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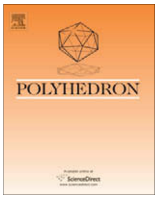

Synthesis, crystal structures and spectral studies of square planar nickel(II) complexes containing an ONS donor Schiff base and triphenylphosphine

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ABSTRACT

Five mononuclear nickel(II) complexes, *viz.* [Ni(L1)(PPh_3)] (**1**), [Ni(L2)(PPh_3)] (**2**), [Ni(L3)(PPh_3)] (**3**), [Ni(L4)(PPh_3)] (**4**) and [Ni(L5)(PPh_3)] (**5**) (where L1, L2, L3, L4 and L5 are dianions of *N*-(2-mercaptophenyl)salicylideneimine, 5-methyl-*N*-(2-mercaptophenyl)salicylideneimine, 5-chloro-*N*-(2-mercaptophenyl)salicylideneimine, 5-bromo-*N*-(2-mercaptophenyl)salicylideneimine and *N*-(2-mercaptophenyl)naphthylideneimine, respectively), have been synthesized and characterized by means of elemental analysis, electronic, IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy. Single crystal X-ray analysis of two of the complexes (**1** and **5**) has revealed the presence of a square planar coordination geometry (ONSP) about nickel. The crystal structures of the complexes are stabilized by intermolecular π–π stacking between the ligands (L) and by various C–H···π interactions.

1. Introduction

The synthesis of geometrically distorted nickel(II) complexes with mixed N and S donor sets is the research interest of many groups [1]. Nickel is present in the active sites of several important classes of metalloproteins, such as 2-mercaptoethanol-inhibited urease and Ni/Fe hydrogenases [2]. The nickel coordination sphere in both of these metalloenzyme systems contains N and S donor sets. These features led to increased interest in the synthesis of nickel(II) complexes with mixed N,S donating chelates as structural and spectroscopic models of the active sites. There are many reports available for nickel(II) complexes with N,S donor ligands [3], but nickel(II) complexes containing N,S donor ligands as well as triphenylphosphine are very rare [4]. Complexes of this kind are interesting in terms of both models of the active sites and homogeneous catalysis.

In addition, *N*-(2-mercaptophenyl)salicylideneimine exhibits different kinds of coordination modes with different metal ions. It behaves as a bifunctional tridentate ligand with Tc(V), Re(V), Ru(II) and Ru(III) [5–7]. The same ligand shows monofunctional tridentate coordination with Co(II), Cu(II) and Zn(II) [8] and monofunctional bidentate coordination with Ru(I) [9]. Hence, we intend to investigate the coordination behaviour of *N*-(2-mercaptophenyl)salicylideneimine, its derivatives and *N*-(2-mercaptophenyl)naphthylideneimine with Ni(II). Here, we report square planar nickel(II) complexes of O,N,S donor ligands and triphenylphosphine. These complexes were characterized by IR, electronic and NMR spectral data. The structures of two complexes have been determined by single crystal X-ray crystallography. The general structures of the ONS Schiff base ligands used in this study are depicted in Fig. 1.

2. Experimental

2.1. Materials

All the chemicals used were of analytical grade. Solvents were purified and dried according to standard procedures [10]. $NiCl_2 \cdot 6H_2O$ was purchased from Qualigens Fine Chemicals and was used without further purification. The starting complex $[NiCl_2(PPh_3)_2]$ was prepared by the reaction between $NiCl_2 \cdot 6H_2O$ and triphenylphosphine in glacial acetic acid [11]. The Schiff base ligands were prepared by the condensation between salicylaldehyde, its derivatives or 2-hydroxy-1-naphthaldehyde and *o*-aminothiophenol in ethanol [5,12].

2.2. Physical measurements

Electronic spectra were measured on a Perkin Elmer EZ 301 UV–Vis double beam spectrophotometer for CH_3CN solutions of the complexes in the 200–800 nm range. FT-IR spectra were recorded

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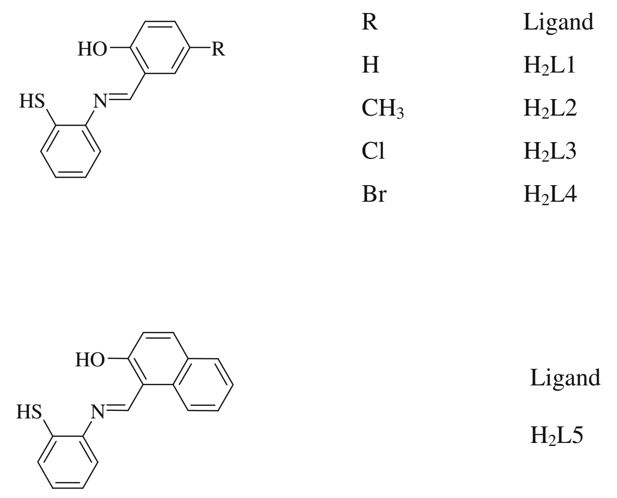

Fig. 1. General structures of the ligands.

on a Perkin Elmer Spectrum One FT-IR spectrometer as KBr pellets in the frequency range 400–4000 cm^{-1}. The C, H, N and S contents were determined by a Thermoflash EA1112 series elemental analyzer. ^{1}H, ^{13}C, HSQC and HMBC NMR spectra were recorded in a Bruker AMX 400 instrument using TMS as the internal standard. ^{31}P NMR spectra were recorded in a Bruker AMX 400 instrument in $CDCl_3$ with H_3PO_4 as a reference. Melting points were determined with a Khora digital melting point apparatus.

2.3. X-ray crystallography

Single crystals of **1** and **5** for X-ray diffraction studies were grown at room temperature from a dichloromethane solution by the diffusion of diethyl ether vapour. Diffraction data were collected on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) [13] and refined by full-matrix least squares fitting based on F^2 using the program SHELXL-97 [14]. 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.

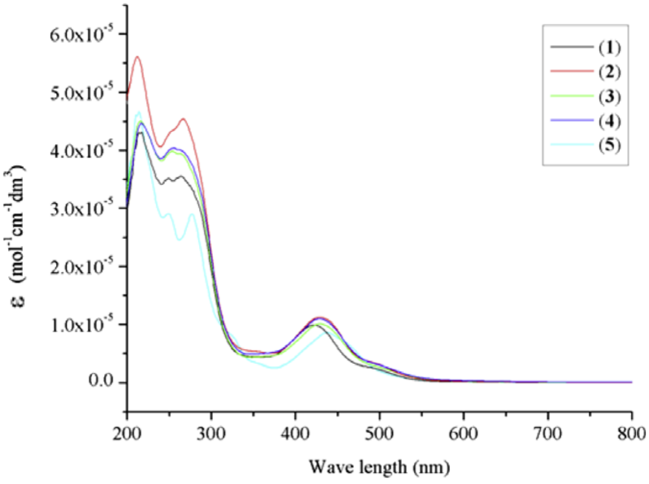

Fig. 2. Electronic spectra of the nickel(II) complexes.

2.4. Synthesis of Ni(II) complexes

All the complexes were prepared by stirring an ethanolic solution of $[NiCl_2(PPh_3)_2]$ with dichloromethane solutions of the ligands in a 1:1 molar ratio for 2 h at 25–27 °C. The resulting dark brown solutions were concentrated to approximately 3 cm^3 and cooled. Hexane (20 cm^3) 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.

$[Ni(L1)(PPh_3)]$ (**1**) is prepared from $[NiCl_2(PPh_3)_2]$ (0.5 g; 0.764 mmol) and H_2L1 (0.175 g; 0.764 mmol). Yield: 59%. *Anal.*Calc.

Table 1
Infrared spectral data (cm^{-1}) for the ligands and their Ni(II) complexes.

Compound	ν(C=N)	ν(C–O)	ν(C–S)	ν(Ni–O)	ν(Ni–N)	Bands due to PPh_3
H_2L1	1614	1316	754			
H_2L2	1622	1323	756			
H_2L3	1621	1321	753			
H_2L4	1612	1317	757			
H_2L5	1610	1304	757			
(**1**)	1607	1334	746	528	457	1433, 1095, 691
(**2**)	1615	1341	744	532	455	1435, 1096, 693
(**3**)	1619	1325	743	527	455	1434, 1093, 695
(**4**)	1603	1326	752	529	459	1437, 1098, 694
(**5**)	1598	1321	750	529	456	1435, 1097, 695

Table 2
^{1}H, ^{13}C and ^{31}P NMR spectral data of the Ni(II) complexes.

Complex	^{1}H (ppm)	^{13}C (ppm)	^{31}P (ppm)
(**1**)	6.4–8.0 (m, 23H, aromatic), 8.9 (d, $J = 10.36$ Hz, 1H, –CH=N–)	163.98, 154.51, 149.82, 143.98, 143.85, 134.84, 134.72, 133.98, 133.00, 130.59, 130.57, 129.43, 129.00, 128.62, 128.60, 128.21, 128.11, 126.70, 121.88, 121.63, 119.30, 115.44, 114.84	22.3
(**2**)	2.3 (s, 3H, $–CH_3$), 6.3–8.0 (m, 22H, aromatic), 8.8 (d, $J = 9.36$ Hz, 1H, –CH=N–)	162.44, 154.25, 149.99, 144.46, 144.32, 135.95, 134.86, 134,72, 132.73, 130.55, 130.42, 129.69, 129.08, 128.63, 128.20, 128.07, 128.02, 126.52, 124.23, 121.83, 121.35, 118.84, 114.76, 20.23	22.3
(**3**)	6.3–8.0 (m, 22H, aromatic), 8.8 (d, $J = 9.03$ Hz, 1H, –CH=N–)	162.53, 153.46, 149.43, 144.48, 144.33, 134.79, 134.66, 133.94, 131.84, 130.70, 130,67, 129.36, 128.74, 128.66, 128.28, 128.14, 127.06, 123.07, 122.03, 119.90, 119.54, 114.95	22.4
(**4**)	6.3–8.0 (m, 22H, aromatic), 8.8 (d, $J = 9.34$ Hz, 1H, –CH=N–)	162.83, 153.39, 149.91, 144.42, 144.24, 136.46, 135.06, 134.79, 134.66, 130.72, 130.67, 129.35, 128.73, 128.66, 128.29, 128.16, 127.09, 123.50, 122.05, 120.83, 114.97, 106.28	22.5
(**5**)	6.3–8.1 (m, 25H, aromatic), 8.8 (d, $J = 10.27$ Hz,1H, –CH=N–)	164.93, 151.12, 148.32, 143.23, 142.96, 134.84, 134.63, 134.19, 130.64, 130.60, 129.70, 129.08, 128.80, 128.32, 128.10, 127.58, 127.06, 126.03, 124.24, 122.77, 121.98, 118.94, 114.85, 110.29	25.2

for $C_{31}H_{24}NNiOPS$: C, 67.90; H, 4.41; N, 2.55; S, 5.85. Found: C, 67.02; H, 3.96; N, 2.41; S, 6.11%. $\lambda_{max}(\varepsilon)$ CH_3CN: 213(42900), 249(35135), 264(35496), 422(9885) nm(dm^3 mol^{-1} cm^{-1}). Decomposition temperature 230 °C.

[Ni(L2)(PPh_3)] (**2**) is prepared from [$NiCl_2(PPh_3)_2$] (0.25 g; 0.382 mmol) and H_2L2 (0.093 g; 0.382 mmol). Yield: 67%. *Anal*Calc. for $C_{32}H_{26}NNiOPS$: C, 68.35; H, 4.66; N, 2.49; S, 5.70. Found: C, 67.99; H, 4.23; N, 2.80; S, 6.00%. $\lambda_{max}(\varepsilon)$ CH_3CN: 216(56603), 253(43880), 267(45735), 431(11252) nm(dm^3 mol^{-1} cm^{-1}). Decomposition temperature 234 °C.

[Ni(L3)(PPh_3)] (**3**) is prepared from [$NiCl_2(PPh_3)_2$] (0.5 g; 0.764 mmol) and H_2L3 (0.202 g; 0.764 mmol). Yield: 58%. *Anal*Calc. for $C_{31}H_{23}ClNNiOPS$: C, 63.90; H, 3.98; N, 2.40; S, 5.32. Found: C, 63.34; H, 3.52; N, 2.56; S, 5.85%. $\lambda_{max}(\varepsilon)$ CH_3CN: 216(45411), 253(40015), 267(39532), 429(10094) nm(dm^3 mol^{-1} cm^{-1}). Decomposition temperature 246 °C.

[Ni(L4)(PPh_3)] (**4**) is prepared from [$NiCl_2(PPh_3)_2$] (0.5 g; 0.764 mmol) and H_2L4 (0.25 g; 0.764 mmol). Yield: 40%. *Anal.* Calc. for $C_{31}H_{23}BrNNiOPS$: C, 59.37; H, 2.23; N, 2.55; S, 5.11. Found: C, 59.18; H, 2.45; N, 2.27; S, 5.71%. $\lambda_{max}(\varepsilon)$ CH_3CN: 212(45269), 253(40509), 267(40334), 428(11001) nm(dm^3 mol^{-1} cm^{-1}). Decomposition temperature 239 °C.

[Ni(L5)(PPh_3)] (**5**) is prepared from [$NiCl_2(PPh_3)_2$] (0.5 g; 0.764 mmol) and H_2L5 (0.214 g; 0.764 mmol). Yield: 57%. *Anal.* Calc. for $C_{35}H_{26}NNiOPS$: C, 70.26; H, 4.38; N, 2.34; S, 5.36. Found: C, 69.66; H, 3.85; N, 2.18; S, 6.53%. $\lambda_{max}(\varepsilon)$ CH_3CN: 199(46749), 249(29007), 276(28964), 328(7516), 438(8550), 468(5901) nm (dm^3 mol^{-1} cm^{-1}). Decomposition temperature 245 °C.

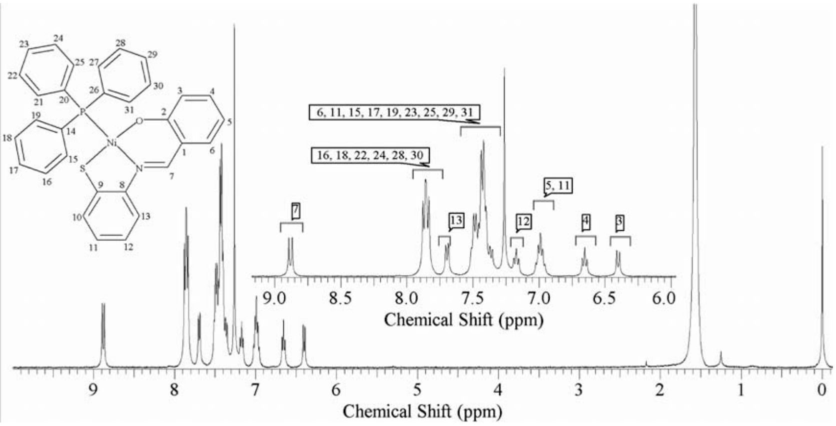

Fig. 3. ^{1}H NMR spectrum of [Ni(L1)(PPh_3)].

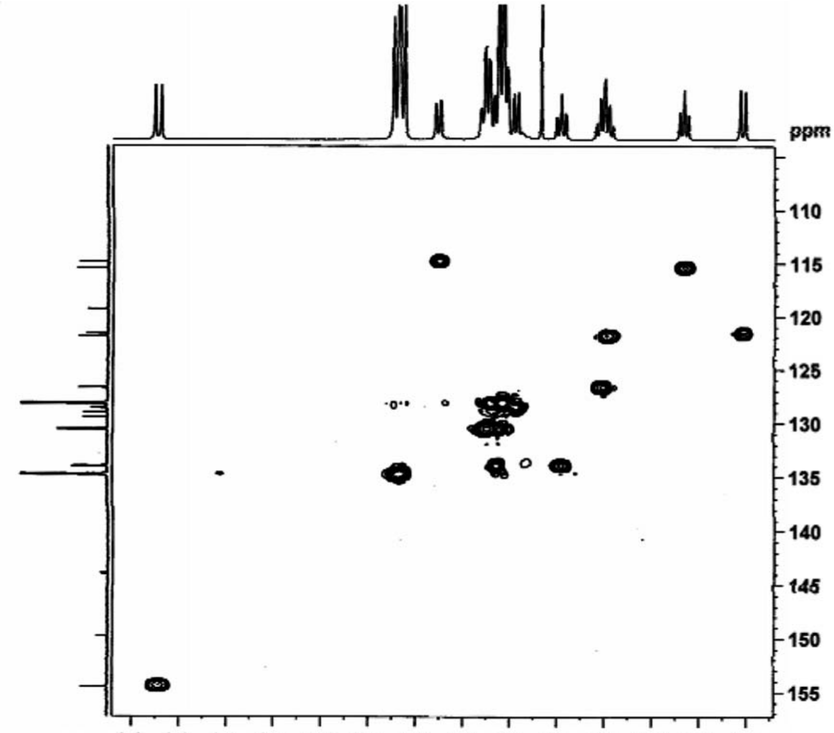

Fig. 4. HSQC spectrum of [Ni(L1)(PPh_3)].

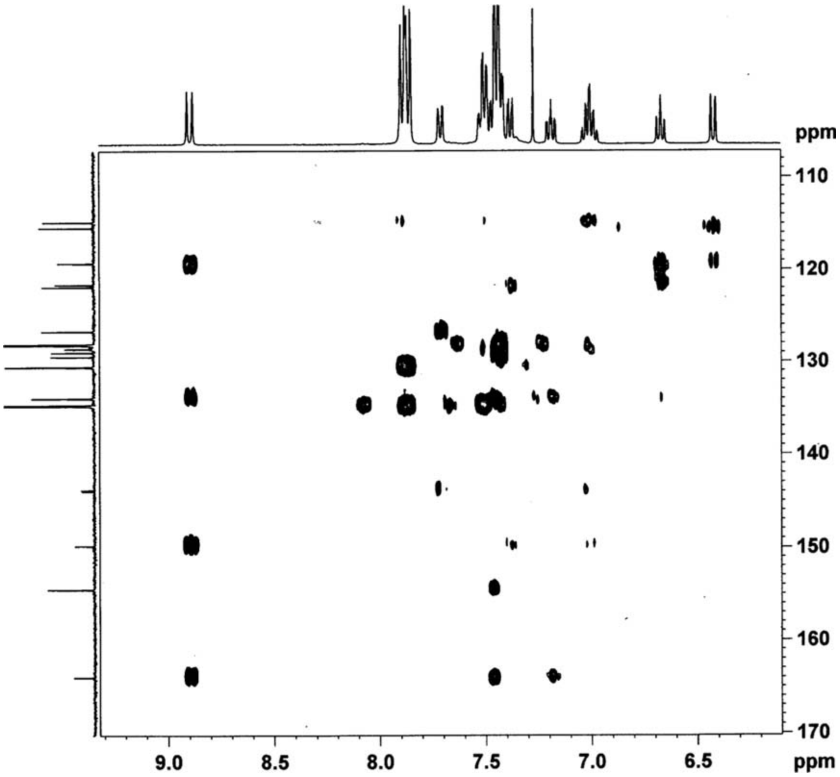

Fig. 5. HMBC spectrum of [Ni(L1)(PPh$_3$)].

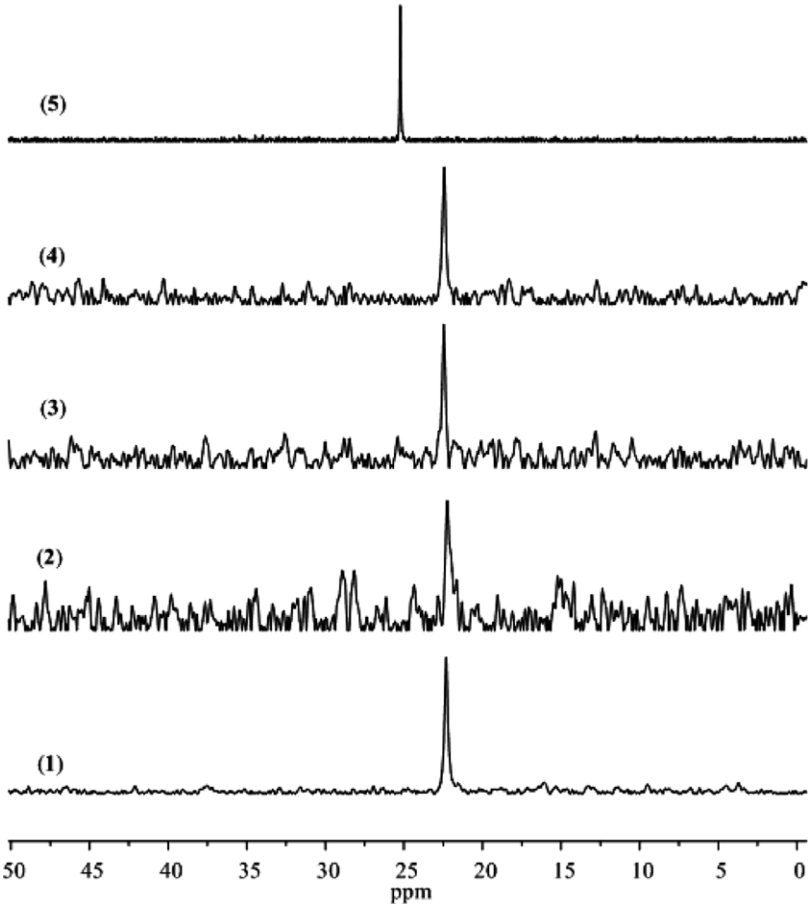

Fig. 6. ^{31}P NMR spectra of the nickel(II) complexes.

Table 3
Crystal data, data collection and structure refinement parameters for (**1**) and (**5**).

Parameters	(**1**)	(**5**)
Empirical formula	$C_{31}H_{24}NNiOPS$	$C_{35}H_{26}NNiOPS$
Formula weight	548.25	598.31
Colour	dark brown	dark brown
Habit	block	block
Crystal dimensions (mm)	0.52 × 0.42 × 0.35	0.59 × 0.55 × 0.48
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	8.9703(4)	13.1734(4)
b (Å)	9.9644(4)	17.2572(6)
c (Å)	14.3335(6)	12.6594(4)
α (°)	99.836(1)	90
β (°)	94.904(1)	130.720(1)
γ (°)	97.785(1)	90
Volume (Å^3)	1242.95(9)	2795.82(16)
Z	2	4
T (K)	100(2)	100(2)
D_C (Mg/m^3)	1.465	1.421
Absorption coefficient (mm^{-1})	0.955	0.856
$F(0\,0\,0)$	568	1240
λ (Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
θ Range (°)	2.58–29.96	2.33–29.99
Scan type	ω, φ	ω, φ
Index ranges	$-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-20 \leqslant l \leqslant 20$	$-18 \leqslant h \leqslant 17$, $-20 \leqslant k \leqslant 24$, $-17 \leqslant l \leqslant 17$
Reflections collected/unique	18 052/7114	29 095/8103
R_{int}	0.0161	0.0185
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Diffractometer	Bruker SMART APEX CCD	Bruker SMART APEX CCD
Absorption correction	multi-scan SADABS	multi-scan SADABS
Final R indices R_1/wR_2 [$I > 2\sigma(I)$]	0.0285/0.0750	0.0244/0.0651
R_1/wR_2 (all data)	0.0302/0.0762	0.0269/0.0665
Goodness-of-fit (GOF) on F^2	1.051	1.038
$\Delta\rho_{max.}$ (e Å^{-3})	0.70 and −0.26	0.42 and −0.33
Data/restraints/parameters	7114/0/325	8103/117/361

3. Results and discussion

The reaction of equimolar ratios of the ligands (H_2L) and [$NiCl_2(PPh_3)_2$] yielded the new complexes of the general formula [$Ni(L)(PPh_3)$] (L = dianionic Schiff base ligand) in moderate to good yield. All the present complexes were brown in colour. They were found to be soluble in CH_2Cl_2, CH_3CN, C_6H_6, DMSO, DMF and C_2H_5OH. The analytical data for these complexes are in good agreement with the above molecular formula. In all the reactions, it has been observed that the Schiff base behaves as a bifunctional tridentate ligand by substituting one of the triphenylphosphine ligands and both the chloride ions from the starting complex.

3.1. Electronic spectra

The electronic spectra of the complexes (Fig. 2) **1**, **2**, **3** and **4** in CH_3CN showed four bands in the region 198–431 nm. The bands appearing in the region 198–267 nm have been assigned to intraligand transitions. A less intense band in range 423–431 nm corresponds to a forbidden $d \rightarrow d$ transition. Complex **5** displayed six bands in the 199–469 nm range. The extra bands are due to the additional phenyl ring present in the ligand. Four bands in the region 199–323 nm are due to intraligand transitions and two bands at 438 and 469 nm are due to forbidden $d \rightarrow d$ transitions. The same behaviour has been observed in the electronic spectra of other similar square planar nickel(II) complexes [4,15].

3.2. IR spectra

Selected IR bands of the ligands and complexes are listed in Table 1. The spectra of the ligands exhibit a strong band around 1610–1622 cm^{-1}, which is assigned to a ν(C=N) vibration. As a result of coordination, this band shifts to a lower wavenumber by *ca.* 10 cm^{-1} in the complexes [4,16]. The band in the region

Table 4
Selected bond lengths (Å) and angles (°).

(**1**)		(**5**)	
Ni(1)–O(1)	1.8496(9)	Ni(1)–O(1)	1.8448(8)
Ni(1)–N(1)	1.9096(10)	Ni(1)–N(1)	1.8956(8)
Ni(1)–S(1)	2.1359(3)	Ni(1)–S(1)	2.1369(3)
Ni(1)–P(1)	2.2164(3)	Ni(1)–P(1)	2.1894(3)
S(1)–C(9)	1.7512(12)	S(1)–C(12)	1.7499(10)
P(1)–C(20)	1.8196(12)	P(1)–C(24)	1.8202(10)
P(1)–C(26)	1.8211(11)	P(1)–C(30)	1.8206(10)
P(1)–C(14)	1.8214(11)	P(1)–C(18)	1.8228(10)
O(1)–C(2)	1.2995(14)	O(1)–C(2)	1.2968(12)
N(1)–C(7)	1.3054(15)	N(1)–C(11)	1.3137(12)
N(1)–C(8)	1.4268(14)	N(1)–C(13)	1.4247(13)
C(1)–C(2)	1.4088(16)	C(1)–C(2)	1.4134(14)
C(8)–C(9)	1.3960(16)	C(12)–C(13)	1.4012(13)
C(1)–C(7)	1.4216(17)	C(1)–C(11)	1.4169(14)
O(1)–Ni(1)–N(1)	95.37(4)	O(1)–Ni(1)–N(1)	94.34(3)
O(1)–Ni(1)–S(1)	173.98(3)	O(1)–Ni(1)–S(1)	175.08(2)
N(1)–Ni(1)–S(1)	89.32(3)	N(1)–Ni(1)–S(1)	90.15(3)
O(1)–Ni(1)–P(1)	82.58(3)	O(1)–Ni(1)–P(1)	85.10(2)
N(1)–Ni(1)–P(1)	174.75(3)	N(1)–Ni(1)–P(1)	177.24(3)
S(1)–Ni(1)–P(1)	93.056(12)	S(1)–Ni(1)–P(1)	90.311(11)
C(9)–S(1)–Ni(1)	98.64(4)	C(12)–S(1)–Ni(1)	97.76(3)
C(20)–P(1)–C(26)	104.11(5)	C(24)–P(1)–C(30)	106.73(5)
C(20)–P(1)–C(14)	104.63(5)	C(24)–P(1)–C(18)	104.79(4)
C(26)–P(1)–C(14)	105.55(5)	C(30)–P(1)–C(18)	102.19(4)
C(20)–P(1)–Ni(1)	113.56(4)	C(24)–P(1)–Ni(1)	105.04(3)
C(26)–P(1)–Ni(1)	107.01(4)	C(30)–P(1)–Ni(1)	117.88(3)
C(14)–P(1)–Ni(1)	120.57(4)	C(18)–P(1)–Ni(1)	119.02(3)
C(2)–O(1)–Ni(1)	128.25(8)	C(11)–N(1)–C(13)	118.87(9)
C(7)–N(1)–C(8)	118.68(10)	C(11)–N(1)–Ni(1)	123.28(7)
C(7)–N(1)–Ni(1)	122.90(8)	C(13)–N(1)–Ni(1)	117.73(6)
C(8)–N(1)–Ni(1)	118.37(8)	C(2)–O(1)–Ni(1)	127.63(7)
N(1)–C(7)–C(1)	127.12(11)	N(1)–C(11)–C(1)	127.45(9)
C(2)–C(1)–C(7)	122.53(11)	C(2)–C(1)–C(11)	120.51(9)
C(8)–C(9)–S(1)	118.42(8)	C(13)–C(12)–S(1)	118.67(8)

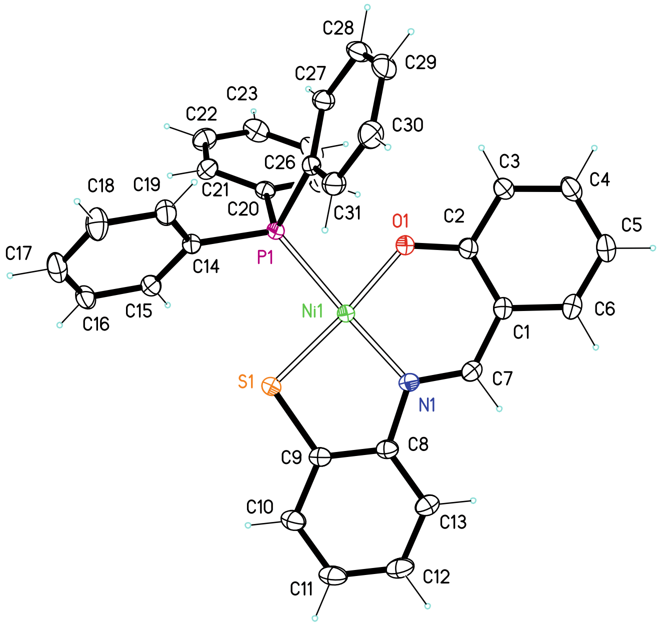

Fig. 7. Molecular structure of complex **1** showing 50% displacement ellipsoids.

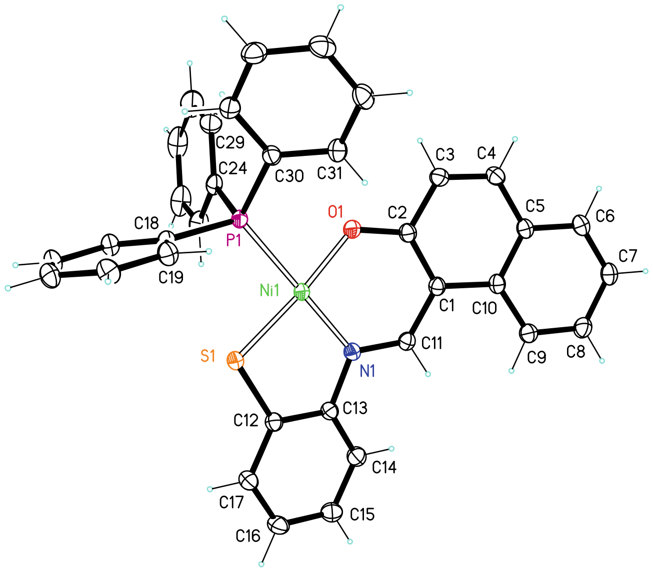

Fig. 8. Molecular structure of complex **5** showing 50% displacement ellipsoids.

1304–1323 cm^{-1}, which is assigned to phenolic ν(C–O) in the free ligand, is shifted to a higher wavenumber in the complexes, suggesting the coordination of the phenolic oxygen atom to the nickel ion [4,16]. A weak band observed in the region 753–757 cm^{-1}, corresponding to ν(C–S) in the ligands, shifts to a lower wavenumber (743–752 cm^{-1}) which supports sulfur coordination with the nickel centre [17]. The bands around 530 and 460 cm^{-1} in all the complexes are assigned to ν(Ni–O) and ν(Ni–N), respectively [18]. Bands due to triphenylphosphine also appear in the expected region [19].

3.3. NMR spectra

^{1}H, ^{13}C and ^{31}P NMR spectral data of the complexes are given in Table 2. All the nickel(II) complexes exhibit a multiplet around 6.3–8.1 ppm, which has been assigned to the protons of the phenyl groups present in triphenylphosphine and the Schiff base ligand. A doublet observed at 8.8 ppm in the complexes has been assigned to the azomethine proton (–C=N–) [20]. Complex **3** exhibits a singlet at 2.3 ppm, corresponding to methyl protons. The absence of a resonance due to phenolic and thiolato hydrogen atoms indicates the deprotonation of these groups and the Schiff bases behave as dianionic ligands. The ^{1}H NMR spectrum of **1** is depicted in Fig. 3. In the ^{13}C NMR spectra of all the complexes, azomethine carbon resonances are observed in the 151.12–154.49 ppm range. The resonances for C–S, C–N, C–O and C–P are observed in the regions 129.00–129.69, 149.32–149.99, 162.44–164.93 and 142.96–144.48 ppm, respectively [21,22]. The ^{13}C NMR and DEPT 135 spectra of **1** revealed the presence of seven different carbons (119.30, 129.00, 129.46, 143.85, 143.98, 149.82 and 163.98 ppm). This indicates that the three quaternary carbons arising from triphenylphosphine aromatic units are in different magnetic environments. The HSQC correlation spectrum of **1** (Fig. 4) establishes the connection between the imine proton (δ_H = 8.89, d, J = 10.36 Hz, 1H) and C-7 (δ_C = 154.51). The interaction of the imine proton (δ_H = 8.89, d, J = 10.36 Hz, 1H) with three quaternary carbons *viz.* C-1 (δ_C = 119.30), C-2 (δ_C = 163.98) and C-8 (δ_C = 149.82) and the methine carbon C-6 (δ_C = 134.00) has been understood from the HMBC correlation spectrum (Fig. 5). The ^{31}P NMR spectra of all the complexes exhibit a singlet around 22.3–25.2 ppm, suggesting the presence of one coordinated triphenylphosphine ligand in these nickel(II) complexes [23]. The ^{31}P NMR spectra of all the complexes are given in Fig. 6.

3.4. X-ray crystallography

The compounds **1** and **5** were structurally determined by X-ray crystallography. The crystallographic and measurement data are shown in Table 3 and representative bond lengths and bond angles are listed in Table 4. Figs. 7 and 8 present thermal ellipsoid representations of complexes **1** and **5**, respectively. In both the complexes, the nickel(II) atom is four coordinated in a square planar geometry by the Schiff base and triphenylphosphine ligands. The Schiff base acts as a tridentate ligand through the thiolato sulfur atom, the imine N and the phenolic O atom. Two units of [Ni(L1)(PPh$_3$)] and four units of [Ni(L5)(PPh$_3$)] are present in their respective unit cells. As expected for four coordinate d^8 metal complexes, the structure of **1** adopts a nearly ideal square planar geometry with O–Ni–S and N–Ni–P bond angles of 173.98(3) and 174.75(3)°, respectively [24]. The other angles around the nickel(II)

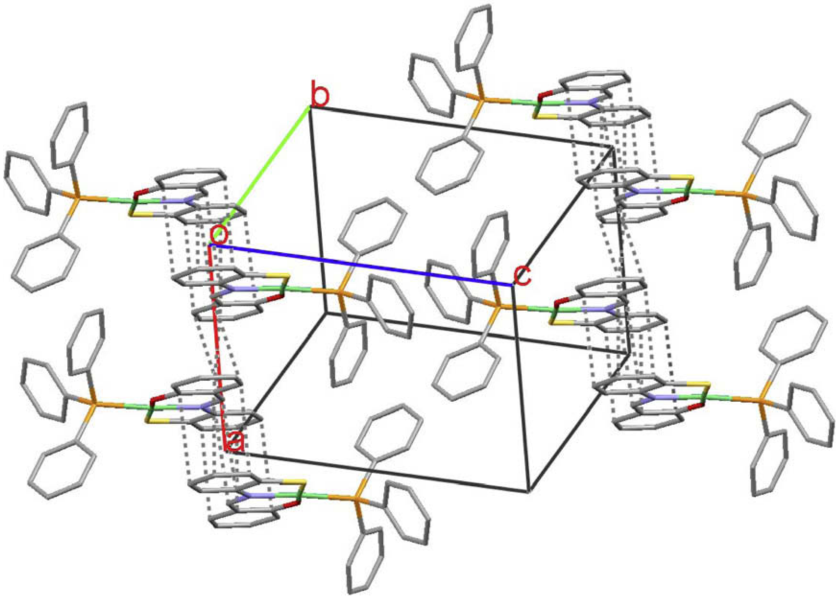

Fig. 9. Schematic drawing of the crystal packing of **1** showing the π–π stacking parallel to the *a*-axis. Hydrogen atoms are omitted.

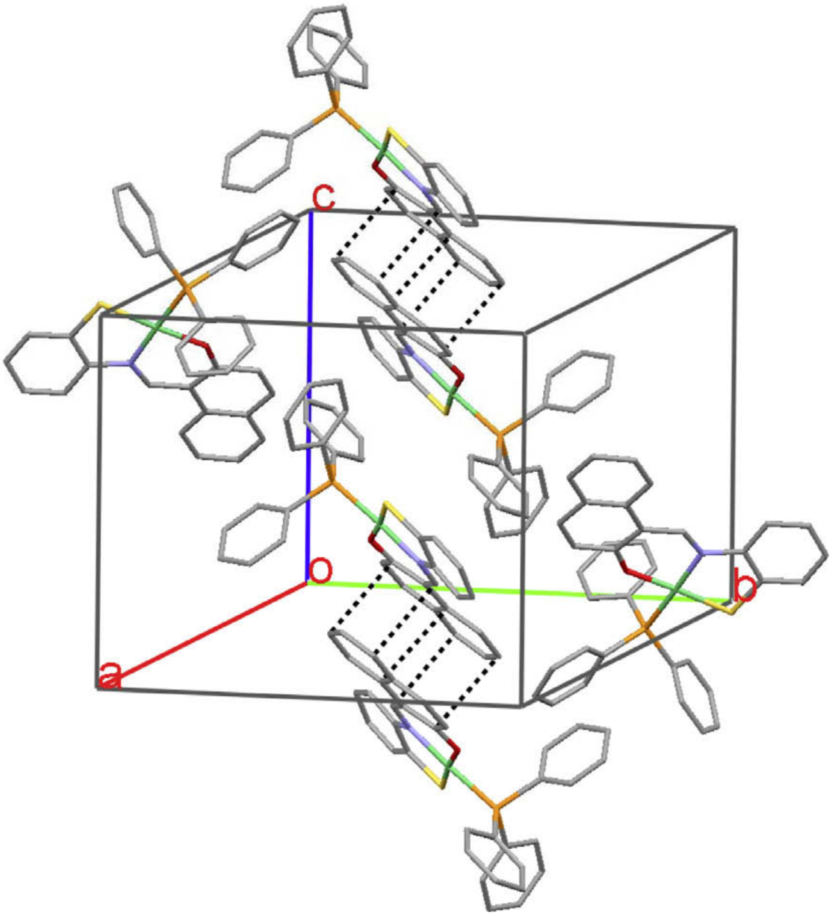

Fig. 10. Schematic drawing of the crystal packing of **5** showing the π–π stacking between pairs of complexes *via* their naphthyl moieties. Hydrogen atoms are omitted.

atom deviate slightly from the ideal value (90°), ranging from 82.58(3) to 95.37(4)°. In structure **5**, the O–Ni–S and N–Ni–P bond angles are 175.08(2) and 177.24(3)°, respectively and other angles around nickel(II) are in the range 85.10(2) to 94.34(3)°. The Ni–P, Ni–O, Ni–N and Ni–S bond distances are in the usual range in both complexes [4]. Disregarding triphenylphosphine, complex **1** is essentially planar, showing a r.m.s. deviation of 0.030 Å of the non-hydrogen atoms from a common least-squares plane, from which the P atom deviates by 0.324(1) Å. Complex **5** is distinctly more aplanar showing for the Ni(L5) moiety a r.m.s. deviation of 0.154 Å from planarity and a significant twist between the phenyl and the naphthyl residues of L5 (interplanar angle 14.15(5)°). These differences between [Ni(L1)(PPh_3)] and [Ni(L5)(PPh_3)] are attributable to differences in crystal packing and intermolecular interactions. The intermolecular interactions in [Ni(L1)(PPh_3)] are characterized by comparatively weak π–π stacks of L1, forming continuous chains along the *a*-axis (Fig. 9). In [Ni(L5)(PPh_3)], there are pairs of complexes π–π stacked via their naphthyl moieties (Fig. 10). The PPh_3 moieties in both [Ni(L1)(PPh_3)] and [Ni(L5)(PPh_3)] do not show π–π stacking but contribute by various C–H⋯π interactions to the coherence of the structures.

4. Conclusion

Mononuclear Ni(II) complexes of the type [Ni(L)(PPh_3)] (L = ONS donor Schiff base ligand) were prepared and characterized by NMR, IR and electronic spectroscopy. Structures of two complexes were determined by X-crystallography, which are stabilized by intermolecular π–π stacking between the ligands (L) and by various C–H⋯π interactions.

Supplementary data

CCDC 663130 and 653443 contain the supplementary crystallographic data for **1** and **5**. 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.

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