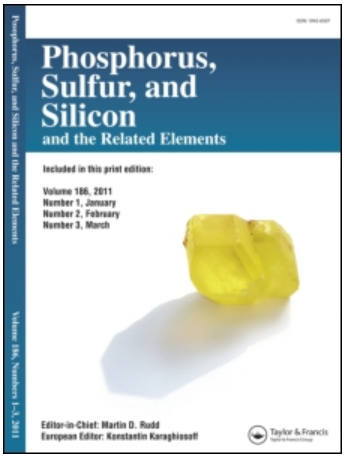

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SYNTHESIS, CHARACTERIZATION, AND BIOCIDAL ASPECTS OF SOME NOVEL ALKYLENE DITHIOPHOSPHATE DERIVATIVES OF MACROCYCLIC COMPLEXES OF Ni(II) HAVING N_2S_2 POTENTIAL DONORS IN 14- to 20-MEMBERED RINGS

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SYNTHESIS, CHARACTERIZATION, AND BIOCIDAL ASPECTS OF SOME NOVEL ALKYLENE DITHIOPHOSPHATE DERIVATIVES OF MACROCYCLIC COMPLEXES OF Ni(II) HAVING N_2S_2 POTENTIAL DONORS IN 14- TO 20-MEMBERED RINGS

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Alkylene dithiophosphate derivatives of macrocyclic complexes of nickel (II), having N_2S_2 potential donors, of the general formula, $[(Ni(mc_1\text{–}mc_5)\ \{(S_2P\langle_{O}^{O}\rangle G\}_2]$, *where mc = macrocyclic ligands and* $G = CH_3\text{—}\underset{|}{\overset{|}{CH}}\text{—}\underset{|}{\overset{|}{CH}}\text{—}CH_3$, $(CH_3)_2\underset{|}{\overset{|}{C}}\text{—}\underset{|}{\overset{|}{C}}(CH_3)_2$, *and* $(CH_3)_2\underset{|}{\overset{|}{C}}\text{—}CH_2CH\text{—}$ *have been synthesized from the reactions of* $[Ni\ (mc_1\text{–}mc_5)\ X_2]$, *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.*

Keywords: Alkylene dithiophosphates; macrocyclic complexes; mixed ligand complexes; nickel (II)

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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 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).[42,43]

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.[44–52] Recently we reported the synthesis, characterization, and antimicrobial aspects of the mixed-ligand macrocyclic complexes of Ni(II) having dialkyldithiophosphate moieties.[53] 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. o-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.[54] 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 in our earlier communication.[42]

Macrocyclic Complex Derived from Template Condensation of Malonic Acid and o-Aminothiophenol in the Presence of Nickel Chloride

A solution of nickel chloride (0.852 g, 0.0035 mmol) in methanol was reacted with o-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°C. The green precipitate obtained on cooling was filtered, washed with methanol, and dried in vacuo.

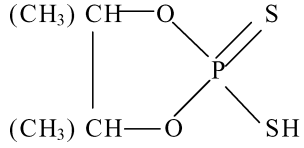
Macrocyclic Complex Derived from Template Condensation of Succinic Acid and o-Aminothiophenol in the Presence of Nickel Chloride

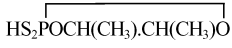
A solution of nickel chloride (1.245 g, 0.0052 mmol) in methanol was reacted with o-aminothiophenol (1.309 g, 0.0104 mmol) dissolved in methanol. This was followed by the addition of a methanolic solution of succinic acid (1.248 g, 0.0105 mmol). Reaction mixture was refluxed for 10 h at 80°C. The green 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 in our earlier communication.[44]

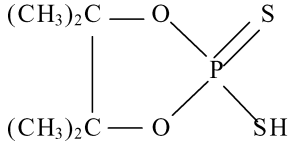
The derivatives of macrocyclic complexes of the following alkylene dithiophosphoric acids have been synthesized. Their trivial name as well as their International Union of Pure and Applied Chemistry (IUPAC) names are given. IUPAC names have been mentioned in parenthesis.

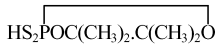
Butylene dithiophosphoric acid **(2-Mercapto-2-thiono-4,5 dimethyl 1,2,3-dioxaphospholane)**



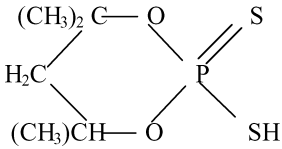


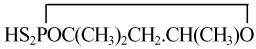
Tetramethylethylene dithiophosphoric acid. **(2-Mercapto-2-thiono-4,4,5,5-tetremethyl-1,3,2-dioxaphospholane)**





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 o-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 ~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 by THF/C_2H_5OH mixture.

Relevant data for the similar syntheses are given in Table I.

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:

$$[\mathrm{Ni(mc_1 - mc_5)X_2}] + 2\mathrm{NH_4S_2P}\begin{array}{c}\mathrm{O}\\ \diamond \\ \mathrm{O}\end{array}\mathrm{G}$$

$$\rightarrow \left[\mathrm{Ni(mc_1 - mc_5)}\left\{\mathrm{S_2P}\begin{array}{c}\mathrm{O}\\ \diamond \\ \mathrm{O}\end{array}\mathrm{G}\right\}_2\right] + 2\mathrm{NH_4X}$$

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

$$\mathrm{G} = \mathrm{CH_3{-}\overset{|}{C}H{-}\overset{|}{C}H{-}CH_3}, \mathrm{(CH_3)_2\overset{|}{C}{-}\overset{|}{C}(CH_3)_2{-}}, \quad \text{and}$$

$$\mathrm{(CH_3)_2\overset{|}{C}{-}CH_2\overset{|}{C}H{-}}, \quad \text{and} \quad \mathrm{X} = \mathrm{Cl^-}, \mathrm{NO_3^-} \quad \text{or} \quad \mathrm{CH_3COO^-}$$

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 pinkish green 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 II). The molecular weight determinations indicate their monomeric nature (Table I). The analytical data of these derivatives are given in Table III.

TABLE I Reactions of Macrocyclic Complexes of Ni (II) with Ammonium Alkylene Dithiophosphates

Sr. no.	Macrocyclic complex [Molecular formula] (Empirical formula) g (mmol)	Ammonium alkylenedithiophosphates g (mmol)	[Product] (Empirical formula) yield (g) %	Color	m.p. (decomp.) °C	m.wt. found (calcd.)
1	[Ni(mc$_1$)Cl$_2$] ($C_{18}H_{14}N_2S_2O_4.NiCl_2$) 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$_1$)] {$S_2POCH(CH_3).CH(CH_3)O\}_2$] ($C_{26}H_{30}N_2P_2S_6O_8.Ni$) 1.080 84%	Shining green	238	824.4 (810.7)
2	[Ni(mc$_1$)Cl$_2$] ($C_{18}H_{14}N_2S_2O_4.NiCl_2$) 0.748 (0.0014)	$NH_4S_2POC(CH_3)_2.C(CH_3)_2O$ ($C_6H_{12}S_2O_2P.NH_4$) 0.665 (0.0029)	[Ni(mc$_1$)] {$S_2POC(CH_3)_2.C(CH_3)_2O\}_2$] ($C_{30}H_{38}N_2P_2S_6O_8.Ni$) 1.080 86%	Dull green	235	856.7 (866.7)
3	[Ni(mc$_1$)Cl$_2$] ($C_{18}H_{14}N_2S_2O_4.NiCl_2$) 0.690 (0.0013)	$NH_4S_2POC(CH_3)_2CH_2.CH(CH_3)O$ ($C_6H_{12}S_2O_2P.NH_4$) 0.613 (0.0026)	[Ni(mc$_1$) {$S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2$] ($C_{30}H_{38}N_2P_2S_6O_8.Ni$) 0.986 89%	Shining green	216	845.7 (866.7)
4	[Ni(mc$_2$)Cl$_2$] ($C_{20}H_{18}N_2S_2O_4.NiCl_2$) 0.814 (0.0014)	$NH_4S_2POCH(CH_3).CH(CH_3)O$ ($C_4H_8S_2O_2P.NH_4$) 0.602 (0.0029)	[Ni(mc$_2$) {$S_2POCH(CH_3).CH(CH_3)O\}_2$] ($C_{28}H_{34}N_2P_2S_6O_8.Ni$) 1.080 81%	Pinkish green	220	820.5 (838.7)
5	[Ni(mc$_2$)Cl$_2$] ($C_{20}H_{18}N_2S_2O_4.NiCl_2$) 0.792 (0.0014)	$NH_4S_2POC(CH_3)_2.C(CH_3)_2O$ ($C_6H_{12}S_2O_2P.NH_4$) 0.668 (0.0029)	[Ni(mc$_2$) {$S_2POC(CH_3)_2.C(CH_3)_2O\}_2$] ($C_{32}H_{42}N_2P_2S_6O_8.Ni$) 1.060 81%	Pinkish green	258	887.7 (894.7)
6	[Ni(mc$_2$)Cl$_2$] ($C_{20}H_{18}N_2S_2O_4.NiCl_2$) 0.806 (0.0014)	$NH_4S_2POC(CH_3)_2CH_2.CH(CH_3)O$ ($C_6H_{12}S_2O_2P.NH_4$) 0.679 (0.0029)	[Ni(mc$_2$) {$S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2$] ($C_{32}H_{42}N_2P_2S_6O_8.Ni$) 1.120 84%	Dull green	232	862.4 (894.7)

7	$[Ni(mc_3)Cl_2]$ $(C_{22}H_{22}N_2S_2O_4.NiCl_2)$ 0.798 (0.0014)	$NH_4S_2POCH(CH_3).CH(CH_3)O$ $(C_4H_8S_2O_2P.NH_4)$ 0.561 (0.0028)	$[Ni(mc_3)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8.Ni)$ 1.050 86%	Shining green	212	902.4 (922.7)
8	$[Ni(mc_3)Cl_2]$ $(C_{22}H_{22}N_2S_2O_4.NiCl_2)$ 0.814 (0.0014)	$NH_4S_2POC(CH_3)_2.C(CH_3)_2O$ $(C_6H_{12}S_2O_2P.NH_4)$ 0.652 (0.0028)	$[Ni(mc_3)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8.Ni)$ 1.080 82%	Pinkish green	208	943.2 (922.7)
9	$[Ni(mc_3)Cl_2]$ $(C_{22}H_{22}N_2S_2O_4.NiCl_2)$ 0.804 (0.0014)	$NH_4S_2POC(CH_3)_2CH_2.CH(CH_3)O$ $(C_6H_{12}S_2O_2P.NH_4)$ 0.644 (0.0028)	$[Ni(mc_3)\{S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8.Ni)$ 1.100 84%	Pinkish green	204	912.4 (922.7)
10	$[Ni(mc_4)Cl_2]$ $(C_{24}H_{26}N_2S_2O_4.NiCl_2)$ 0.805(0.0013)	$NH_4S_2POCH(CH_3).CH(CH_3)O$ $(C_4H_8S_2O_2P.NH_4)$ 0.540 (0.0026)	$[Ni(mc_4)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8.Ni)$ 1.200 78%	Dull green	218	878.8 (894.7)
11	$[Ni(mc_4)Cl_2]$ $(C_{24}H_{26}N_2S_2O_4.NiCl_2)$ 0.814 (0.0013)	$NH_4S_2POC(CH_3)_2.C(CH_3)_2O$ $(C_6H_{12}S_2O_2P.NH_4)$ 0.621 (0.0027)	$[Ni(mc_4)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8.Ni)$ 1.100 85%	Shining green	229	967.4 (950.7)
12	$[Ni(mc_4)Cl_2]$ $(C_{24}H_{26}N_2S_2O_4.NiCl_2)$ 0.788 (0.0013)	$NH_4S_2POC(CH_3)_2CH_2.CH(CH_3)O$ $(C_6H_{12}S_2O_2P.NH_4)$ 0.602 (0.0026)	$[Ni(mc_4)\{S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8.Ni)$ 0.982 79%	Pinkish green	220	938.2 (950.7)

(Continued on next page)

TABLE I Reactions of Macrocyclic Complexes of Ni (II) with Ammonium Alkylene Dithiophosphates *(Continued)*

Sr. no.	Macrocyclic complex [Molecular formula] (Empirical formula) g (mmol)	Ammonium alkylenedithiophosphates g (mmol)	[Product] (Empirical formula) yield (g) %	Color	m.p. (decomp.) °C	m.wt. found (calcd.)
13	[Ni(mc_5)Cl_2] ($C_{28}H_{18}N_2S_2O_4.NiCl_2$) 0.804 (0.0012)	$NH_4S_2POCH(CH_3).CH(CH_3)O$ ($C_4H_8S_2O_2P.NH_4$) 0.505 (0.0025)	[Ni(mc_5) {$S_2POCH(CH_3).CH(CH_3)O$}$_2$] ($C_{36}H_{34}N_2P_2S_6O_8.Ni$) 0.964 82%	Shining green	221	920.2 (934.7)
14	[Ni(mc_5)Cl_2] ($C_{28}H_{18}N_2S_2O_4.NiCl_2$) 0.811 (0.0012)	$NH_4S_2POC(CH_3)_2.C(CH_3)_2O$ ($C_6H_{12}S_2O_2P.NH_4$) 0.580 (0.0025)	[Ni(mc_5) {$S_2POC(CH_3)_2.C(CH_3)_2O$}$_2$] ($C_{40}H_{42}N_2P_2S_6O_8.Ni$) 1.080 86%	Dull green	218	1012.5 (990.7)
15	[Ni(mc_5)Cl_2] ($C_{28}H_{18}N_2S_2O_4.NiCl_2$) 0.818 (0.0012)	$NH_4S_2POC(CH_3)_2CH_2.CH(CH_3)O$ ($C_6H_{12}S_2O_2P.NH_4$) 0.585(0.0025)	[Ni(mc_5) {$S_2POC(CH_3)_2CH_2.CH(CH_3)O$}$_2$] ($C_{40}H_{42}N_2P_2S_6O_8.Ni$) 1.040 82%	Shining green	228	982.6 (990.7)

mc_1, Macrocyclic ligand derived from o-aminothiophenol and malonic acid; mc_2, Macrocyclic ligand derived from o-aminothiophenol and succinic acid; mc_3, Macrocyclic ligand derived from o-aminothiophenol and glutaric acid; mc_4, Macrocyclic ligand derived from o-aminothiophenol and adipic acid; mc_5, Macrocyclic ligand derived from o-aminothiophenol and phthalic acid.

TABLE II Physico-Chemical Properties of the Alkylene Dithiophosphate Derivatives of Macrocyclic Complexes of Ni (II)

Sr. no.	Compound	Magnetic moment μ_{eff} (B.M.)	Electronic spectra λ max (nm)		Conductivity $\hat{M}$ (ohm^{-1} cm^2 mol^{-1})	$^{31}P_{NMR}$ chemical shift (δ)
			ν_2	ν_3		
1	$[Ni(mc_1)]\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{26}H_{30}N_2P_2S_6O_8.Ni)$	3.14	660	420	3.48	96.80 (95.49)
2	$[Ni(mc_1)]\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8.Ni)$	3.20	665	400	6.20	—
3	$[Ni(mc_1)\{S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8.Ni)$	3.20	650	410	4.50	—
4	$[Ni(mc_2)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{28}H_{34}N_2P_2S_6O_8.Ni)$	3.04	650	415	7.14	—
5	$[Ni(mc_2)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8.Ni)$	3.14	660	400	6.80	98.24 (93.07)
6	$[Ni(mc_2)\{S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8.Ni)$	3.08	680	410	6.42	—
7	$[Ni(mc_3)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8.Ni)$	3.20	655	400	5.74	—
8	$[Ni(mc_3)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8.Ni)$	2.98	660	410	5.14	—

(Continued on next page)

TABLE II Physico-Chemical Properties of the Alkylene Dithiophosphate Derivatives of Macrocyclic Complexes of Ni (II) *(Continued)*

Sr. no.	Compound	Magnetic moment μ_{eff} (B.M.)	Electronic spectra λ max (nm) ν_2	ν_3	Conductivity $\hat{}M$ (ohm^{-1} cm^2 mol^{-1})	$^{31}P_{NMR}$ chemical shift (δ)
9	[Ni(mc$_3$) {S$_2$POC(CH$_3$)$_2$CH$_2$.CH(CH$_3$)O}$_2$] ($C_{34}H_{46}N_2P_2S_6O_8Ni$)	3.02	680	400	7.40	86.12 (73.20)
10	[Ni(mc$_4$) {S$_2$POCH(CH$_3$).CH(CH$_3$)O}$_2$] ($C_{32}H_{42}N_2P_2S_6O_8Ni$)	3.14	680	410	5.15	—
11	[Ni(mc$_4$) {S$_2$POC(CH$_3$)$_2$.C(CH$_3$)$_2$O}$_2$] ($C_{36}H_{50}N_2P_2S_6O_8Ni$)	3.20	665	420	6.52	98.15 (93.07)
12	[Ni(mc$_4$) {S$_2$POC(CH$_3$)$_2$CH$_2$.CH(CH$_3$)O}$_2$] ($C_{36}H_{50}N_2P_2S_6O_8Ni$)	3.04	670	400	5.42	—
13	[Ni(mc$_5$) {S$_2$POCH(CH$_3$).CH(CH$_3$)O}$_2$] ($C_{36}H_{34}N_2P_2S_6O_8Ni$)	3.20	760	420	4.23	98.24 (95.49)
14	[Ni(mc$_5$) {S$_2$POC(CH$_3$)$_2$.C(CH$_3$)$_2$O}$_2$] ($C_{40}H_{42}N_2P_2S_6O_8Ni$)	2.98	655	415	4.33	—
15	[Ni(mc$_5$) {S$_2$POC(CH$_3$)$_2$CH$_2$.CH(CH$_3$)O}$_2$] ($C_{40}H_{42}N_2P_2S_6O_8Ni$)	2.98	670	400	5.74	84.78 (73.20)

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

TABLE III Analytical Data of Alkylene Dithiophosphate Derivatives of Macrocyclic Complexes of Ni(II)

Sr. no.	Compound	Found (calcd.) C	H	N	P	S	Ni
1	$[Ni(mc_1)]\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{26}H_{30}N_2P_2S_6O_8Ni)$	38.23 (38.48)	3.23 (3.70)	3.55 (3.45)	7.54 (7.64)	23.65 (23.68)	7.54 (7.24)
2	$[Ni(mc_1)]\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$	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	$[Ni(mc_1)\{S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$	41.34 (41.53)	4.02 (4.38)	3.25 (3.23)	7.43 (7.15)	23.15 (22.15)	6.45 (6.77)
4	$[Ni(mc_2)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{28}H_{34}N_2P_2S_6O_8Ni)$	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	$[Ni(mc_2)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$	42.26 (42.92)	4.84 (4.69)	3.50 (3.13)	7.34 (6.93)	21.73 (21.46)	6.84 (6.56)
6	$[Ni(mc_2)\{S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$	42.67 (42.92)	4.27 (4.69)	3.68 (3.13)	6.45 (6.93)	21.65 (21.46)	6.60 (6.56)
7	$[Ni(mc_3)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8Ni)$	41.34 (41.53)	4.27 (4.38)	3.65 (3.23)	7.42 (7.15)	21.78 (22.15)	7.25 (6.77)

(Continued on next page)

TABLE III Analytical Data of Alkylene Dithiophosphate Derivatives of Macrocyclic Complexes of Ni(II) *(Continued)*

Sr. no.	Compound	Found (calcd.) C	H	N	P	S	Ni
8	$[Ni(mc_3)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8Ni)$	44.65 (44.22)	4.84 (4.99)	3.76 (3.03)	6.12 (6.72)	20.56 (20.81)	6.83 (6.36)
9	$[Ni(mc_3)\{S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8Ni)$	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	$[Ni(mc_4)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8Ni)$	42.34 (42.92)	4.36 (4.69)	3.54 (3.13)	6.52 (6.93)	21.83 (21.46)	6.88 (6.56)
11	$[Ni(mc_4)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8Ni)$	45.76 (45.44)	5.42 (5.26)	3.90 (2.95)	6.84 (6.52)	20.40 (20.20)	6.83 (6.17)
12	$[Ni(mc_4)\{S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8Ni)$	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	$[Ni(mc_5)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{36}H_{34}N_2P_2S_6O_8Ni)$	46.98 (46.22)	3.45 (3.64)	3.52 (3.00)	7.20 (6.63)	21.54 (20.54)	6.02 (6.28)
14	$[Ni(mc_5)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{40}H_{42}N_2P_2S_6O_8Ni)$	48.65 (48.45)	4.90 (4.24)	3.56 (2.83)	6.02 (6.25)	19.40 (19.38)	5.67 (5.93)
15	$[Ni(mc_5)\{S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{40}H_{42}N_2P_2S_6O_8Ni)$	48.21 (48.45)	4.54 (4.24)	2.31 (2.83)	6.80 (6.25)	19.55 (19.38)	5.07 (5.93)

Infrared Spectra

Characteristic IR absorption frequencies of these derivatives are given in Table IV. 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.[55] A broad band present in the region 3278–3150 cm^{-1} has been assigned to ν(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.[56] The bands present between 1000–950 cm^{-1} may be attributed to the ring vibrations of dioxaphospholanes and dioxaphosphorinanes[57,58] respectively, which are probably coupled with C—C staching 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.[59,60] The presence of sharp bands in the region 460–410 cm^{-1} and 360–315 cm^{-1} have been assigned to ν(Ni—N) and ν(Ni—S) vibrations, respectively.[47]

^{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.[46,47] 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,[46,47] 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 II. 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.[59,60]

TABLE IV IR Spectral Data of Alkylene Dithiophosphates Derivatives of Macrocyclic Complexes of Ni (II)

Sr. no.	[Molecular formula] (Empirical formula)	Amide-I	Amide-II	Amide-III	Amide-IV	ν(NH)	(P)—O—C	P—O—(C)	Ring vibration	P = S	P—S	ν(Ni—N)	ν(Ni—S)
1	[Ni(mc$_1$)] {$S_2POCH(CH_3).CH(CH_3)O\}_2$] ($C_{26}H_{30}N_2P_2S_6O_8.Ni$)	1668 m	1562 m	1260 s	650 w	3190 w	1040 m	865 m	950 s	670 s	560 w	420 s	326 w
2	[Ni(mc$_1$)] {$S_2POC(CH_3)_2.C(CH_3)_2O\}_2$] ($C_{30}H_{38}N_2P_2S_6O_8.Ni$)	1670 s	1555 m	1274 s	648 w	3200 w	1045 m	880 m	965 s	700 s	540 w	456 s	318 w
3	[Ni(mc$_1$) {$S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2$] ($C_{30}H_{38}N_2P_2S_6O_8.Ni$)	1650 s	1558 m	1268 s	656 w	3258 w	1058 m	890 m	955 s	680 s	550 w	475 s	348 w
4	[Ni(mc$_2$) {$S_2POCH(CH_3).CH(CH_3)O\}_2$] ($C_{28}H_{34}N_2P_2S_6O_8.Ni$)	1690 s	1559 m	1252 m	636 w	3240 m	1062 m	870 m	950 s	685 s	560 w	418 s	364 w
5	[Ni(mc$_2$) {$S_2POC(CH_3)_2.C(CH_3)_2O\}_2$] ($C_{32}H_{42}N_2P_2S_6O_8.Ni$)	1650 m	1560 m	1250 m	688 w	3238 m	1070 m	860 m	970 s	700 s	545 w	428 s	318 w
6	[Ni(mc$_2$) {$S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2$] ($C_{32}H_{42}N_2P_2S_6O_8.Ni$)	1680 m	1523 m	1262 s	695 w	3190 m	1050 m	890 m	1000 s	710 s	555 w	460 s	348 w
7	[Ni(mc$_3$) {$S_2POCH(CH_3).CH(CH_3)O\}_2$] ($C_{30}H_{38}N_2P_2S_6O_8.Ni$)	1690 m	1575 m	1252 m	605 w	3278 w	1065 m	870 m	970 s	670 s	550 w	422 s	345 w

8	[Ni(mc$_3$) {$S_2POC(CH_3)_2.C(CH_3)_2O$}$_2$] ($C_{34}H_{46}N_2P_2S_6O_8.Ni$)	1682 s	1555 m	1259 m	658 w	3145 m	1040 m	880 m	980 s	690 s	560 w	458 s	377 w
9	[Ni(mc$_3$) {$S_2POC(CH_3)_2CH_2.CH(CH_3)O$}$_2$] ($C_{34}H_{46}N_2P_2S_6O_8.Ni$)	1689 s	1587 m	1256 m	657 w	3162 m	1075 m	890 m	965 s	700 s	545 w	483 s	320 w
10	[Ni(mc$_4$) {$S_2POCH(CH_3).CH(CH_3)O$}$_2$] $C_{32}H_{42}N_2P_2S_6O_8.Ni$)	1682 m	1555 m	1260 s	647 w	168 w	1070 m	878 m	1000 s	670 s	560 w	420 s	335 w
11	[Ni(mc$_4$) {$S_2POC(CH_3)_2.C(CH_3)_2O$}$_2$] ($C_{36}H_{50}N_2P_2S_6O_8.Ni$)	1690 m	1562 m	1274 s	632 w	3200 w	1062 m	860 m	965 s	680 s	540 w	430 s	340 w
12	[Ni(mc$_4$) {$S_2POC(CH_3)_2CH_2.CH(CH_3)O$}$_2$] ($C_{36}H_{50}N_2P_2S_6O_8.Ni$)	1660 m	1537 m	1268 m	640 w	3210 w	1055 m	850 m	955 s	700 s	550 w	460 s	318 w
13	[Ni(mc$_5$) {$S_2POCH(CH_3).CH(CH_3)O$}$_2$] ($C_{36}H_{34}N_2P_2S_6O_8.Ni$)	1673 m	1568 m	1252 s	648 w	3208 w	1070 m	890 m	950 s	690 s	560 w	460 s	350 w
14	[Ni(mc$_5$) {$S_2POC(CH_3)_2.C(CH_3)_2O$}$_2$] ($C_{40}H_{42}N_2P_2S_6O_8.Ni$)	1685 s	1570 m	1252 s	650 w	3200 m	1050 m	870 m	1000 s	700 s	555 w	460 s	348 w
15	[Ni(mc$_5$) {$S_2POC(CH_3)_2CH_2.CH(CH_3)O$}$_2$] ($C_{40}H_{42}N_2P_2S_6O_8.Ni$)	1690 s	1568 m	1270 s	660 w	3208 m	1055 m	850 m	950 s	670 s	540 w	418 s	340 w

s, strong; m, medium; w, weak.

Electronic Spectra

Electronic spectra were recorded on GBC 911 spectrophotometer in the range of 380–1000 nm. Only two bands, ν_2 and ν_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.[61] Data are given in Table II.

Magnetic Susceptibility

The magnetic moments of the dithiophosphate derivatives are given in Table II. 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.[62]

STRUCTURAL INFORMATION

The above spectral and magnetic data indicate the following octahedral geometry (Figures 1 and 2) for the above derivatives 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 occupies the axial position, binding the central nickel ion in unidentate manner through strong electrostatic attraction.

ANTIMICROBIAL ACTIVITY

Antimicrobial activities of o-aminothiophenol, dicarboxylic acids, nickel salts, and the parent macrocyclic complexes (mc_1 to mc_5) were reported in our earlier communication.[42] For the sake of comparison the antimicrobial activities of o-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 V and VI. 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,

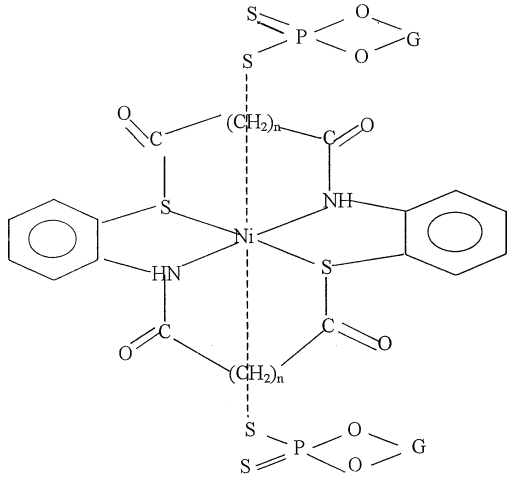


FIGURE 1 Dithiophosphate derivatives of macrocyclic complexes of Ni(II) derived by the template condensation of o-aminothiophenol with malonic, succinic, glutaric, or adipic acid.

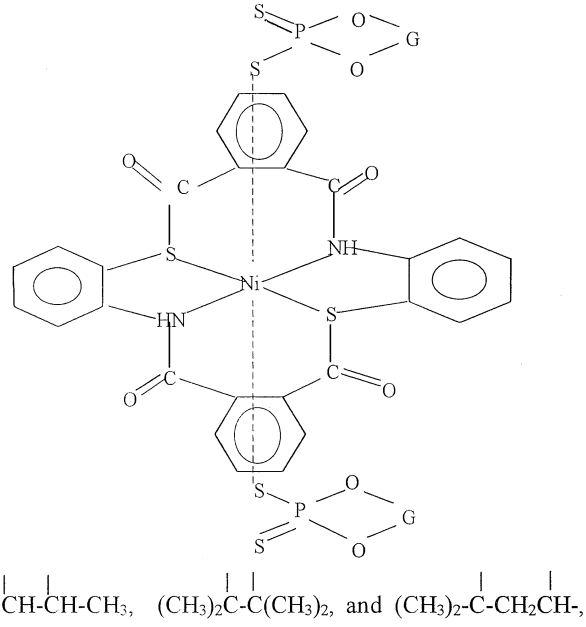


FIGURE 2 Dithiophosphate derivatives of macrocyclic complexes of NI(II) derived by the template condensation of o-aminothiophenol with pthalic acid.

TABLE V 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)

Sr. no.	Compound	Aspergillus flavus			Fusarium oxysporum			Trichoderma harzianum		
		100	125	200	100	125	200	100	125	200
1	o-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	$HOOC{-}CH_2{-}COOH$	18	20	24	20	24	28	24	28	30
6	$HOOC{-}(CH_2)_2{-}COOH$	20	23	27	21	24	26	25	28	32
7	$HOOC{-}(CH_2)_3{-}COOH$	21	24	28	19	21	24	20	23	27
8	$HOOC{-}(CH_2)_4{-}COOH$	20	24	27	21	24	27	23	25	28
9	$HS_2POCH(CH_3).CH(CH_3)O$	**60**	**66**	**62**	**63**	**65**	**71**	**62**	**66**	**72**
10	$HS_2POC(CH_3)_2.C(CH_3)_2O$	**62**	**68**	**64**	**67**	**68**	**70**	**64**	**68**	**71**
11	$HS_2POC(CH_3)_2CH_2.CH(CH_3)O$	**62**	**66**	**66**	**65**	**70**	**73**	**63**	**67**	**71**
12	$[Ni(mc_1)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{26}H_{30}N_2P_2S_6O_8.Ni)$	**76** (54)	**68** (57)	**82** (61)	**64** (54)	**84** (58)	**85** (62)	**84** (58)	**85** (62)	**85** (70)
13	$[Ni(mc_1)]\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8.Ni)$	**74**	**74**	**80**	**75**	**88**	**84**	**79**	**87**	**86**
14	$[Ni(mc_1)\{S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8.Ni)$	**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$_2$) {$S_2POC(CH_3)_2.C(CH_3)_2O$}$_2$] ($C_{32}H_{42}N_2P_2S_6O_8.Ni$)	**75**	**74**	**86**	**74**	**87**	**85**	**85**	**84**	**86**
17	[Ni(mc$_2$) {$S_2POC(CH_3)_2CH_2.CH(CH_3)O$}$_2$] ($C_{32}H_{42}N_2P_2S_6O_8.Ni$)	**74**	**77**	**80**	**78**	**83**	**86**	**81**	**84**	**87**
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)	**79** (49)	**83** (49)	**85** (61)
19	[Ni(mc$_3$) {$S_2POC(CH_3)_2.C(CH_3)_2O$}$_2$] ($C_{34}H_{46}N_2P_2S_6O_8.Ni$)	**78**	**77**	**85**	**73**	**86**	**85**	**80**	**84**	**84**
20	[Ni(mc$_3$) {$S_2POC(CH_3)_2CH_2.CH(CH_3)O$}$_2$] ($C_{34}H_{46}N_2P_2S_6O_8.Ni$)	**75**	**78**	**83**	**78**	**81**	**85**	**84**	**86**	**86**
21	[Ni(mc$_4$) {$S_2POCH(CH_3).CH(CH_3)O$}$_2$] ($C_{32}H_{42}N_2P_2S_6O_8.Ni0$)	**73** (51)	**77** (58)	**80** (63)	**79** (52)	**80** (55)	**83** (61)	**84** (49)	**86** (53)	**86** (60)
22	[Ni(mc$_4$) {$S_2POC(CH_3)_2.C(CH_3)_2O$}$_2$] ($C_{36}H_{50}N_2P_2S_6O_8.Ni$)	**73**	**76**	**85**	**73**	**82**	**87**	**85**	**87**	**86**
23	[Ni(mc$_4$) {$S_2POC(CH_3)_2CH_2.CH(CH_3)O$}$_2$] ($C_{36}H_{50}N_2P_2S_6O_8.Ni$)	**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$_5$) {$S_2POC(CH_3)_2.C(CH_3)_2O$}$_2$] ($C_{40}H_{42}N_2P_2S_6O_8.Ni$)	**77**	**75**	**84**	**74**	**84**	**84**	**81**	**87**	**87**
26	[Ni(mc$_5$) {$S_2POC(CH_3)_2CH_2.CH(CH_3)O$}$_2$] ($C_{40}H_{42}N_2P_2S_6O_8.Ni$)	**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 VI 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)

		B. subtili		*S. typhi*	
Sr. no.	Compound	500	1000	500	1000
1	Streptomycin (standard)	16	19	18	20
2	$NiCl_2 \cdot 6H_2O$	10	12	10	14
3	$Ni(NO_3)_2 \cdot 6H_2O$	12	14	11	15
4	$Ni(CH_3COO)_2 \cdot 4H_20$	11	14	9	13
5	o-Aminothiophenol	14	17	11	14
6	HOOC—(CH_2)—COOH	5	7	6	9
7	HOOC—$(CH_2)_2$—COOH	8	10	8	11
8	HOOC—$(CH_2)_3$—COOH	6	4	7	9
9	HOOC—$(CH_2)_4$—COOH	7	9	6	8
10	HOOC—(C_6H_4)—COOH	7	11	9	11
11	$HS_2POCH(CH_3) \cdot CH(CH_3)O$	**18**	**21**	**16**	**18**
12	$HS_2POC(CH_3)_2.C(CH_3)_2O$	**17**	**21**	**20**	**24**
13	$HS_2POC(CH_3)_2CH_2.CH(CH_3)O$	**17**	**22**	**20**	**24**
14	$[Ni(mc_1)\ \{S_2POCH(CH_3) \cdot CH(CH_3)O\}_2]$ $(C_{26}H_{30}N_2P_2S_6O_8.Ni)$	**20** (18)	**22** (21)	**21** (17)	**26** (20)
15	$[Ni(mc_1)]\ \{S_2POC(CH_3)_2 \cdot C(CH_3)_2O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8.Ni)$	**22**	**25**	**21**	**24**
16	$[Ni(mc_1)\ \{S_2POC(CH_3)_2CH_2 \cdot CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8.Ni)$	**24**	**27**	**23**	**28**
17	$[Ni(mc_2)\ \{S_2POCH(CH_3) \cdot CH(CH_3)O\}_2]$ $(C_{28}H_{34}N_2P_2S_6O_8.Ni)$	**23** (18)	**27** (21)	**23** (18)	**28** (20)

18	$[Ni(mc_2)\{S_2POC(CH_3)_2{\cdot}C(CH_3)_2O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8{.}Ni)$	**24**	**27**	**23**	**27**
19	$[Ni(mc_2)\{S_2POC(CH_3)_2CH_2{\cdot}CH(CH_3)O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8{.}Ni)$	**23**	**26**	**24**	**27**
20	$[Ni(mc_3)\{S_2POCH(CH_3){\cdot}CH(CH_3)O\}_2]$ $(C_{30}H_{38}N_2P_2S_6O_8{.}Ni)$	**26** (18)	**29** (20)	**25** (18)	**27** (21)
21	$[Ni(mc_3)\{S_2POC(CH_3)_2{\cdot}C(CH_3)_2O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8{.}Ni)$	**23**	**27**	**22**	**26**
22	$[Ni(mc_3)\{S_2POC(CH_3)_2CH_2{\cdot}CH(CH_3)O\}_2]$ $(C_{34}H_{46}N_2P_2S_6O_8{.}Ni)$	**24**	**24**	**25**	**28**
23	$[Ni(mc_4)\{S_2POCH(CH_3){\cdot}CH(CH_3)O\}_2]$ $(C_{32}H_{42}N_2P_2S_6O_8{.}Ni)$	**20** (18)	**22** (21)	20 (19)	24 (21)
24	$[Ni(mc_4)\{S_2POC(CH_3)_2{\cdot}C(CH_3)_2O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8{.}Ni)$	**23**	**23**	**21**	**22**
25	$[Ni(mc_4)\{S_2POC(CH_3)_2CH_2{\cdot}CH(CH_3)O\}_2]$ $(C_{36}H_{50}N_2P_2S_6O_8{.}Ni)$	**22**	**27**	**20**	**21**
26	$[Ni(mc_5)\{S_2POCH(CH_3){\cdot}CH(CH_3)O\}_2]$ $(C_{36}H_{34}N_2P_2S_6O_8{.}Ni)$	**27** (20)	**23** (22)	**24** (18)	**23** (22)
27	$[Ni(mc_5)\{S_2POC(CH_3)_2{\cdot}C(CH_3)_2O\}_2]$ $(C_{40}H_{42}N_2P_2S_6O_8{.}Ni)$	**24**	**27**	**24**	**25**
28	$[Ni(mc_5)\{S_2POC(CH_3)_2CH_2{\cdot}CH(CH_3)O\}_2]$ $(C_{40}H_{42}N_2P_2S_6O_8{.}Ni)$	**23**	**22**	**22**	**26**

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

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 V. 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.[63] The values obtained are presented in Table VI. 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.

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