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# NMR (1D and 2D) and X-ray crystallographic studies of Ni(II) complex with *N*-(2-mercaptophenyl)-4-methoxysalicylideneimine and triphenylphosphine

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This paper is dedicated to Professor K. Natarajan on the occasion of his 60th birthday.

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#### 1. Introduction

A large number of Schiff base complexes have been studied for their interesting and important properties such as their ability to reversibly bind oxygen [1], catalytic activity in hydrogenation of olefins [2], transfer of an amino group [3], photochromic properties [4], complexing ability towards some toxic metals [5], etc. They also exhibit interesting stereochemical, electrochemical and electronic properties [6]. Complexation of nickel by Schiff base ligands with N, S donor atoms has been of particular interest because of the fact that coordination sphere of nickel in metalloproteins such as 2-mercaptoethanol-inhibited urease and Ni/Fe hydrogenases contains N and S donor sets. Recently we devoted our efforts to the synthesis of several Schiff base complexes with nickel to obtain information on the chemical behaviour of the metal with these ligands [7]. In continuation of our efforts, we herein report the synthesis, spectral studies including detailed 2D NMR and crystal structure of Ni(II) complex containing dianion of N-(2-mercaptophenyl)-4-methoxysalicylideneimine) and triphenylphosphine (Scheme 1).

#### ABSTRACT

Mononuclear nickel(II) complex, *viz.* [Ni(L)(PPh<sub>3</sub>)] (where L is dianion of *N*-(2-mercaptophenyl)-4-methoxysalicylideneimine) has been synthesized and characterized by means of elemental analysis, electronic, IR and NMR [<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H}, DEPT, <sup>1</sup>H–<sup>1</sup>H COSY, ge-HSQC, ge-HMBC] spectroscopic techniques. Structural analysis of the complex by single crystal X-ray crystallography indicated the presence of square planar coordination geometry (ONSP) about nickel. One of the phenyl rings of triphenylphosphine involve in C–H… $\pi$  interactions with H6b, H13 and H32 to form a three dimensional network which stabilizes the structure of complex.

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#### 2. Experimental

#### 2.1. Materials and methods

All the reagents and solvents employed were commercially available and used with no further purification. Schiff base ligands [8] and  $[NiCl_2(PPh_3)_2]$  [9] were prepared by following literature method.

#### 2.2. Physical measurements

Electronic spectrum was measured on a PerkinElmer EZ 301 UV–vis double beam spectrophotometer in CH<sub>3</sub>CN solution of the complex in the 200–800 nm range. FT-IR spectrum was recorded on a PerkinElmer Spectrum One FT-IR spectrometer as KBr pellet in the frequency range of 400–4000 cm<sup>-1</sup>. The C, H, N and S contents were determined by Thermoflash EA1112 series elemental analyzer. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectrum were recorded in CDCl<sub>3</sub> solution on Bruker Avance 500 spectrometer at 500.13 (<sup>1</sup>H) and 125.76 (<sup>13</sup>C) MHz using TMS as internal standard. DEPT spectrum was recorded in a standard manner using only a  $\Theta$  = 135 pulse program. The 2D-COSY, ge-HSQC and ge-HMBC spectra were obtained by using the standard Bruker pulse programs. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum was recorded in CDCl<sub>3</sub> solution on Bruker Avance 500 spectrometer at 202.46 (<sup>31</sup>P) MHz using H<sub>3</sub>PO<sub>4</sub> as external

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Fig. 1. <sup>1</sup>H NMR spectrum.

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H and <sup>13</sup> C NMR data, and <sup>1</sup> H- <sup>1</sup> H COSY, <sup>1</sup> H- <sup>13</sup> C HSQC and <sup>1</sup> H- <sup>13</sup> C HMBC correlations.

Carbon number	Chemical shift (ppm)		<sup>1</sup> H– <sup>1</sup> H COSY	<sup>1</sup> H– <sup>13</sup> C HSQC	<sup>1</sup> H– <sup>13</sup> C HMBC		
	$\delta_{ m H}$	δ <sub>c</sub>	_		<sup>2</sup> J	3Ј	<sup>4</sup> J
C1	_	117.80	-	-	-	-	-
C2	-	160.00	-	-	-	_	-
C3	6.35 (1H, d, J=9.14 Hz)	122.58 <sup>b</sup>	H4	122.58	160.00(C2)	117.80(C1), 149.62(C5)	112.27(C7) <sup>a</sup> , 153.63(C14)
C4	6.89 (1H, dd, J=9.14, 3.15 Hz)	125.39 <sup>b</sup>	H3	125.39	149.62(C5)	112.27(C7), 160.00(C2)	-
C5	-	149.62	-	-	-	-	_
C6	3.78 (3H, s)	55.94 <sup>b</sup>	-	55.94		149.62(C5)	-
C7	6.84 (1H, d, J=2.84 Hz)	112.27 <sup>b</sup>	-	112.27	149.62(C5)	125.39(C4), 153.63(C8), 160.00(C2)	-
C8	8.85 (1H, d, /=10.4 Hz).	153.63 <sup>b</sup>	-	153.63	117.80(C1)	112.17(C7), 149.89(C9), 160.00(C2)	-
C9	- ,	149.89	-	-	-	-	-
C10	7.36 (1H, d, /=7.57 Hz)	128.61 <sup>b</sup>	H11	128.60	149.89(C9)	121.81(C11)	-
C11	6.93-7.04 (2H, m)	121.81 <sup>b</sup>	H10	121.81	128.60(C10)	114.76(C13), 149.89(C14) <sup>a</sup>	143.9(C14)
C12		126.46 <sup>b</sup>	H13	126.46	114.76(C13)	128.60(C10), 143.90(C14) <sup>a</sup>	149.89(C9)
C13	7.70 (1H, d, J=8.20 Hz)	114.76 <sup>b</sup>	H12	114.76	143.90(C14)	126.46(C12)	149.89(C9), 121.81(C11) <sup>a</sup>
C14		143.90	-	-	-	-	-
Cq	-	129.13	-	-	-	-	-
		129.50					
Со	7.78–7.94 (6H, m)	134.71 <sup>b</sup> 134.80 <sup>b</sup>	Ho-Hm	134.71, 134.80	(128.09–128.17)–(Cn	n) (130.53–130.55)–(Cp), (134.71–134.80)–(Co	)) –
Cm	7.40-7.46 (6H, m)	128.08 <sup>b</sup> , 128.16 <sup>b</sup>	Hm-Ho, Hm-Hp	128.08, 128.16	(134.71–134.80)–(Cq	) (129.13–129.53)–(Cq)	-
Ср	7.49 (3H, t, J=7.09 Hz)	130.53 <sup>b</sup> , 130.55 <sup>b</sup>	Hp-Hm	130.53, 130.55	(128.09–128.17)–(Cn	n) (134.71–134.80)–(Co)	-

Cq=(C15, C21, C27); Co=(C16, C22, C28, C20, C26, C32); Cm=(C17, C23, C29, C19, C25, C21); Cp=C18, C24, C30. Ho=(H16, H22, H28, H20, H26, H32); Hm=(H17, H23, H29, H19, H25, H21); Hp=(H18, H24, H30).

<sup>a</sup> Weak signal. <sup>b</sup> <sup>13</sup>C resonances appeared in DEPT135.



standard. Melting point was determined with Khora digital melting point apparatus.

#### 2.3. Determination and refinement of structure

Single crystals of Ni complex for X-ray diffraction studies were grown at room temperature from a dichloromethane–ethanol solution by the diffusion of diethyl ether vapour. Diffraction data were collected on a Bruker Axs Kappa ApexII CCD diffractometer using graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The structures were solved by direct methods (SHELXS-97) [10] and refined by full-matrix least-squares fitting based on  $F^2$  using the program SHELXL-97 [11]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were located by difference Fourier syntheses and were then included in the refinement with idealized geometry riding on the atoms to which they were bonded.

#### 2.4. Synthesis of Ni(II) complex

The complex was prepared by stirring an ethanolic solution  $(10 \text{ cm}^3)$  of  $[\text{NiCl}_2(\text{PPh}_3)_2]$  (0.5 g, 0.764 mmol) with dichloromethane solution  $(10 \text{ cm}^3)$  of ligand (0.198 g, 0.764 mmol) for 2 h at 25–27 °C. The resulting dark brown solutions were concentrated to approximately 3 cm<sup>3</sup> and cooled. Hexane (20 cm<sup>3</sup>)



**Scheme 1.** Structure of Ni(II) complex (numbering is given for better understanding of discussions).





was then added whereupon the product complex separated. The brown coloured complex was filtered, washed with ethanol and then with hexane and dried in vacuo. The formation of complex was checked by TLC. Yield: 274 mg (62%). Decomposition temperature 230°C. Anal. Found: C, 66.46; H, 4.53; N, 2.42; S, 5.54. Calc. for C<sub>31</sub>H<sub>24</sub>NNiOPS: C, 66.90; H, 4.41; N, 2.55; S, 5.95%. UV-vis  $(CH_3CN) \lambda_{max} (nm) (\varepsilon (dm^3 mol^{-1} cm^{-1})): 213 (4708), 255 (3638),$ 273 (3716), 444 (863), 507 (209). IR (KBr disk), cm<sup>-1</sup>: ν(C=N) 1591, v(C-O) 1358, v(C-S) 750, v(Ni-O) 533, v(Ni-N) 461, bands due to PPh<sub>3</sub> 1435, 1096, 692. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.78 (3H, s), 6.35 (1H, d, J=9.14 Hz), 6.84 (1H, d, J=2.84 Hz) 6.89 (1H, dd, J=9.14, 3.15 Hz), 6.93-7.04 (2H, m), 7.36 (1H, d, J=7.57 Hz), 7.41–7.45 (6H, m), 7.49 (3H, t, J=7.09 Hz), 7.70 (1H, d, J=8.20 Hz), 7.78–7.94 (6H, m), 8.85 (1H, d, J=10.40 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (202.46 MHz, CDCl<sub>3</sub>, 25 °C),  $\delta$  (ppm): 22.7 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (125.76 MHz, CDCl<sub>3</sub>, 25 °C): 55.94, 76.77, 77.03, 77.28, 112.27, 114.76, 117.80, 121.81, 122.58, 125.39, 126.46, 128.08, 128.16, 128.61, 129.13, 129.50, 130.53, 130.55, 134.71, 134.80,

143.90,149.62, 149.89, 153.63, 160.00 ppm.  $^{13}\text{C}\text{-DEPT}$  135 NMR (125.76 MHz, CDCl<sub>3</sub>, 25 °C): 55.94, 112.22, 114.76, 121.83, 122.61, 125.39, 126.48, 128.09, 128.17, 128.62, 130.54, 130.56, 134.72, 134.80, 153.63 ppm.

#### 3. Results and discussion

The reaction of equimolar ratios of the ligand  $(H_2L)$  and  $[NiCl_2(PPh_3)_2]$  yielded the new brown coloured complex of the general formula  $[Ni(L)(PPh_3)]$  [L = dianionic *N*-(2-mercaptophenyl)-4-methoxysalicylideneimine] in good yield. It was found to be soluble in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, C<sub>6</sub>H<sub>6</sub>, DMSO, DMF and C<sub>2</sub>H<sub>5</sub>OH. The analytical data for the complexes are in good agreement with the above molecular formula. In the reaction, it has been observed that the Schiff base behaves as a bifunctional tridentate ligand by substituting one of the triphenylphosphines and both the chloride ions from the starting complex.





#### 3.1. UV-vis and IR spectra

The electronic spectrum of complex in  $CH_3CN$  showed four bands in the region 213–507 nm. The bands appearing in the region 213–273 nm have been assigned to intraligand transitions. A less intense band at 444 nm corresponds to forbidden d  $\rightarrow$  d transition. The same behaviour has been observed in the electronic spectra of other similar square planar nickel(II) complexes [12].

The spectrum of ligand exhibits a strong band at  $1622 \text{ cm}^{-1}$ , which is assigned to  $\nu(C=N)$  vibration. As a result of coordination, this band shifts to lower wave number by *ca*.  $30 \text{ cm}^{-1}$  in complex [12]. A band at  $1358 \text{ cm}^{-1}$  which is assigned to phenolic  $\nu(C=O)$  in the free ligand, is shifted to higher wave number in the complex

suggesting the coordination of phenolic oxygen to nickel ion [12]. A weak band observed at 756 cm<sup>-1</sup> corresponding to  $\nu$ (C–S) in the ligands, shifts to lower wave number which supports sulfur coordination with the nickel centre [13]. The bands at 533 and 461 cm<sup>-1</sup> in the complex are assigned to  $\nu$ (Ni–O) and  $\nu$ (Ni–N) respectively [14]. Bands due to triphenylphosphine are also appearing in the expected region [15].

#### 3.2. 1D and 2D NMR spectra

In <sup>1</sup>H NMR spectrum of complex (Fig. 1), five doublets were observed at  $\delta_{\rm H}$  = 6.35 (1H, d, *J* = 9.14 Hz),  $\delta_{\rm H}$  = 6.84 (1H, d, *J* = 2.84 Hz),  $\delta_{\rm H}$  = 7.36 (1H, d, *J* = 7.57 Hz),  $\delta_{\rm H}$  = 7.70 (1H, d, *J* = 8.20 Hz) and



Fig. 5. Stack plot of <sup>13</sup>C and DEPT 135 NMR spectrum.

 $\delta_{\rm H}$  = 8.85 (1H, d, /= 10.40 Hz) which has been assigned to H3, H7, H10, H13 and H8 (azomethine proton) respectively. The *I* value of azomethine proton indicates that two aromatic units of Schiff base are trans to each other [16]. A doublet of doublet observed at  $\delta_{\rm H}$  = 6.89 ppm (1H, dd, *J* = 9.14, 3.15 Hz) in the complex has been assigned to H4. Complex exhibits a singlet at 3.78 ppm with three proton count, corresponds to methoxy protons (H6). In the <sup>13</sup>C NMR spectra of the complex, methoxy (C6) and azomethine (C7) carbon resonances observed at 55.94 and 153.63 ppm respectively. <sup>1</sup>H–<sup>1</sup>H COSY spectrum (Fig. 2) displayed scalar couplings for adjacent protons like H3  $\leftrightarrow$  H4, H10  $\leftrightarrow$  H11 and H12  $\leftrightarrow$  H13. Further, the connection between these nine protons and its parent carbons namely C3 (δ<sub>C</sub> 122.58), C7 (δ<sub>C</sub> 112.27), C10 (δ<sub>C</sub> 128.61), C13  $(\delta_{C} 114.76)$ , C8  $(\delta_{C} 153.61)$ , C4  $(\delta_{C} 125.39)$  and C6  $(\delta_{C} 55.94)$  is confirmed by direct couplings in HSQC spectrum (Fig. 3). A quintet shaped multiplet observed in the 6.93-7.04 ppm region with a proton count of two is assigned to H11 and H12. This multiplet shows scalar couplings with H10 ( $\delta_{\rm H}$  = 7.36) and H13 ( $\delta_{\rm H}$  = 7.70) in its <sup>1</sup>H–<sup>1</sup>H COSY spectrum. It is difficult to find out coupling for H11  $\leftrightarrow$  H12 due to merged resonances. The connection of H11 and H12 with its parent carbon atoms, C11 ( $\delta_{C}$  121.81) and C12 ( $\delta_{C}$  126.46), is established by HSQC spectrum. Nickel(II) complex exhibits three multiplets in the regions of  $\delta_{\rm H}$  7.41–7.45 (6H, m),  $\delta_{\rm H}$ 7.49 (3H, m) and  $\delta_{\rm H}$  7.78–7.94 (6H, m) which has been assigned to meta, para and ortho protons respectively, of three phenyl rings of triphenylphosphine. This assignment is based on scalar couplings in <sup>1</sup>H–<sup>1</sup>H COSY spectrum, which shows correlation only between Ho  $\leftrightarrow$  Hm and Hp  $\leftrightarrow$  Hm [Ho = (H16, H22, H28, H20, H26, H32); Hm = (H17, H23, H29, H19, H25, H21); Hp = (H18, H24, H30)]. The absence of resonances due to phenolic and thiolato hydrogen indicates the deprotonation of these groups and the Schiff base behaves as dianionic ligands. The <sup>13</sup>C NMR resonances for C14–S1, C5-O2, C9-N1 and C2-O1 are observed at 143.90, 149.62, 149.89 and 160.01 ppm respectively [17,18]. It is interesting that HMBC spectrum (Fig. 4) was very much useful to distinguish the resonances due to C5 ( $\delta_{C}$  149.62) and C9 ( $\delta_{C}$  149.89). The DEPT 135 spectrum shows disappearance of resonances at 117.80, 129.13, 129.50, 143.90, 149.62, 149.89, and 160.01 ppm. The <sup>13</sup>C resonances at 129.13 and 129.50 are assigned to quaternary carbons present in triphenylphosphine. This indicates that three guaternary carbons arising from aromatic units of triphenylphosphine are in two dif-





ferent magnetic environments. Stack plot of <sup>13</sup>C and DEPT 135 NMR spectrum is depicted in Fig. 5. <sup>31</sup>P NMR spectrum (Fig. 6) of the complex exhibits a singlet at 22.72 ppm suggesting the presence of one coordinated triphenylphosphine in nickel(II) complex [7]. In HMBC correlation spectrum, methoxy protons (H6,  $\delta_{\rm H}$  3.78 (3H, s)) show a strong three bond coupling with C5 ( $\delta_{\rm C}$  149.62) which was a rare observation as coupling occurs through an oxygen atom. In addition, the coupling of imine proton ( $\delta_{\rm H}$  8.89) with three quaternary carbons, *viz.* C1 ( $\delta_{\rm C}$  117.80), C2 ( $\delta_{\rm C}$  160.00), C9 ( $\delta_{\rm C}$  149.89) and C7 ( $\delta_{\rm C}$  112.17) has been understood from HMBC correlation spectrum. <sup>1</sup>H and <sup>13</sup>C NMR data, and <sup>1</sup>H–<sup>1</sup>H COSY, <sup>1</sup>H–<sup>13</sup>C HSQC and <sup>1</sup>H–<sup>13</sup>C HMBC correlations are given in Table 1.

#### 3.3. X-ray crystallography

ORTEPIII view [19] of structure of complex is shown in Fig. 7. The nickel atom in this complex has approximate square planar coordination with S1, N1, O1 of Schiff base and P1 of triphenylphosphine with the metal atom having maximum deviation of 0.029(5)Å from the mean plane. Table 2 shows crystal data, data collection and structure refinement parameters. The bond angles O1–Ni1–S1, N1–Ni1–P1, O1–Ni1–P1, O1–Ni1–N1, N1–Ni1–S1 and S1–Ni1–P1 are 175.08(3)°, 177.17(5)°, 85.22(4)°, 94.96(6)°, 89.72(5)° and 90.03(19)° respectively. The Ni1–P1, Ni1–O1, Ni1–N1 and Ni1–S1 bond distances are in the usual range [12]. Table 3 shows selected bond lengths and bond angles. The



Fig. 7. Molecular structure of complex showing 50% displacement ellipsoids.

#### Table 2

Parameters	$[Ni(L)(PPh_3)]$
Empirical formula	C <sub>32</sub> H <sub>26</sub> NNiO <sub>2</sub> PS
Formula weight	578.28
Colour	Black
Habit	Block
Crystal dimension	$0.25mm \times 0.20mm \times 0.20mm$
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
a (Å)	13.1300(5)
b (Å)	17.3071(6)
c (Å)	12.4713(5)
α (°)	90
β(°)	104.5210(10)
γ (°)	90(1)
Volume (Å <sup>3</sup> )	2743.48(18)
Ζ	4
Temperature	293(2)K
$D_C (Mg/m^3)$	1.400
Absorption coefficient (mm <sup>-1</sup> )	0.872
F(000)	1200
λ (Mo Kα) (Å)	0.71073
$\theta$ range (°)	1.6-28.7
Scan type	ω, φ
Index ranges	$-17 \le h \le 17, -23 \le k \le 21, -16 \le l \le 14$
Reflections collected/unique	33535/7081
R <sub>int</sub>	0.0300
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Diffractometer	Bruker axs kappa APEX2 CCD
Absorption correction	Multi-scan SADABS
Final R indices $R_1/wR_2$ [I > $2\sigma(I)$ ]	0.0326/0.0841
$R_1/wR_2$ (all data)	0.0510/0.0992
Goodness-of-fit on F <sup>2</sup>	1.079
$\Delta  ho_{\rm max}$ and $\Delta  ho_{\rm min}$ (eÅ <sup>-3</sup> )	0.30 and -0.26
Data/restraints/parameters	7081/0/344

Schiff base moiety of the complex is not planar with dihedral angle between aminothiophenol moiety and 5-methoxysalicylidene moiety being 16.72(6) Å. The phenyl ring (C21...C26) form fairly strong C—H··· $\pi$  contacts with H6b\_\$1 (2.586(12) Å, symm\_\$1: 1 – *x*, –*y*, –*z*), H13\_\$2 (2.794(3) Å, symm\_\$2: 2 – *x*, –*y*, 1 – *z*) and H32\_\$3 (2.619(3) Å, symm\_\$3: *x*, -1/2 - y, -1/2 + z) to form a three dimensional network. Packing diagram (Fig. 8) was produced using the program MERCURY [20]. The dihedral angles between phenyl

## Table 3 Selected bond lengths (Å) and angles (°).

Bond lengths (Å)		Bond angles (°)	
Ni1-01	1.8461(13)	01-Ni1-N1	94.96(6)
Ni1-N1	1.9028(15)	01-Ni1-S1	175.08(3)
Ni1-S1	2.1297(5)	N1-Ni1-S1	89.72(5)
Ni1—P1	2.1875(5)	01-Ni1-P1	85.22(4)
S1-C14	1.7481(19)	N1-Ni1-P1	177.17(5)
P1-C15	1.8276(17)	S1-Ni1-P1	90.03(19)
P1-C21	1.8132(19)	C14-S1-Ni1	98.23(6)
P1-C27	1.8142(19)	C27-P1-C21	107.60(9)
01-C2	1.307(3)	C27-P1-C15	102.41(8)
N1-C8	1.298(15)	C21-P1-C15	105.04(8)
N1-C9	1.430(14)	C27—P1—Ni1	116.57(6)
C1-C2	1.405(3)	C21-P1-Ni1	104.66(6)
C1-C8	1.415(3)	C15-P1-Ni1	119.61(6)
C9-C14	1.389(3)	C8-N1-C9	119.31(16)
C5—02	1.375(2)	C8-N1-Ni1	122.95(13)
02—C6	1.410(3)	C9-N1-Ni1	117.57(11)
		C2-01-Ni1	126.12(13)
		N1-C8-C1	126.87(18)
		C2-C1-C8	122.13(18)
		C9-C14-S1	118.66(14)
		C7-C5-02	114.90(19)
		02-C5-C4	125.4(2)
		C5-02-C6	116.75(18)



**Fig. 8.** Schematic drawing of the crystal packing showing  $C \rightarrow H \cdots \pi$  interactions. The hydrogen atoms except those involved in interactions are omitted for clarity.

rings of the triphenylphosphine and the mean plane of Schiff base are  $39.85(7)^{\circ}$  (C27...C32),  $86.00(5)^{\circ}$  (C21...C26),  $88.11(5)^{\circ}$  (C15...C20) showing their asymmetric orientation with respect to Schiff base which is in agreement with the <sup>13</sup>C NMR data which reveal that two of the phenyl rings of triphenylphosphine are almost chemically similar and other one is different.

#### 4. Conclusion

Mononuclear Ni(II) complex of the type [Ni(L)(PPh<sub>3</sub>)] [H<sub>2</sub>L=N-(2-mercaptophenyl)-4-methoxysalicylideneimine] was prepared and characterized by 2D NMR, IR and electronic spectroscopy. Structure of the complex was determined by X-ray crystallography, which is stabilized by various strong C–H··· $\pi$  interactions. <sup>13</sup>C NMR and X-ray crystal structure of complex reveal that two of the phenyl rings of triphenylphosphine are almost chemically similar and other one is different which was supported by 2D NMR studies.

#### Supplementary data

CCDC 749110 contains the supplementary crystallographic data of the complex. These data can be obtained free of charge via www.ccdc.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.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2010.06.004.

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