| **2** | $[Ni(mc_1)\overline{\{S_2POC(CH_3)_2C(CH_3)_2O\}_2}]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$ | 41.20 (41.53) | 4.17 (4.38) | 3.76 (3.23) | 7.54 (7.15) | 22.65 (22.15) | 6.43 (6.77) |
| **3** | $[Ni(mc_1)\overline{\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2}]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$ | 41.34 (41.53) | 4.02 (4.38) | 3.25 (3.23) | 7.42 (7.15) | 23.14 (22.15) | 6.45 (6.77) |
| **4** | $[Ni(mc_2)\overline{\{S_2POCH(CH_3)CH(CH_3)O\}_2}]$ $(C_{28}H_{34}N_2P_2S_6O_8Ni)$ | 40.54 (40.06) | 4.73 (4.05) | 3.07 (3.33) | 7.52 (7.39) | 22.72 (22.89) | 6.39 (7.00) |
| **5** | $[Ni(mc_2)\overline{\{S_2POC(CH_3)_2C(CH_3)_2O\}_2}]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$ | 42.25 (42.92) | 4.85 (4.69) | 3.51 (3.13) | 7.35 (6.93) | 21.74 (21.46) | 6.85 (6.56) |
| **6** | $[Ni(mc_2)\overline{\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2}]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$ | 42.66 (42.92) | 4.26 (4.69) | 3.68 (3.13) | 6.45 (6.93) | 21.66 (21.46) | 6.61 (6.56) |
| **7** | $[Ni(mc_3)\overline{\{S_2POCH(CH_3)CH(CH_3)O\}_2}]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$ | 41.33 (41.53) | 4.25 (4.38) | 3.65 (3.23) | 7.48 (7.15) | 21.75 (22.15) | 7.22 (6.77) |
| **8** | $[Ni(mc_3)\overline{\{S_2POC(CH_3)_2C(CH_3)_2O\}_2}]$ $(C_{34}H_{46}N_2P_2S_6O_8Ni)$ | 44.65 (44.22) | 4.86 (4.99) | 3.76 (3.03) | 6.11 (6.72) | 20.56 (20.81) | 6.39 (6.36) |
| **9** | $[Ni(mc_3)\overline{\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2}]$ $(C_{34}H_{46}N_2P_2S_6O_8Ni)$ | 44.35 (44.22) | 4.31 (4.99) | 2.67 (3.03) | 6.38 (6.72) | 20.54 (20.81) | 6.06 (6.36) |
| **10** | $[Ni(mc_4)\overline{\{S_2POCH(CH_3)CH(CH_3)O\}_2}]$ $(C_{32}H_{342}N_2P_2S_6O_8Ni)$ | 42.33 (42.92) | 4.36 (4.69) | 3.55 (3.13) | 6.50 (6.93) | 21.80 (21.46) | 6.80 (6.56) |
| **11** | $[Ni(mc_4)\overline{\{S_2POC(CH_3)_2C(CH_3)_2O\}_2}]$ $(C_{36}H_{50}N_2P_2S_6O_8Ni)$ | 45.75 (45.44) | 5.30 (5.26) | 2.40 (2.95) | 6.50 (6.52) | 21.55 (20.20) | 6.42 (6.17) |
| **12** | $[Ni(mc_4)\overline{\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2}]$ $(C_{36}H_{50}N_2P_2S_6O_8Ni)$ | 45.76 (45.44) | 5.32 (5.26) | 2.45 (2.95) | 6.53 (6.52) | 21.50 (20.20) | 6.44 (6.17) |
| **13** | $[Ni(mc_5)\overline{\{S_2POCH(CH_3)CH(CH_3)O\}_2}]$ $(C_{36}H_{34}N_2P_2S_6O_8Ni)$ | 46.98 (46.22) | 3.45 (3.64) | 3.52 (3.00) | 7.20 (6.63) | 21.55 (20.54) | 6.20 (6.28) |
| **14** | $[Ni(mc_5)\overline{\{S_2POC(CH_3)_2C(CH_3)_2O\}_2}]$ $(C_{40}H_{42}N_2P_2S_6O_8Ni)$ | 48.60 (48.45) | 4.90 (4.24) | 3.55 (2.83) | 6.08 (6.25) | 19.40 (19.38) | 5.65 (5.93) |
| **15** | $[Ni(mc_5)\overline{\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2}]$ $(C_{40}H_{42}N_2P_2S_6O_8Ni)$ | 48.22 (48.45) | 4.54 (4.24) | 2.32 (2.83) | 6.82 (6.25) | 19.47 (19.38) | 5.09 (5.93) |

**Table 4: IR Spectral Data of the Alkylene Dithiophosphates derivatives of Macrocyclic Complexes of Ni (II)**

| S. No. | [Molicular formula] (Empirical formula) | Amide-I | Amide-II | Amide-III | Amide-IV | ν(N-H) | (P)-O-C | P-O-(C) | Ring vibration | P=S | P-S | (Ni-N) | (NI-S) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | $[Ni(mc_1)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{26}H_{30}N_2P_2S_6O_8Ni)$ | 1668m | 1562m | 1260s | 650w | 3190w | 1040m | 865m | 850s | 670s | 560w | 420s | 326w |
| **2** | $[Ni(mc_1)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$ | 1670s | 1555m | 1274s | 648w | 3200w | 1045m | 880m | 865s | 700s | 540 | 456s | 318w |
| **3** | $[Ni(mc_1)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$ | 1650s | 1558m | 1268s | 656w | 3258w | 1058m | 890m | 855s | 680s | 550 | 475s | 348w |
| **4** | $[Ni(mc_2)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{28}H_{34}N_2P_2S_6O_8Ni)$ | 1690s | 1559m | 1252m | 636w | 3240m | 1062m | 870m | 850s | 685s | 560 | 418s | 364w |
| **5** | $[Ni(mc_2)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$ | 1650m | 1560m | 1250m | 688w | 3238m | 1070m | 860m | 870s | 700s | 545 | 428s | 318w |
| **6** | $[Ni(mc_2)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$ | 1680m | 1523m | 1262s | 695w | 3190m | 1050m | 890m | 950s | 710s | 555 | 460s | 348w |
| **7** | $[Ni(mc_3)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$ | 1690m | 1575m | 1252m | 605w | 3278w | 1065m | 870m | 870s | 670s | 550 | 422s | 345w |

Cont…

| S. No. | [Molicular formula] (Empirical formula) | Amide-I | Amide-II | Amide-III | Amide-IV | ν (N-H) | (P)-O-C | P-O-(C) | Ring vibration | P=S | P-S | (Ni-N) | (NI-S) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **8** | $[Ni(mc_3)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8Ni)$ | 1682s | 1555m | 1259m | 658w | 3145m | 1040m | 880m | 880s | 690s | 560w | 458s | 377w |
| **9** | $[Ni(mc_3)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8Ni)$ | 1689s | 1587m | 1256m | 657w | 3162m | 1075m | 890m | 865s | 700s | 545w | 483s | 320w |
| **10** | $[Ni(mc_4)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$ | 1682m | 1555m | 1260s | 647w | 168w | 1070m | 878m | 970s | 670s | 560w | 420s | 335w |
| **11** | $[Ni(mc_4)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8Ni)$ | 1690m | 1562m | 1274s | 632w | 3200w | 1062m | 860m | 865s | 680s | 540w | 430s | 340w |
| **12** | $[Ni(mc_4)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8Ni)$ | 1660m | 1537m | 1268m | 640w | 3210w | 1055m | 850m | 855s | 700s | 550w | 460s | 318w |
| **13** | $[Ni(mc_5)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{36}H_{34}N_2P_2S_6O_8Ni)$ | 1673m | 1568m | 1252s | 648w | 3208w | 1070m | 890m | 850s | 690s | 560w | 460s | 350w |
| **14** | $[Ni(mc_5)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{42}H_{40}N_2P_2S_6O_8Ni)$ | 1685s | 1570m | 1252s | 650w | 3200m | 1050m | 870m | 960s | 700s | 555w | 460s | 348w |
| **15** | $[Ni(mc_5)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{40}H_{42}N_2P_2S_6O_8Ni)$ | 1690s | 1568m | 1270s | 660w | 3208m | 1055m | 850m | 850s | 670s | 540w | 418s | 340w |

## Electronic spectra

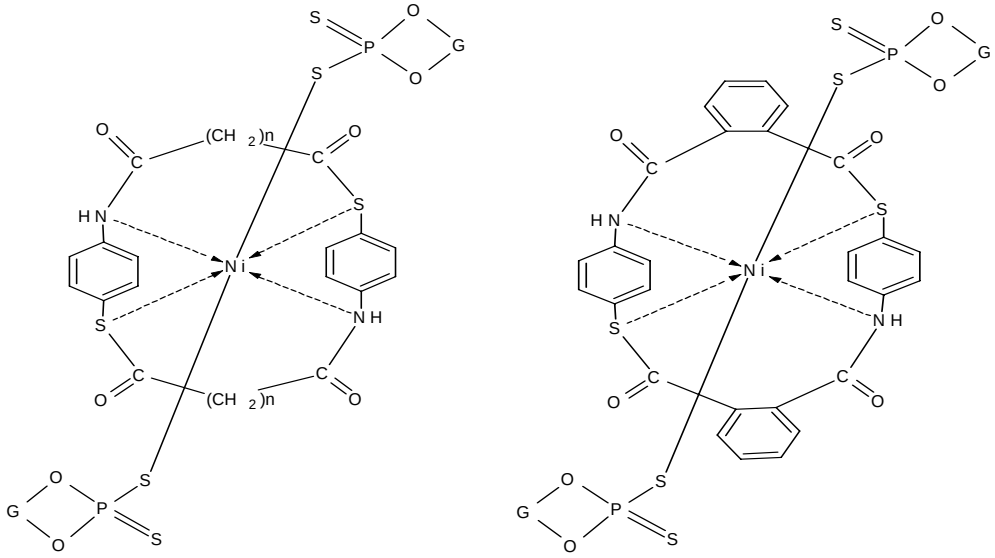
Electronic spectra were recorded on GBC 911 spectrophotometer in the range of 380-1000 nm. Only two bands, $\nu_2$ and $\nu_3$, were observed at around 630-685 and 390-440 nm, this may be attributed to the $3A_2g \rightarrow 3T_1g$ (F) and $3A_2g \rightarrow 3T_1g$ (P) transitions, respectively. These transitions indicate the six coordination of central nickel atom.[59] Data are given in Table 2.

## Magnetic susceptibility

The magnetic moments of the dithiophosphate derivatives are given in Table 2. The magnetic susceptibility was measured at Faraday balance using $Hg[Co(CNS)_4]$ as a calibrant. Pascal constants were used for diamagnetic corrections. The complexes show magnetic moment values of 2.98-3.20 B.M. at room temperature, which correspond to the two unpaired electrons expected for Ni (II) complexes[60].

## Structural information

The above spectral and magnetic data indicate the following octahedral geometry (Fig. 1 and 2) for the above derivatives in which two sulpher atoms and two nitrogen atoms of the macrocyclic ring coordinate to the central nickel ion in the square planar form, and each dithiophosphate moiety occupies the axial position, binding the central nickel ion in unidentate manner through strong electrostatic attraction.



Where n = 1, 2, 3 or 4

**Fig. 1: Dithiophosphate derivatives of macrocyclic complexes of Ni (II) derived by the template condensation of p-aminothiophenol with malonic, succinic, glutaric or adipic acid**

G = $CH_3$-CH-CH-$CH_3$, $(CH_3)_2$-C-C-$(CH_3)_2$, and $(CH_3)_2$- C-$CH_2$-CH-

**Fig. 2: Dithiophosphate derivatives of macrocyclic complexes of Ni (II) derived by the template condensation of p-aminothiophenol with pthalic acid**

## Antimicrobial activity

Antimicrobial activities of dicarboxylic acids, nickel salts and the parent macrocyclic complexes ($mc_1$ to $mc_5$) were reported earlier by Bhasin and Panchal[42] For the sake of comparison the antimicrobial activities

of *p*-aminothiophenol, dicarboxylic acids, nickel salts, their macrocyclic complexes ($mc_1$ to $mc_5$) and of butylene, pinacoline (tetramethylethylene) and hexylene dithiophosphoric acids are mentioned in Tables 5 and 6.

Antifungal activities and antibacterial activities of alkylene dithiophosphate derivatives are shown in bold. However, the activity of parent macrocyclic complexes is mentioned in the parenthesis. Like their parent macrocyclic complexes, the antifungal activities of alkylene dithiophosphate derivatives were tested against three fungi, namely *Aspergillus flavus*, *Fusarium oxysporum* and *Trichoderma harzianum*. The screening data for the average percentage inhibition of the fungi at 100, 125 and 200 ppm concentrations are given in Table 5.

The values obtained suggest that alkylene dithiophosphate derivatives of macrocyclic complexes are more fungitoxic than their parent macrocyclic complexes, as well as alkylene dithiophosphoric acids. Furthermore, the data also indicate that with the increase in concentration the fungitoxicity also increases. The antibacterial activity against two bacterias, namely *S. typhi* and *B. subtili*, were tested by inhibition zone technique[61]. The values obtained are presented in Table 6. The values suggest that alkylene dithiophosphate derivatives of macrocyclic complexes are found to be more antibacterial than their parent macrocyclic complexes ($mc_1$ to $mc_5$). of course, the dithiophosphate moieties behave as a monodentate in all the derivatives, but substitution of anions ($Cl^-$, $NO_3^-$ and $CH_3COO^-$) by the dithiophosphate moieties may reduce the polarity of the central atom by the partial sharing of its positive charge.

**Table 5: Antifungal activity of alkylene dithiophosphate derivatives of macrocyclic complexes of Ni (II), average % of inhibition after 72 h at 30°C ± 2 (conc. in ppm)**

| S. No. | Compound | *Aspergillus flavus* | | | *Fusariunm oxysporum* | | | *Trichoderma harzianum* | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | **100** | **125** | **200** | **100** | **125** | **200** | **100** | **125** | **200** |
| **1** | *p*-Aminothiophenol | 40 | 48 | 52 | 36 | 40 | 43 | 39 | 42 | 45 |
| **2** | $NiCl_2.6H_2O$ | 21 | 30 | 42 | 24 | 32 | 38 | 23 | 34 | 42 |
| **3** | $Ni(NO_3)_2.6H_2O$ | 24 | 32 | 40 | 24 | 29 | 42 | 26 | 30 | 37 |
| **4** | $Ni(CH_3COO)_2.4H_2O$ | 23 | 29 | 40 | 28 | 36 | 41 | 24 | 32 | 40 |
| **5** | $HOOCCH_2COOH$ | 18 | 20 | 24 | 20 | 24 | 28 | 24 | 28 | 30 |
| **6** | $HOOC(CH_2)_2COOH$ | 20 | 23 | 27 | 21 | 24 | 26 | 25 | 28 | 32 |
| **7** | $HOOC(CH_2)_3COOH$ | 21 | 24 | 28 | 19 | 21 | 24 | 20 | 23 | 27 |
| **8** | $HOOC(CH_2)_4COOH$ | 20 | 24 | 27 | 21 | 24 | 27 | 23 | 25 | 28 |
| **9** | $\overline{HS_2POCH(CH_3)CH(CH_3)O}$ | 60 | 66 | 62 | 63 | 65 | 71 | 62 | 66 | 72 |
| **10** | $\overline{HS_2POC(CH_3)_2C(CH_3)_2O}$ | 62 | 68 | 64 | 67 | 68 | 70 | 64 | 68 | 71 |
| **11** | $\overline{HS_2POC(CH_3)_2CH_2CH(CH_3)O}$ | 62 | 66 | 66 | 65 | 70 | 73 | 63 | 67 | 71 |
| **12** | $[Ni(mc_1)\{\overline{S_2POCH(CH_3)CH(CH_3)O}_2]$ $(C_{26}H_{30}N_2P_2S_6O_8.Ni)$ | 76 (54) | 68 (57) | 82 (61) | 64 (54) | 84 (58) | 85 (64) | 84 (58) | 85 (62) | 85 (70) |

Cont…

| S. No. | Compound | *Aspergillus flavus* | | | *Fusariunm oxysporum* | | | *Trichoderma harzianum* | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | **100** | **125** | **200** | **100** | **125** | **200** | **100** | **125** | **200** |
| **13** | $[Ni(mc_1)]\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ ($C_{30}H_{38}N_2P_2S_6O_8.Ni$) | 74 | 74 | 80 | 75 | 88 | 84 | 79 | 88 | 86 |
| **14** | $[Ni(mc_1)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ ($C_{30}H_{38}N_2P_2S_6O_8.Ni$) | 76 | 74 | 81 | 76 | 80 | 83 | 78 | 81 | 84 |
| **15** | $[Ni(mc_2)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ ($C_{28}H_{34}N_2P_2S_6O_8.Ni$) | 78 (53) | 78 (57) | 84 (67) | 73 (52) | 85 (57) | 83 (62) | 84 (53) | 84 (59) | 87 (64) |
| **16** | $[Ni(mc_2)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ ($C_{32}H_{42}N_2P_2S_6O_8.Ni$) | 75 | 74 | 86 | 74 | 87 | 85 | 85 | 84 | 86 |
| **17** | $[Ni(mc_2)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ ($C_{32}H_{42}N_2P_2S_6O_8.Ni$) | 74 | 77 | 80 | 78 | 83 | 86 | 81 | 85 | 84 |
| **18** | $[Ni(mc_3)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ ($C_{30}H_{38}N_2P_2S_6O_8.Ni$) | 77 (42) | 78 (48) | 85 (55) | 74 (47) | 83 (52) | 87 (57) | 89 (49) | 85 (50) | 83 (61) |
| **19** | $[Ni(mc_3)\ \{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ ($C_{34}H_{46}N_2P_2S_6O_8.Ni$) | 78 | 77 | 85 | 73 | 86 | 85 | 80 | 84 | 84 |
| **20** | $[Ni(mc_3)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ ($C_{34}H_{46}N_2P_2S_6O_8.Ni$) | 75 | 78 | 83 | 78 | 81 | 85 | 84 | 86 | 86 |
| **21** | $[Ni(mc_4)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ ($C_{32}H_{42}N_2P_2S_6O_8.Ni$) | 73 (51) | 77 (58) | 80 (63) | 79 (52) | 80 (55) | 83 (61) | 84 (49) | 86 (53) | 86 (60) |
| **22** | $[Ni(mc_4)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ ($C_{36}H_{50}N_2P_2S_6O_8.Ni$) | 73 | 76 | 85 | 73 | 82 | 87 | 85 | 87 | 86 |
| **23** | $[Ni(mc_4)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ ($C_{36}H_{50}N_2P_2S_6O_8.Ni$) | 74 | 77 | 80 | 78 | 81 | 85 | 81 | 84 | 87 |
| **24** | $[Ni(mc_5)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ ($C_{36}H_{34}N_2P_2S_6O_8.Ni$) | 72 (49) | 76 (54) | 80 (59) | 77 (49) | 82 (55) | 84 (60) | 84 (59) | 86 (63) | 88 (68) |
| **25** | $[Ni(mc_5)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ ($C_{40}H_{42}N_2P_2S_6O_8.Ni$) | 77 | 78 | 84 | 74 | 84 | 84 | 81 | 87 | 87 |
| **26** | $[Ni(mc_5)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ ($C_{40}H_{42}N_2P_2S_6O_8.Ni$) | 74 | 77 | 81 | 76 | 80 | 84 | 80 | 84 | 86 |

Antifungal activity of the parent macrocyclic complexes (average of $Cl^-$, $NO_3^-$, $CH_3COO^-$) are shown in parenthesis.

**Table 6: Antibacterial activity of alkylene dithiophosphate derivatives of macrocyclic complexes of Ni (II), percentage growth inhibition after 24 h at 30°C ± 2 (conc. in ppm)**

| S. No. | Compound | *B. subtili* | | *S. typhi* | |
|---|---|---|---|---|---|
| | | 500 | 1000 | 500 | 1000 |
| **1** | Streptomycin (standerd) | 17 | 20 | 19 | 20 |
| **2** | $NiCl_2.6H_2O$ | 11 | 12 | 11 | 14 |
| **3** | $Ni(NO_3)_2.6H_2O$ | 12 | 15 | 12 | 15 |
| **4** | $Ni(CH_3COO)_2.4H_2O$ | 10 | 14 | 9 | 16 |
| **5** | *p*-aminothiophenol | 15 | 18 | 12 | 14 |
| **6** | HOOC $CH_2$ COOH | 5 | 8 | 6 | 9 |
| **7** | HOOC $(CH_2)_2$ COOH | 8 | 10 | 9 | 12 |
| **8** | HOOC $(CH_2)_3$ COOH | 66 | 5 | 7 | 8 |
| **9** | HOOC $(CH_2)_4$ COOH | 7 | 9 | 6 | 9 |
| **10** | HOOC $(C_6H_4)$ COOH | 8 | 12 | 9 | 12 |
| **11** | $\overline{HS_2POCH(CH_3)CH(CH_3)O}$ | 17 | 22 | 17 | 18 |
| **12** | $\overline{HS_2POC(CH_3)_2C(CH_3)_2O}$ | 18 | 21 | 20 | 24 |
| **13** | $\overline{HS_2POC(CH_3)_2CH_2CH(CH_3)O}$ | 18 | 23 | 20 | 25 |
| **14** | $[Ni(mc_1)\{\overline{S_2POCH(CH_3)CH(CH_3)O}\}_2]$ $(C_{26}H_{30}N_2P_2S_6O_8.Ni)$ | 21 | 22 | 21 | 26 |
| **15** | $[Ni(mc_1)]\{\overline{S_2POC(CH_3)_2C(CH_3)_2O}\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8.Ni)$ | 22 | 25 | 21 | 24 |
| **16** | $[Ni(mc_1)\{\overline{S_2POC(CH_3)_2CH_2CH(CH_3)O}\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8.Ni)$ | 24 | 27 | 24 | 29 |
| **17** | $[Ni(mc_2)\{\overline{S_2POCH(CH_3)CH(CH_3)O}\}_2]$ $(C_{28}H_{34}N_2P_2S_6O_8.Ni)$ | 25 | 28 | 25 | 29 |
| **18** | $[Ni(mc_2)\{\overline{S_2POC(CH_3)_2C(CH_3)_2O}\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8.Ni)$ | 24 | 27 | 23 | 28 |
| **19** | $[Ni(mc_2)\{\overline{S_2POC(CH_3)_2CH_2CH(CH_3)O}\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8.Ni)$ | 23 | 25 | 26 | 28 |
| **20** | $[Ni(mc_3)\{\overline{S_2POCH(CH_3)CH(CH_3)O}\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8.Ni)$ | 26 | 25 | 27 | 28 |

Cont…

| S. No. | Compound | *B. subtili* | | *S. typhi* | |
|---|---|---|---|---|---|
| | | 500 | 1000 | 500 | 1000 |
| **21** | $[Ni(mc_3)\ \{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8.Ni)$ | 23 | 25 | 22 | 28 |
| **22** | $[Ni(mc_3)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8.Ni)$ | 24 | 24 | 25 | 28 |
| **23** | $[Ni(mc_4)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8.Ni)$ | 20 | 22 | 20 | 24 |
| **24** | $[Ni(mc_4)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8.Ni)$ | 22 | 23 | 21 | 22 |
| **25** | $[Ni(mc_4)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8.Ni)$ | 22 | 27 | 20 | 21 |
| **26** | $[Ni(mc_5)\{S_2POCH(CH_3)CH(CH_3)O\}_2]$ $(C_{36}H_{34}N_2P_2S_6O_8.Ni)$ | 27 | 22 | 28 | 24 |
| **27** | $[Ni(mc_5)\{S_2POC(CH_3)_2C(CH_3)_2O\}_2]$ $(C_{40}H_{42}N_2P_2S_6O_8.Ni)$ | 25 | 24 | 27 | 25 |
| **28** | $[Ni(mc_5)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{40}H_{42}N_2P_2S_6O_8.Ni)$ | 23 | 22 | 22 | 26 |

Antibacterial activity of the parent macrocyclic complexes (average of $Cl^-$, $NO_3^-$, $CH_3COO^-$) are shown in parenthesis.

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