

Ni(II) complexes of dithiophosphonic acids

AFSHIN SAADAT^a, ALIREZA BANAEI^b, PATRICK McARDLE^c, KARIM ZARE^a,
KHODAYAR GHOLIVAND^{d,*} and ALI ASGHAR EBRAHIMI VALMOOZI^d

^aDepartment of Chemistry, Science and Research Branch, Islamic Azad University, P.O. Box 14515-775, Tehran, Iran

^bDepartment of Chemistry, Payame Noor University, P.O. Box 56199-14814, Tehran, Iran

^cDepartment of Chemistry, NUI Galway, P.O. Box 2386, Galway, Ireland

^dDepartment of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran
e-mail: gholi_kh@modares.ac.ir

MS received 14 December 2013; revised 17 February 2014; accepted 21 February 2014

Abstract. The reaction of 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson reagent) with isobutanol, cyclohexylamine and phenylethylamine produced (4-methoxy-phenyl)-phosphono-dithioic acid o-isobutyl ester $\text{HS}_2\text{P}(\text{p-C}_6\text{H}_4\text{OMe})(\text{OCH}_2\text{CH}(\text{CH}_3)_2)$ (**I**), $[\text{S}_2\text{P}(\text{C}_6\text{H}_{11}\text{NH})(\text{p-C}_6\text{H}_4\text{OMe})\text{H}_3\text{N}^+\text{C}_6\text{H}_{11}]$ (**II**) and $[\text{S}_2\text{P}(\text{phCH}_2\text{CH}_2\text{NH})(\text{p-C}_6\text{H}_4\text{OMe})\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{ph}]$ (**III**), respectively. The reaction of alcohol with Lawesson reagent produced neutral product (**I**) while that with amines led to an ion pair (**II**, **III**). Furthermore, reaction of **I**, **II** and **III** with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in methanol produced novel complexes: **IV**, **V** and **VI**. The compounds were characterized by ^1H , ^{13}C and ^{31}P NMR, IR spectroscopy and elemental analysis. The single crystal X-ray structures of **IV** and **V** showed that the nickel complexes are square planar. Compound **V** formed a three-dimensional supramolecular structure via intermolecular $\text{P}=\text{O} \cdots \text{H}-\text{N}$ hydrogen bonds. The X-ray crystallography of **V** showed that those three hydrogens of $^+\text{NH}_3$ cation produced three hydrogen bonds with different distances. The new compounds were additionally tested in view of their anti-bacterial properties. The ligands containing amine substituents exhibited more activity toward tested bacteria than their alcohol substituents, while the Ni(II) complexes including alcohol substituents exhibited high potential.

Keywords. Dithiophosphonic acid; Ni(II) complexes; crystal structures; isobutanol; cyclohexylamine; anti-bacterial activity.

1. Introduction

Thiophosphorus derivatives exhibit various biological activities such as anti-bacterial, anti-tumour and anti-fungal.^{1–3} Some of the thiophosphorus analogues are used in agriculture as insecticide and herbicides.⁴ This category which includes dithiophosphonates and dithiophosphinate (scheme 1) are among well-known bidentate ligands and have been widely investigated.^{5–10} The above mentioned biological and synthetic significance of dithiophosphonates derivatives prompted us to synthesize some dithiophosphonic acid ligands and their complexes. Previous studies have shown that the reaction of amines and alcohols with Lawesson reagent produces an ion pair and neutral ligand, respectively.^{11,12} The aim of this study was to design and synthesize Ni(II) complexes with new dithiophosphonic acid ligand and compare them with those reported in the literature, in view of structural aspects and also study anti-bacterial properties.

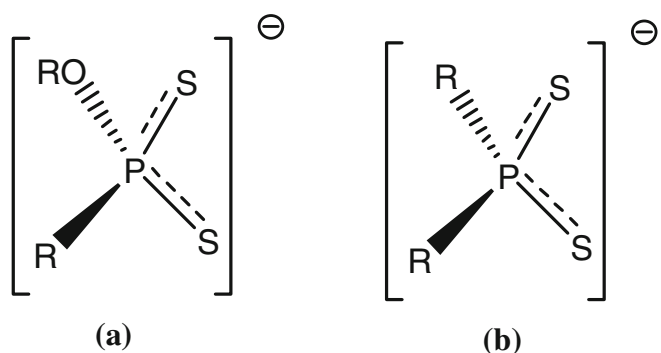
Three novel dithiophosphinates with the formula $\text{HS}_2\text{P}(\text{p-C}_6\text{H}_4\text{OMe})(\text{OCH}_2\text{CH}(\text{CH}_3)_2)$ (**I**), $[\text{S}_2\text{P}(\text{C}_6\text{H}_{11}\text{NH})(\text{p-C}_6\text{H}_4\text{OMe})\text{H}_3\text{N}^+\text{C}_6\text{H}_{11}]$ (**II**) and $[\text{S}_2\text{P}(\text{phCH}_2\text{CH}_2\text{NH})(\text{p-C}_6\text{H}_4\text{OMe})\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{ph}]$ (**III**) were synthesized and characterized by ^{31}P , ^{13}C , ^1H NMR, IR spectroscopy and elemental analysis. Furthermore, the reaction of these ligands with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ led to **IV**, **V** and **VI** (see schemes 2 and 3). Solid state structures of **IV** and **V** were solved by X-ray crystallography. Also, the behaviour of the **IV** (alcohol moiety) and **V** (amine moiety) were compared. Finally, anti-bacterial activities of ligands and complexes against *Pseudomonas aeruginosa*, *Escherichia coli* and *Acinetobacter baumannii* were measured.

2. Experimental

2.1 General methods and materials

Solvents were dried and purified before being used according to published procedures.¹³ Lawesson reagent was prepared as described in the literature.¹⁴ Isobutanol,

*For correspondence



Scheme 1. (a) Dithiophosphonates and (b) Dithiophosphinate.

toluene, cyclohexylamine, methanol, acetonitrile, and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from Merck. NMR spectra of compounds **I**, **II** and **III** were obtained from their freshly prepared solutions. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. ^{31}P NMR spectra were recorded on a Bruker Advance DRS 500 spectrometer. ^1H and ^{13}C chemical shifts were determined relative to internal TMS and ^{31}P chemical shifts relative to 85% H_3PO_4 as an external standard. IR spectrum was obtained using KBr pellets on a Shimadzu IR-60 model spectrometer. Elemental analysis was performed using a Heraeus CHN-ORAPID apparatus. Crystal structures of **IV** and **V** were solved by direct methods¹⁵ and refined by full matrix least squares using SHELXL-97,¹⁶ SHELX operations were automated using ORTEP, which was also used to obtain the drawings.¹⁷ Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. Data were collected on a Marresearch image plate using monochromatized Mo K_α radiation (0.71069\AA) at 298 K.

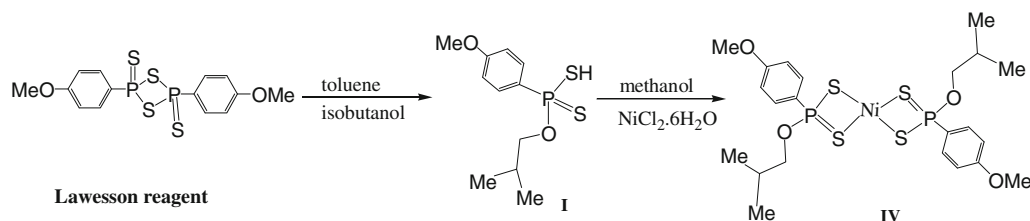
2.2 Synthesis of **I**

To a solution of (6.067 g, 15 mmol) Lawesson reagent in dry toluene at 67°C , (2.22 g, 30 mmol) isobutanol was added dropwise and the mixture was stirred for 2 h. After evaporating the solvent, the yellow oil product

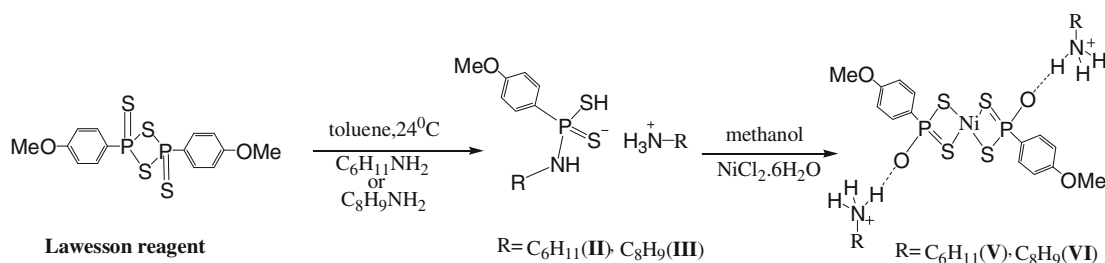
was formed, washed with diethyl ether and dried under vacuum. Yield: 84%. *Anal.* calcd. for $\text{C}_{11}\text{H}_{15}\text{O}_2\text{PS}_2$ (276.3 g mol^{-1}): C, 47.81; H, 6.2%; found: C, 47.7; H, 5.9%; ^1H NMR (400.13 MHz, CDCl_3 , 25°C): δ 1.02 (6H, s, H6 and H6'), 1.9 (1H, m, H5), 3.4 (2H, m, H4), 3.7 (3H, m, ArO-CH_3), 6.8 (2H, d, $^3J(\text{P,H})=3.2$, H2 and H2'), 7.2 (2H, d, $^4J(\text{P,H})=12.7$, H3 and H3'); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ 18.5 (s, C6 and C6'), 29.4 (s, C5), 56 (s, ArO-CH_3), 70.2 (s, C4), 114 (d, $^3J(\text{P,C})=12.5$, C2 and C2'), 118 (d, $^1J(\text{P,C})=112.3$, P-C), 136 (d, $^2J(\text{P,C})=15.3$, C3 and C3'), 165 (s, C1). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.45 MHz, CDCl_3 , 25°C , H_3PO_4 external): δ 98 (s) ppm. IR (KBr, cm^{-1}): 1590 (m), 1490 (m), 1290 (m), 1270 (s), 1056 (s) for $\nu_s(\text{P-O})$, 970 (w), 673 (m), 565 (m) for $\nu_s(\text{P-S})$. The structure of ligand **I** is given in scheme 2 and figure 1.

2.3 Synthesis of **II**

To a suspension of (2.022 g, 5 mmol) Lawesson reagent in 40 mL dry toluene at 25°C , (0.99 g, 10 mmol) cyclohexylamine was added and the mixture was stirred for overnight. The colourless precipitated solid was filtered off and washed several times with dry toluene. mp: 190°C , Yield: 78%. *Anal.* calcd. for $\text{C}_{19}\text{H}_{33}\text{N}_2\text{OPS}_2$ (400.58 g mol^{-1}): C, 56.9; H, 8.3; N, 6.9%; found: C, 56.8; H, 8.4; N, 6.9%. ^1H NMR (400.13 MHz, $\text{DMSO-}d_6$, 25°C): δ 1.08 (4H, m, H6 and H6'), 1.2 (2H, m, H7), 1.3 (4H, m, H10 and H10'), 1.6 (2H, m, H11), 1.7 (4H, m, H5 and H5'), 2.05 (4H, q, H9 and H9'), 2.5 (1H, m, H4), 2.8 (1H, m, H8), 3.8 (s, 3H, $\text{CH}_3\text{-OAr}$), 6.8 ($^+\text{NH}_3$), 7.8 (2H, m, $^3J(\text{P,H})=8.5$, H2 and H2'), 8.02 (2H, m, $^4J(\text{P,H})=8.6$, H3 and H3'), 8.1 (br, 1H, NH); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$, 25°C): δ 23.3 (d, C6, C6', C10 and C10'), 23.6 (d, C7 and C11), 30 (d, C5, C5', C9 and C9'), 49.6 (d, C4 and C8), 54.2 (s, $\text{CH}_3\text{-OAr}$), 111 (d, $^3J(\text{P,C})=14.6$, C2 and C2'), 130 (d, $^1J(\text{P,C})=109.7$, P-C), 112 (d, $^2J(\text{P,C})=14.9$, C3 and C3'), 159 (s, C1). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.45 MHz, $\text{DMSO-}d_6$, 25°C , H_3PO_4 external): δ 76 (s) ppm. IR (KBr, cm^{-1}): 3233 (s) for $\nu_{\text{as}}(\text{N-H})$, 1595 (s), 1494 (s), 1251 (s), 1010 (vs) for $\nu_{\text{as}}(\text{C-N})$, 999 (vs) for $\nu_{\text{as}}(\text{P-N})$, 624 (s), 545 (m) for $\nu_{\text{as}}(\text{P-S})$. The structure of **II** is given in scheme 3 and figure 1.



Scheme 2. Schematic representation for reaction of isobutanol with Lawesson reagent.



Scheme 3. Schematic representation for reaction of cyclohexylamine and phenylethylamine with Lawesson reagent.

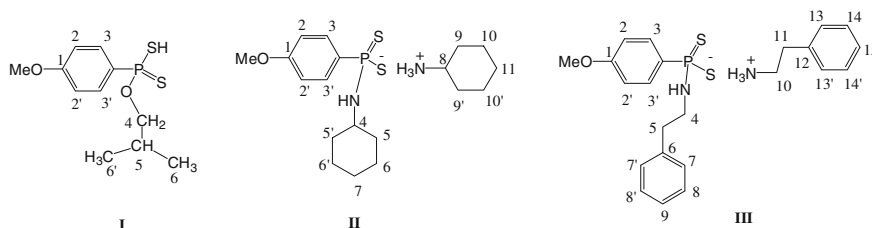


Figure 1. Numbering scheme for I, II and III.

2.4 Synthesis of **III**

In a manner similar to a suspension of (2.022 g, 5 mmol) Lawesson reagent in 40 mL dry toluene at 25°C, (1.21 g, 10 mmol) phenylethylamine was added and the mixture was stirred overnight. The colourless precipitated solid was filtered off and washed several times with dry toluene. mp: 155°C, Yield: 82%. *Anal.* calcd. for C₂₃H₃₀N₂OPS₂ (445.60 g mol⁻¹): C, 61.9; H, 6.7; N, 6.2%; found: C, 61.9; H, 6.7; N, 6.3%. ¹H NMR (400.13 MHz, DMSO-*d*₆, 25°C): δ 2.5 (2H, t, H5), 2.8 (2H, t, H4), 2.9 (2H, t, H11), 3 (2H, t, H10), 3.7 (3H, s, CH₃-OAr), 6.8 (2H, d, ³J(P,H)=2.1, H2 and H2'), 7.02 (2H, m, H9 and H15), 7.1 (4H, m, H7, H7', H13 and H13'), 7.3 (6H, m, H8, H8', H14, H14', H3 and H3'), 8 (3H, m, ⁺NH₃); ¹³C NMR (100 MHz, DMSO-*d*₆, 25°C): δ 56 (s, CH₃-O-Ar), 42 (d, C4), 39 (s, C10), 36 (d, C5), 32 (s, C11), 112 (d, ¹J(P,C)=13.4, C2 and C2'), 132-133 (d, ¹J(P,C)=101.2, P-C), 127.3 (d, C9 and C15), 127.9 (d, C8, C8', C7, C7', C13, C13', C14 and C14'), 131 (d, ²J(P,C)=29.9, C3 and C3'), 135 (s, C6), 138 (s, C12), 159 (s, C1). ³¹P{¹H} NMR (202.45 MHz, DMSO-*d*₆, 25°C, H₃PO₄ external): δ 79 (s) ppm. IR (KBr, cm⁻¹): 3028 (s) for ν_{as}(N-H), 1589 (m), 1490 (m), 1246 (s), 1091 (vs) for ν_{as}(C-N), 1029 (s) for ν_{as}(P-N), 601 (s), 575 (s) for ν_{as}(P-S). The structure of **III** is given in scheme 3 and figure 1.

2.5 Synthesis of complex **IV**

A methanolic solution of the ligand **I** (1.65 g, 6 mmol) was added dropwise to a solution of (0.71 g, 3 mmol) NiCl₂·6H₂O in 30 mL methanol. The resulting purple

solution was stirred and refluxed at 65°C for 2 h. The solvent was evaporated under reduced pressure to give a purple solid which was crystallized from acetonitrile to give purple X-ray quality crystals. mp: 146°C, Yield: 86%. *Anal.* calcd. for C₂₂H₃₀NiO₄P₂S₄ (609.39 g mol⁻¹): C, 43.3; H, 5.2%; found: C, 43.5; H, 5.3%. Selected IR (KBr, cm⁻¹): 1590 (m), 1485 (s), 1124 (s), 836 (w), 662 (m), 654 (m) cm⁻¹ for ν_s(P-S). The structure of complex **IV** is given in scheme 2 and figure 2.

2.6 Synthesis of complex **V**

A methanolic solution of the ligand **II** (2.40 g, 6 mmol) was added dropwise to a solution of (0.71 g, 3 mmol) NiCl₂·6H₂O in 30 mL methanol. The resulting purple solution was stirred and refluxed at 65°C for 2 h. The solvent was evaporated under reduced pressure to give a purple solid which was crystallized from methanol to give purple X-ray quality crystals. mp: 225°C Yield: 77%. *Anal.* calcd. for C₂₆H₄₂N₂NiO₄P₂S₄ (695.51 g mol⁻¹): C, 44.9; H, 6.1; N, 4.0%; found: C, 44.8; H, 6.1; N, 4.0%. Selected IR (KBr, cm⁻¹): 3228 (s) cm⁻¹ for ν_{as}(N-H), 1591 (m), 1111 (s), 1055 (vs) cm⁻¹ for ν_{as}(C-N), 831 (w), 601 (m), 559 (m) cm⁻¹ for ν_s(P-S). The structure of complex **V** is given in scheme 3 and figure 3.

2.7 Synthesis of complex **VI**

A methanolic solution of the ligand **III** (2.67 g, 6 mmol) was added dropwise to a solution of (0.71 g, 3 mmol)

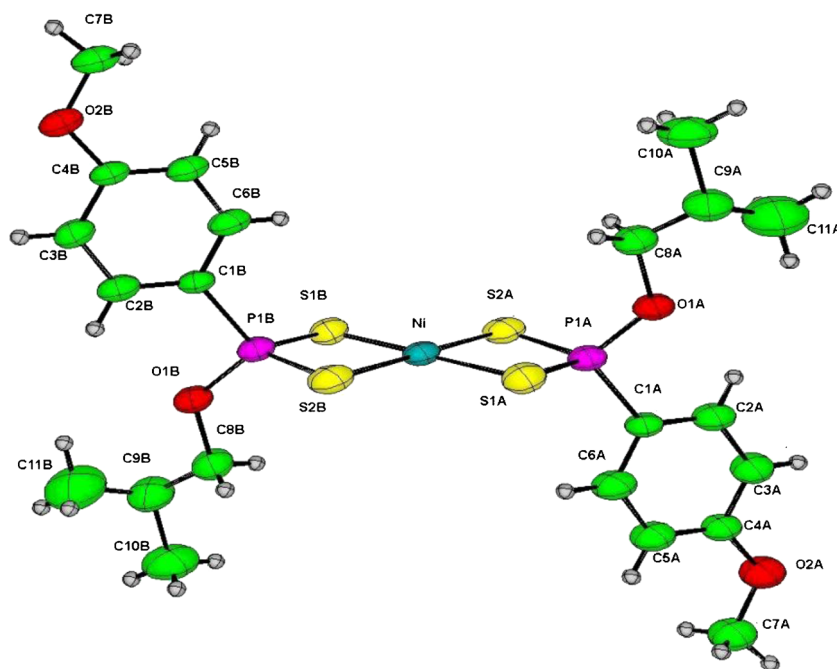


Figure 2. Displacement ellipsoid plot (at the 40% probability level) and atom labeling for the IV. Carbon, green; hydrogen, grey; oxygen, red; phosphorus, pink; sulphur, yellow; nickel, turquoise.

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 30 mL methanol. The resulting purple solution was stirred and refluxed at 65°C for 2 h. The solvent was evaporated under reduced pressure to give a purple solid which was crystallized from acetonitrile to give purple crystals. mp: 185°C , Yield: 79%. *Anal.* calcd. for $\text{C}_{30}\text{H}_{38}\text{N}_2\text{NiO}_4\text{P}_2\text{S}_4$ ($739.53 \text{ g mol}^{-1}$): C, 48.7; H, 5.2; N, 3.8%; found: C, 48.8; H, 5.2; N, 3.7%. Selected IR (KBr, cm^{-1}): 3230 (s) cm^{-1} for $\nu_{\text{as}}(\text{N-H})$, 1589 (m) , 1490 (s) , 1246 (s) , 1091 (vs) cm^{-1} for $\nu_{\text{as}}(\text{C-N})$, 825 (w) , 601 (m) , 565 (m) cm^{-1} for $\nu_{\text{s}}(\text{P-S})$. The structure of complex VI is given in scheme 3.

2.8 Determination of anti-bacterial activity

Synthesized compounds were tested for their anti-bacterial activities by the standardized disk diffusion method.¹⁸ The assayed collection included the following microorganisms: *Pseudomonas aeruginosa* (ATCC 27853), *Escherichia coli* (ATCC 25922), and *Acinetobacter baumannii* (ATCC 19606). In the disk diffusion method, sterile paper discs (6.4 mm diameter) impregnated with compounds tested (solutions in DMSO) to a load $500 \mu\text{g}$ of a compound per disc were placed on

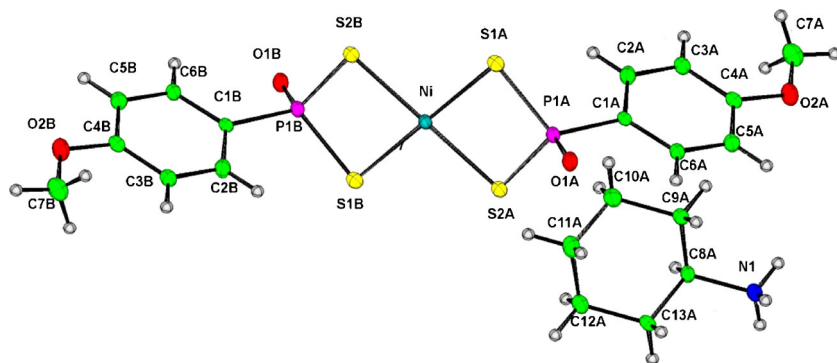


Figure 3. Displacement ellipsoid plot (at the 40% probability level) and atom labeling for the V. Carbon, green; hydrogen, grey; nitrogen, blue; oxygen, red; phosphorus, pink; sulphur, yellow; nickel, turquoise.

the surface of the media inoculated with the microorganisms. Discs containing DMSO were used as negative control. Gentamycin was used as standard drug. Diameter of the growth inhibition zone was read after 24 h of incubation at 35°C. These compounds were further examined by the broth dilution method to determine their MIC (minimal inhibitory concentration) and MBC (minimum bactericidal concentration).¹⁹ Concentrations of the agents tested in solid medium ranged from 0.5 to 500 $\mu\text{g}/\text{cm}^3$. Minimal inhibitory concentrations were read after 24 h of incubation at 35°C.

3. Results and discussion

3.1 Spectra study

Ligands **I**, **II** and **III** were synthesized and characterized by ^{31}P , ^{13}C , ^1H NMR, IR spectroscopy and elemental analyses. The IR spectrum of **I** shows a band at about 1010–1040 cm^{-1} that can be assigned to the

$\nu(\text{P}-\text{O}-\text{C})$ vibrations.²⁰ Beside, the band in 673 cm^{-1} is related to the $(\text{PS})_{\text{asym}}$ vibration.²¹ Unlike the reaction of alcohols with the Lawesson reagent, the reaction of amines with this reagent led to the formation of an ion pair. In the presence of water, or moisture, **II** and **III** hydrolyse very quickly and this process caused the water molecule in nickel chloride to attack the P–N bond and the hydrolysis process led to the formation of P–O bond (scheme 2).¹¹ In the IR spectrum of **II** and **III**; the N–H stretching frequency was observed at 3233 and 3028 cm^{-1} and P–N stretching frequency was observed at 999 and 1029 cm^{-1} , respectively. Considering P–N bond hydrolysis in **V** and **VI** complexes, stretching frequency of this bond was absent in IR spectroscopy.

3.2 Crystal structures of complexes **IV** and **V**

The structures of **IV** and **V** are shown in figures 2 and 3, respectively. Crystal data and details of the X-ray analysis for **IV** and **V** are given in table 1. In these

Table 1. Crystallographic data of the complexes **IV** and **V**.

Forms	IV	V
Empirical formula	$\text{C}_{22} \text{H}_{30} \text{Ni O}_4 \text{P}_2 \text{S}_4$	$\text{C}_{26} \text{H}_{42} \text{N}_2 \text{Ni O}_4 \text{P}_2 \text{S}_4$
Formula weight	607.35	695.51
Temperature (K)	299.4	150.0
Wavelength (Å)	0.7107	0.7107
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Unit cell dimensions		
a (Å)	8.2174(5)	9.5940(7)
b (Å)	9.1940(7)	9.6312(8)
c (Å)	11.1625(8)	10.2736(10)
α (°)	105.595(7)	72.976(8)
β (°)	103.156(6)	73.300(7)
γ (°)	109.222(7)	61.384(8)
V (Å ³)	719.18(9)	784.49(12)
Z Calculated density ($\text{Mg}\cdot\text{m}^{-3}$)	1, 1.402	1, 1.472
Absorption coefficient (mm^{-1})	1.101	1.021
$F(000)$	316	366
Crystal size (mm)	$0.40 \times 0.35 \times 0.15$	$0.50 \times 0.3 \times 0.2$
Θ range for data collection (°)	3.5028–29.0438	3.52–29.1610
Limiting indices	$-11 \leq h \leq 10$ $-12 \leq k \leq 12$ $-14 \leq l \leq 14$	$-10 \leq h \leq 11$ $-12 \leq k \leq 10$ $-9 \leq l \leq 9$
Reflections collected/unique (R_{int})	5322/2624(0.0316)	7116/2831(0.0209)
Absorption correction	Empirical	Empirical
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2624/0/154	2831/0/180
Goodness-of-fit on F^2	1.038	1.059
Final R indices	$R_1=0.0590$, $wR_2=0.1369$	$R_1=0.0353$, $wR_2=0.0775$
R indices (all data)	$R_1=0.0976$, $wR_2=0.1674$	$R_1=0.0438$, $wR_2=0.0863$
Largest diff. peak and hole ($\text{e}\cdot\text{\AA}^{-3}$)	0.682 and -0.379	0.453 and -0.438

Table 2. Experimental geometrical parameters for **IV**.

Bond lengths (Å)			
Ni- S2A	2.2184(13)	P1A-S2A-Ni	85.45(6)
Ni- S2B	2.2185(13)	C8A-O1A-P1A	121.9(3)
Ni- S1A	2.2198(12)	O1A-P1A-C1A	100.49(19)
Ni- S1B	2.2198(12)	O1A-P1A-SA	115.10(16)
S2A- P1A	2.0182(17)	O1A-P1A-S2A	113.41(16)
P1A -O1A	1.574(3)		
P1A- S1A	2.0033(18)		
Bond angles (°)		Dihedral angles (°)	
S1A-Ni-S1B	180.0 2	S1A-P1A-O1A-C8A	−51.93
S1A-Ni-S2A	88.48(5)	S2A-P1A-O1A-C8A	63.29
C1A-P1A-S1A	113.70(17)	P1A-O1A-C8A-C9A	−165.21
S1A-Ni-S2B	91.52(5)	O1A-C8A-C9A-C11A	−45.25
S1B-Ni-S2A	91.52(5)	S1A-P1A-C1A-C6A	76.96
S1B-Ni-S2B	88.48(5)	S1A-P1A-C1A-C2A	−100.08
S2A-Ni-S2B	180.0 2	O1A-P1A-C1A-C2A	21.60
P1A-S2A-Ni	85.14(6))	S2B-Ni-S1A-P1A	176.60
S2A-P1A-S1A	100.70(7)	Ni-S1A-P1A-O1A	127.35

complexes, the metal centre was tetracoordinated in square planar geometry by four sulphur atoms belonging to the ligand. In **IV** complex, the torsion angles, namely Ni-S2A-P1A-S1A (3.42°) and Ni-S2B-P1B-S1B (3.83°) were strong indications of co-planarity of the two four-membered chelate rings. Torsion angles S1A-P1A-O1A-C8A and S1B-P1B-O1B-C8B are −63.29 and 63.29, respectively. (Similarly, compare the torsion angles of Ni-P1A-O1A-C8A and Ni-P1B-O1B-C8B that are −4.92 and 4.92, respectively). Bond lengths Ni-S1A, Ni-S2A are about 2.2317 Å, 2.2168 Å and bond angle of S–Ni–S is about 87.42°. Selected bond lengths, bond angles and torsion angles are presented in table 2. In complex **V** (with the amine moiety), bond lengths, Ni–S1A, Ni–S2A, Ni–S1B and

Ni–S2B, were in order of 2.218, 2.220, 2.218 and 2.220 Å. Angles between S2A–Ni–S2B, S1A–Ni–S1B and S2A–Ni–S1B were 180°, 180° and 91.53°, respectively. Selected bond lengths, bond angles and torsion angles are presented in table 3.

In **V**, cyclohexylamine was not coordinated to the metal centre. Three hydrogens of cyclohexyl amine cation gave three hydrogen bonds with P–O and OMe group and with different distances (figure 4). Details of the hydrogen bonding interactions for **V** are summarized in table 4. Interactions of P–O and OCH₃ with cyclohexylamine cation led to different hydrogen bonding patterns. These interactions caused the formation of three different polymeric chains cyclic with different sizes. In polymeric chains with cyclics R_4^+ (24)

Table 3. Experimental geometrical parameters for the **V**.

Bond lengths (Å)			
Ni-S2A	2.2168(7)	O1A-P1A-C1A	107.34(11)
Ni-S2B	2.2168(7)	C1A-P1A-S1A	111.74(9)
Ni-S1A	2.2317(7)	O1A-P1A-S2A	112.91(8)
Ni-S1A	2.2317(7)	C1A-P1A-S2A	110.03(9)
S1A-P1A	2.0284(10)	S1A-P1A-S2 A	98.32(4)
S2A-P1A	2.0348(9)		
Bond angles (°)		Dihedral angles (°)	
S2A-Ni-S2B	179.999(1)	S2A-Ni-S1B-P1B	172.21(3)
S2A-Ni-S1B	92.58(3)	S2A-Ni-S1A-P1A	−7.79(3)
S2A-Ni-S1A	87.42(3)	S1B-Ni-S1A-P1A	−18.16
S2B-Ni-S1B	87.42(3)	S2B-Ni-S2A-P1A	35(100)
S2B-Ni-S1A	92.58(3)	Ni-S1A-P1A-O1A	−112.18(18)
S1A-Ni-S1B	179.999(1)	Ni-S1A-P1A-C1A	124.10(9)
P1A-S1A-Ni	86.43(3)	Ni-S2A-P1A-O1A	114.62(8)
P1A-S2A-Ni	86.67(3)	O1A-P1A-C1A-C6A	27.5(2)
O1A-P1A-S1A	116.32(8)	S1A-P1A-C1A-C6A	156.15(19)

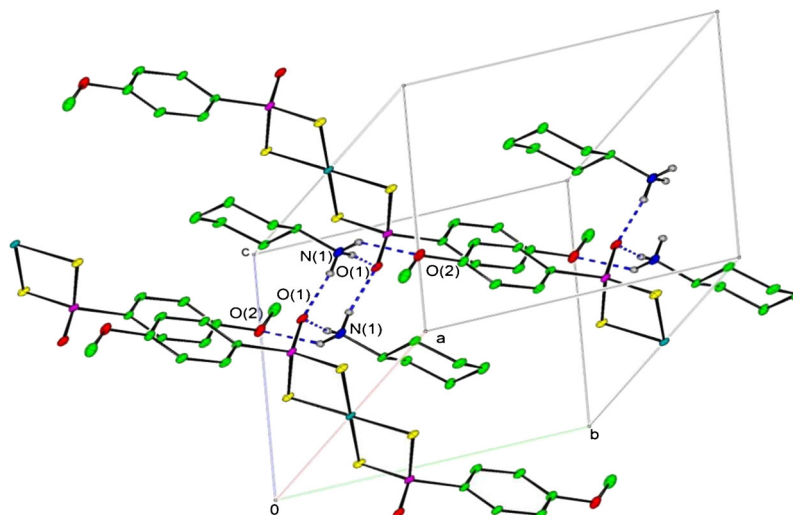


Figure 4. Representation of hydrogen bonded (dashed blue lines) in the crystal structures of **V**. Carbon, green; nitrogen, blue; oxygen, red; phosphorus, pink; sulphur, yellow; nickel, turquoise.

Table 4. Hydrogen-bond distances (Å) and angles (°) for **V**.

D-H	d(D-H)	d(H...A)	< DHA	d(D...A)
N(1)–H(1)A–O(1)	0.89	1.92	172.3	2.806(3)
N(1)–H(1)B–O(2)	0.89	2.20	141.4	2.950(3)
N(1)–H(1)C–O(1)	0.89	1.87	163.8	2.740(3)

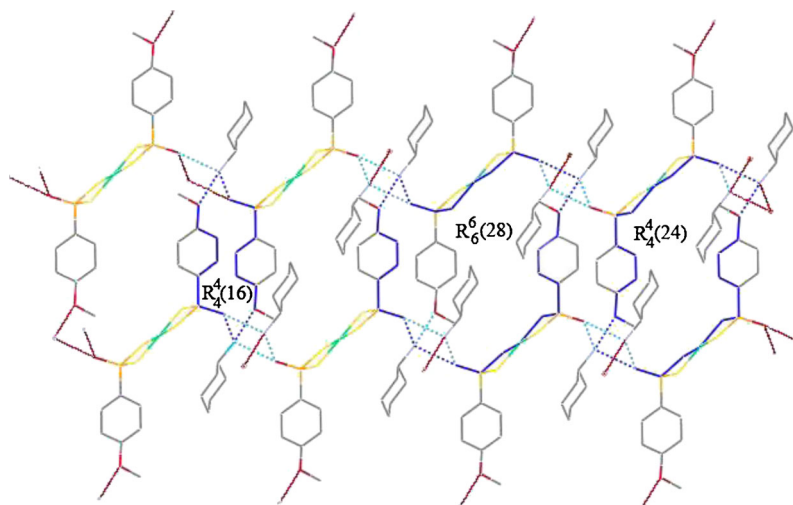


Figure 5. Illustration of $R_4^4(16)$, $R_4^4(24)$ and $R_6^6(28)$ graph sets in the **V**.

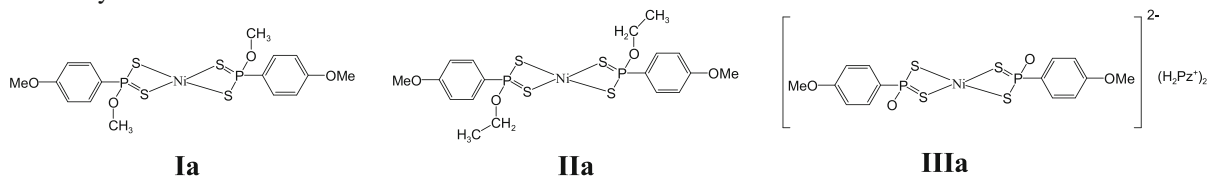
and $R_4^4(16)$ motif, the monomers were connected to each other *via* two P–O...H–N and two Me–O...H–N hydrogen bonds with donor–acceptor distance of 2.740 and 2.950 Å, respectively, where the $R_Y^X(Z)$ graph-set notation is descriptive of a Z-membered ring produced by X hydrogen bonds between Y donor–acceptor units²² also, cyclic $R_6^6(28)$ are connected to each other *via* four P–O...H–N and two Me–O...H–N hydrogen bonds

with donor–acceptor distance of 2.740 and 2.950 Å, respectively (figure 5).

Comparison of obtained data with reported similar structures data is given in table 5. The P1A–S1A bond length in **IV** (with the $\text{OCH}_2\text{CH}(\text{CH}_3)_2$ moiety) (2.0180(17) Å) was longer than those found in the tetra-coordinate nickel (II) complexes **Ia** (with the OCH_3 moiety) (2.0019(17)) and **IIa** (with the OCH_2CH_3

Table 5. Selected geometric parameters for Ni complexes and similar structures.

Comp.	Ni–S(2)A	S(1)A–Ni–S(2)A	P(1)A–Ni	S(1)A–Ni–S(2)B	P(1)A–S(1)A	P–O	N...O	Ref.
IV	2.2168(7)	87.42(3)	2.870(4)	91.52(5)	2.0180(17)	1.574(3)	–	a
Ia	2.2307(1)	88.75(5)	2.809(5)	91.25(5)	2.0019(17)	1.582(3)	–	12
IIa	2.2257(1)	88.04(7)	2.831(2)	91.96(7)	2.0080(2)	1.585(5)	–	12
V	2.2168(7)	87.42(3)	2.921(6)	92.58(3)	2.0348(9)	1.513(2)	2.740(3)	a
IIIa	2.2205(8)	92.14(3)	–	92.14(3)	2.019(1)	1.538(2)	2.657(3)	11

^aPresent study**Table 6.** Anti-bacterial activity of compounds (zone of inhibition in mm).

Compound	<i>E. Coli</i>	<i>A. Baumannii</i>	<i>P. Aeruginosa</i>
I	13	14	12
II	18	18	16
III	14	16	15
IV	15	18	16
V	16	20	19
VI	16	19	18
Gentamycin	40	31	29

Table 7. Anti-microbial activity (MIC ^a/MBC ^b) (μg/cm³) of compound.

Compound	<i>E. Coli</i>		<i>A. Baumannii</i>		<i>P. Aeruginosa</i>	
	MIC	MBC	MIC	MBC	MIC	MBC
I	160	250	65	140	130	145
II	90	135	85	120	90	135
III	140	210	90	135	150	230
IV	150	230	80	120	90	140
V	90	140	70	105	75	130
VI	90	140	75	115	80	120

^aMIC – minimum inhibitory concentration^bMBC – minimum bactericidal concentration

moiety) (2.008(2) Å).¹² This is consistent with decrease in electron density between phosphorus and sulphur atoms in nickel complexes; and also this difference depends on electron donation ability of oxo substituents on ligands (OCH₂CH(CH₃)₂>OCH₂CH₃>OCH₃). The S1A–Ni–S2A bond length in **V** (amine moiety) 87.42(3) was shorter than complex **IIIa** (92.14(3)).¹¹

3.3 Anti-bacterial activity results

The ligands and complexes were screened for *in vitro* anti-microbial activities against three gram negative bacteria *E. coli*, *A. baumannii* and *P. aeruginosa*. The

results are presented in tables 6 and 7. Ligands containing amine substituents exhibited more activity towards tested bacteria than their alcohol substituents. Comparing the obtained results to the standard antibiotic, Gentamycin, ligand **II** exhibited stronger anti-bacterial effect against *E. coli*. Moreover, anti-bacterial activities of Ni (II) complexes are higher than their ligands (see tables 6 and 7).

4. Conclusions

The reaction of Lawesson reagent with isobutanol, cyclohexylamine and phenylethylamine produced HS₂P

(p-C₆H₄OMe)(OCH₂CH(CH₃)₂) (I), S₂P(C₆H₁₁NH)(p-C₆H₄OMe)H₃N⁺C₆H₁₁ (II) and S₂P(phCH₂CH₂NH)(p-C₆H₄OMe)H₃N⁺CH₂CH₂ph (III). The reaction of alcohol with LR produced neutral ligand (I) while amines reacted with LR as an ion pair (II, III). Further reaction of I, II and III with NiCl₂·6H₂O in methanol led to novel complexes: IV, V and VI. The single crystal X-ray structures of IV, V showed that the nickel complexes are square planar. The P = S bond length in IV (with the OCH₂CH(CH₃)₂ moiety) is longer than those found in the tetracoordinate nickel (II) complexes with the OCH₃ and the OCH₂CH₃ moieties. The X-ray crystallography of V shows that R₄⁴ (24) and R₄⁴ (16) motifs in the monomers are connected to each other via two P–O...H–N and two CH₃–O...H–N hydrogen bonds with donor–acceptor distance of 2.740 and 2.950 Å, respectively. From studies on anti-bacterial activity, it was concluded that the most sensitive bacterial species on compounds tested is gram-negative bacteria, *E. coli*, *A. baumannii* and *P. aeruginosa*. Also, ligands containing amine substituents exhibited more activity toward tested bacteria than their alcohol substituents, while Ni(II) complexes exhibited higher potential than their ligands.

Supplementary Information

CCDC 936628 and 936629 contain supplementary crystallographic data for V and IV. These data can be obtained free of charge via <http://www.Ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgement

We thank Islamic Azad University of Tehran, Science and Research Branch for supporting this research work.

References

1. Khajuria R, Syed A, Kumar S and Pandey S 2013 *Bioinorg. Chem. Appl.* **2013** 261731
2. Bara A C, Silvestru C and Haiduc I 1991 *Anticancer Res.* **11** 1651
3. Shabana R and Atrees SS 1995 *Phosphorus, Sulfur Silicon Relat. Elem.* **105** 57
4. Roy N 1990 *Pesticides A* **13** 1989
5. Aragoni M, Demartin F, Demartin F, Devillanova A, Graiff C, Isaia F, Lippolis V, Tiripicchio A and Verani G 2001 *J. Chem. Soc. Dalton Trans.* **18** 2671
6. Sağlam E, Yılmaz H, Celik O and Ide S 2010 *Transition Met. Chem.* **35** 399
7. Sanchez G, Garcia J, Meseguer D, Serrano J, Perez J, Molins E and Lopez G 2004 *Inorg. Chim. Acta* **357** 677
8. Santana M, Garcia G, Navarro C, Lozano A, Perez J, Garcia L and Lopez G 2002 *Polyhedron* **21** 1935
9. Karakus M and Yilmaz H 2006 *Russian J. Coord. Chem.* **32** 437
10. Karakus M, Yilmaz H and Bulak E 2005 *Russian J. Coord. Chem.* **31** 338
11. Alberti E, Ardizzoia G, Brenna S, Castelli F, Galli S and Maspero A 2007 *Polyhedron* **26** 958
12. Liu H, Mao H, Xu C, Zhang H, Hou H, Wu Q, Zhu Y, Ye B and Yuan L 2004 *Polyhedron* **23** 1799
13. Armarego W and Perrin D 1988 *Purification of laboratory chemicals* (Oxford: Pergamon Press)
14. Clausen K, El Barbary A and Lawesson S 1981 *Tetrahedron* **37** 1019
15. Sheldrick G 2008 *Acta Crystallogr.* **64** 112
16. Sheldrick G 1997 SHELXL-97 *A computer program for crystal structure determination*. University of Gottingen
17. McArdle P 1995 *J. Appl. Cryst.* **28** 65
18. Greenwood D 1989 *Antimicrobial chemotherapy* (New York: Oxford University Press)
19. Vincent J and Vincent H 1994 *Proc. Soc. Exp. Biol. Med.* **55** 162
20. Santana M, Garcia G and Navarro C 2002 *Polyhedron* **21** 1935
21. Haiduc I, David L and Cozar O 1999 *J. Mol. Struct.* **482** 153
22. Bernstein J, Davis R, Shimoni L and Chang N 1995 *Angew. Chem. Int. Ed.* **34** 1555