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Synthesis, crystal structure, fluorescence and electrochemical studies of a new tridentate Schiff base ligand and its nickel(II) and palladium(II) complexes

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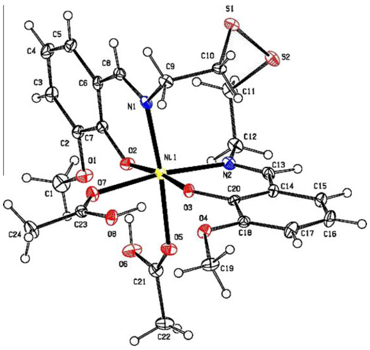
HIGHLIGHTS

- An unsymmetrical tridentate Schiff base with SNO donor atoms was synthesized.
- Two new complexes of nickel and palladium were synthesized with 2:1 (L:M) ratio.
- S–S coupling was occurred in these complexes.
- X-ray structure, ^{1}H NMR, IR and elemental analysis were used for characterization.
- Fluorescence and electrochemistry of the synthesized compounds were investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

A new unsymmetrical tridentate Schiff base ligand was derived from the 1:1 M condensation of ortho-vanillin with 2-mercaptoethylamine. Nickel and palladium complexes were obtained by the reaction of the tridentate Schiff base ligand with nickel(II) acetate tetrahydrate and palladium(II) acetate in 2:1 M ratio. In nickel and palladium complexes the ligand was coordinated to metals via the imine N and enolic O atoms. The S groups of Schiff bases were not coordinated to the metals and S–S coupling was occured. The complexes have been found to possess 1:2 Metal:Ligand stoichiometry and the molar conductance data revealed that the metal complexes were non-electrolytes. The complexes exhibited octahedral coordination geometry. The emission spectra of the ligand and its complexes were studied in methanol. Electrochemical properties of the ligand and its metal complexes were investigated in the CH_3CN solvent at the 100 mV s^{-1} scan rate. The ligand and metal complexes showed both reversible and quasi-reversible processes at this scan rate. The Schiff base and its complexes have been characterized by IR, ^{1}H NMR, UV/Vis, elemental analyses and conductometry. The crystal structure of nickel complex has been determined by single crystal X-ray diffraction.

Introduction

Schiff bases represent one of the most widely utilized classes of ligands in metal coordination chemistry and the chemistry of Schiff bases is an area of increasing interest [1,2]. Schiff bases are capable

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of forming coordinate bonds with many metal ions via azomethine or phenolic groups, and so they have been used for synthesis of metal complexes due to their easy formation and strong metal-binding ability [3–5]. Schiff bases have wide applications in food and dye industries, analytical chemistry, catalysis, fungicidal, agrochemical and biological activities [6–8]. The interest in Schiff base compounds as analytical reagents is increasing since they enable simple and inexpensive determinations of different organic and inorganic substances [9]. Moreover, it was reported that the Schiff bases containing ONS-donors have an important role in biochemistry [10].

Particular attention has been devoted to the metal Schiff base complexes in the last two decades. Schiff bases have been widely used as ligands because of the high stability of coordination compounds with different oxidation states [11]. There is a continuing interest in metal complexes of Schiff bases, because of the presence of hard nitrogen or oxygen and soft sulfur donor atoms in the backbone of these ligands. They readily coordinate with wide range of transition metal ions yielding stable and intense colored metal complexes, some of which have been shown to exhibit interesting physical and chemical properties [12]. Many Schiff base complexes show excellent catalytic activity in various reactions at high temperature and in the presence of moisture and so over the past few years, there have been many reports on their applications in homogeneous and heterogeneous catalysis [13–15]. Moreover, Schiff-base complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety [16]. On the other hand, Schiff base metal complexes have numerous applications such as anticancer [17,6], bactericide agents [18,19], antivirus [20–22] and fungicide agents [23,24]. Many of tridentate Schiff base ligands showed enhanced carcinostatic activity when complexed to transition metal ions [25,26]. Therefore a lot of different Schiff base complexes of metal ions such as Co(II), Cu(II) and Zn(II) have been frequently prepared and their biochemical properties was studied [27].

The chemistry of nickel and palladium complexes with multidentate Schiff base ligands has attracted huge attention because such complexes play an important role in bioinorganic chemistry and redox enzyme systems, and may provide the basis of models for active sites of biological systems or act as catalyst [28]. Although, a lot of Schiff bases with different structures have been synthesized and characterized, however, little attention has been given to Schiff bases which include the SNO-donor system. Thus, in this paper we synthesized a new tridentate Schiff base containing SNO donor atoms and its relevant nickel and palladium complexes. The Schiff base ligand and its complexes were characterized by the FT-IR, ^{1}H NMR, UV–Vis spectroscopy, elemental analysis, magnetic susceptibility, molar conductance and X-ray crystallography. Electrochemical and emission behavior of the Schiff base and its metal complexes were studied by cyclic voltammetry and fluorescence spectroscopy.

Experimental

Materials and physical measurements

All chemicals were reagent grade quality purchased from commercial sources and used as received. Elemental analyses (C, H, N) and metal analyses (Ni and Pd) were performed on a Perkin Elmer 2400 elemental analyzer and GBS Integra XL ICP–OES, respectively. UV–Vis and fluorescence spectra were recorded on an Analytik Jena Specord 205 spectrophotometer and FP-6200 spectrofluorometer, respectively. FT-IR spectra were obtained as KBr pellets on a Perkin–Elmer spectrum RXI FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Avance DPX 500 MHz spectrophotometer, using TMS as an internal standard. The microanalyses were performed using a Perkin–Elmer 2400 series II. Melting points were determined on a Barnstead Electrothermal 9100. Conductivity was measured in DMSO solution (3×10^{-4} M) using a 712 conductometer (Metrohm).

Cyclic voltammograms were performed using a Metrohm Autolab/PGSTAT302N system equipped with a three-compartment cell and a personal computer for data storage and processing. An Ag/AgCl (saturated KCl) reference electrode (Metrohm), a Pt-rod as counter electrode and a platinum disk electrode (i.d. = 2 mm) as working electrode (Metrohm Pt-disk, 0.0314 cm^2) were employed for the electrochemical studies. Voltammetric measurements were performed at room temperature in acetonitrile solution with 0.2 M tetrabutylammonium perchlorate as the supporting electrolyte.

Syntheses

Synthesis of the tridentate Schiff base ligand, *1*

To a solution of 2-mercaptoethylamine (0.050 g, 0.32 mmol) in methanol (6 mL) was added a solution of ortho-vanillin (0.0986 g, 0.32 mmol) in methanol (6 mL) and the mixture was stirred and heated on a water bath at 54 °C (optimum obtained temperature) for 10 h. Then, the solvent was evaporated slowly and a yellow crystalline product separated and washed twice with methanol, dichloromethane and n-hexane. Then, the precipitate was dried in vacuum. (yield: 71%), yellow, m.p: 78 °C, Anal. Calc. for [$C_{10}H_{13}NO_2S$] (**1**): (M.W: 211.28), C, 56.85; H, 6.20; N, 6.63%. Found: C, 56.79; H, 6.12; N, 6.64%; IR (KBr, υ/cm^{-1}): 1629 υ(CN) (imine), 1077 υ(CO) (phenolic), 3436 υ(OH), 1477, υ(C=C) (aromatic), 776 υ(CS), 2847 υ(SH). ^{1}H NMR (400 MHz, DMSO-d$_6$, δ/ppm): 13.42 (1H, s, —OH), 8.52 (1H, s, CH=N), 3.27 (1H, s, S—H), 3.04 (2H, t, S—CH$_2$), 3.85 (2H, t, N—CH$_2$), 6.80–7.00 (phenylic hydrogen group), 3.74 (3H, s, —OCH$_3$).

Synthesis of nickel Schiff base complex, *2*

A methanolic solution (5 mL) containing $Ni(OAc)_2 \cdot 4H_2O$ (0.0176 g, 0.071 mmol) was added slowly to a solution (5 mL) of Schiff base (0.030 g, 0.142 mmol) and the mixture was stirred and heated on a water bath at 56 °C (optimum obtained temperature) for 5 h. A green–brown solution of complex was left to stand for a night. An oily brown precipitate was washed with methanol and ether, and then dried in vacuum. (yield: 80%), m.p: 98 °C, Anal. Calc. for: [$C_{24}H_{30}N_2NiO_8S_2$] (**2**): (M.W: 597.33), C, 48.26; H, 5.06; N, 4.69; Ni, 9.83%. Found: C, 48.18; H, 4.97; N, 4.76, Ni; 9.64%. IR (KBr, υ/cm^{-1}): 1614 υ(CN) (imine), 1108 υ(CO) (phenolic), 1485, υ(C=C) (aromatic), 734 υ(CS), 480 υ(Ni—O), 577 υ(Ni—N). μ_{eff} (298 K): 1.82 B.M.

Synthesis of palladium Schiff base complex, *3*

The synthetic procedure was analogous to that of **2**, except that an ethanolic solution of $Pd(OAc)_2$ (0.030 g, 0.073 mmol) was used instead of $Ni(OAc)_2 \cdot 4H_2O$ and heated on a water bath at 58 °C (optimum obtained temperature) for 10 h. A brown precipitate was obtained and washed with n-hexane, then dried in vacuum. (yield: 68%), m.p: 150 °C (decomp.), Anal. Calc. for [$C_{24}H_{30}N_2PdO_8S_2$] (**3**): (M.W: 645.057), C, 44.69; H, 4.69; N, 4.34; Pd, 16.50%. Found: C, 44.24; H, 4.56; N, 4.28; Pd, 16.20%. IR (KBr, υ/cm^{-1}): 1622 υ(CN) (imine), 1112 υ(CO) (phenolic),1448 υ(C=C) (aromatic), 738 υ(CS), 405 υ(Pd—O), 487 υ(Pd—N). ^{1}H NMR (400 MHz, DMSO-d$_6$, δ/ppm):8.17 (1H, s, CH=N), 2.34 (2H, t, S—CH$_2$), 3.87 (2H, t, N—CH$_2$), 6.65–7.23 (phenylic hydrogens group), 2.96 (3H, s, —OCH$_3$). μ_{eff} (B.M.) (298 K): diamagnetic.

Crystal structure determination and refinement

The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo Kα radiation. For complex **2**, green prismatic shape crystal was chosen using a polarizing microscope and was mounted on a glass fiber which was used for data collection. Cell constants and orientation matrices for data collection were obtained by least-squares refinement of diffraction data from 7076 unique reflections. Data were collected to a maximum 2θ value of 58.34° in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [29] software package. A numerical absorption correction was applied using X-RED [30] and X-SHAPE [31] software. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods [32] and subsequent difference Fourier maps and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [33]. The atomic factors were taken from the International Tables for X-ray Crystallography [34]. All refinements were performed using the X-STEP32 crystallographic software package [35]. A summary of crystal data, experimental details, and refinement results was given in Table 1.

Results and discussion

Synthesis and characterization of compounds

The unsymmetrical tridentate Schiff base ligand was synthesized by the condensation of 2-mercaptoethylamine with ortho-vanillin in MeOH, in a 1:1 M ratio under heating on a water bath and the yellow crystals of the ligand were obtained (Scheme 1). In order to construct the metal complexes, the Schiff base ligand was reacted with nickel(II) acetate tetrahydrate and palladium(II) acetate in 2:1 M ratio in methanol and ethanol respectively. When a 2:1 Ligand:Metal stoichiometry was used, an interesting product formed which S groups of the two Schiff bases were coupled. A strong covalent bond, —S—S—, was important in linking two Schiff bases in nickel and palladium complexes. This linkage was aroused as a result of the oxidation of the thiol groups in the air during the reaction. Also, the crystal structure of the nickel complex showed the formation of —S—S— bond [36–38]. Based on the X-ray crystallography data a distorted octahedral geometry was suggested for the nickel complex. In suggested structure the Schiff base ligands were coordinated to the nickel via the imine N and enolic O atoms. Moreover, based on the spectroscopy data, we suggested that the structure of the palladium complex is similar to the nickel complex. It should be noted that when a 1:1 Ligand:Metal stoichiometry was used, dimer complexes through sulfur bridge can be formed.

Table 1
Crystallographic and structure refinement data for 2.

Empirical formula	$C_{24}H_{30}N_2NiO_8S_2$
Formula weight	597.33
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size (mm^3)	0.17 × 0.15 × 0.15
a (Å)	8.5826(17)
b (Å)	10.957(2)
c (Å)	15.287(3)
α (°)	75.25(3)
β (°)	89.65(3)
γ (°)	72.33(3)
Volume (Å^3)	1320.7(5)
Z	2
Density$_{calc}$ (g cm^{-1})	1.502
θ Ranges for data collection (°)	2.50–29.17
$F(000)$	624
Absorption coefficient (mm^{-1})	0.943
Index ranges	$-11 \leqslant h \leqslant 11$
	$-15 \leqslant k \leqslant 15$
	$-18 \leqslant l \leqslant 20$
Data collected	14808
Unique data, (R_{int})	7076, (0.1161)
Parameters/restrains	346/0
Final R_1/wR_2[a] ($I > 2\sigma(I)$)	0.0839/0.1143
Final R_1/wR_2[a] (all data)	0.1603/0.1337
Goodness-of-fit on F^2 (S)	1.039
Largest diff. peak and hole (e Å^{-3})	0.605, −0.485

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = \left[\sum\left(w(F_o^2 - F_c^2)^2\right)/\sum w(F_o^2)^2\right]^{1/2}$.

Single crystals of **2** were grown by slow diffusion of petroleum ether into a saturated CH_2Cl_2 solution during 7 days at room temperature, whereas suitable single crystals could not be grown for **1** and **3**.

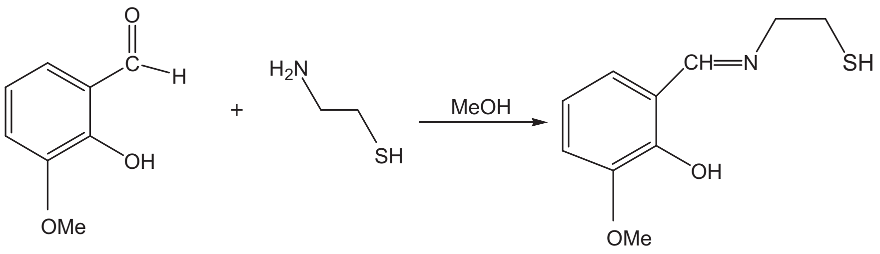
Spectroscopy

IR spectra

In the IR spectra (Fig. 1), all the compounds displayed the characteristic peak in the region 1614–1629 cm^{-1} indicated the formation of Schiff base (—H—C=N) [39]. A comparison of the spectra of the free ligand and the complexes indicated that the ligand was coordinated to the metal centers. Coordination of the azomethine nitrogen to the metals was suggested by the shift of the υ(C=N) band to lower frequencies band in the IR spectra of the nickel and palladium complexes compared with the Schiff base ligand [40,41]. Additional support for the formation of the complexes were provided by the existence of weak intensity bands at 577 and 480 cm^{-1} were attributed to the formation of Ni—N and Ni—O, respectively. Also, two new weak bands at 487 and 405 cm^{-1} were attributed to Pd—N and Pd—O, respectively [42]. The υ(C—O) band in these complexes was shifted approximately 31 cm^{-1} toward a higher frequency, compared with the free ligand, which suggested coordination of the deprotonated phenolic oxygen to the nickel and palladium ions [43]. A weak band in 2848 cm^{-1} due to —SH group in the free Schiff base ligand was not observed in the IR-spectra of the nickel and palladinum complexes [44], revealed that thiolate groups in two moles of Schiff base were deprotonated and coupled to each other in order to form a —S—S— covalent bond. This coupling can be seen in the X-ray structure of the nickel complex. Also, in these compounds the common bands at 620 cm^{-1} and about 734 cm^{-1} were assigned to the S—S and C—S stretches, respectively [45].

^{1}H NMR spectra

The structural assignments were further supported by their ^{1}H NMR spectra. ^{1}H NMR spectra of the compounds were obtained in DMSO-d_6 at room temperature using TMS as the internal standard. In the ^{1}H NMR spectra, the integral intensities of each signal were found to agree with the number of different types of protons present in the Schiff base ligand and its palladium complex. The most important peak in the Schiff base ligand was attributed to a singlet signal due to azomethine proton at the 8.52 ppm that confirmed the formation of Schiff base. Chemical shift of the imine in the Schiff base ligand comparing with the CH=N value of the imines in palladium complex at 8.17 ppm supported nitrogen coordination to the metal center [46]. In the Schiff base ligand and its palladium complex, the protons peaks of O—CH_3 were appeared in 3.74 and 2.96 ppm, respectively. The singlet signal at 13.42 ppm showed the presence of OH proton in the Schiff base ligand and was not observed in palladium Schiff base complex. Moreover, a singlet signal at 3.27 ppm confirmed the presence of SH proton in the Schiff base ligands and was disappeared in the metal Schiff base complex which revealed deprotonation of —SH groups due to the easily S—S coupling. The multiplets of the aromatic protons in **1** and **3** appeared in the range of 6.65–7.23 ppm with different multiplicity and coupling constants. On the other hand, ^{1}H NMR spectrum of Schiff base and its palladium complex indicated the aliphatic protons of —S—CH_2— as a triplet signal at 2.49 and



Scheme 1. The synthetic route of the tridentate Schiff base ligand.

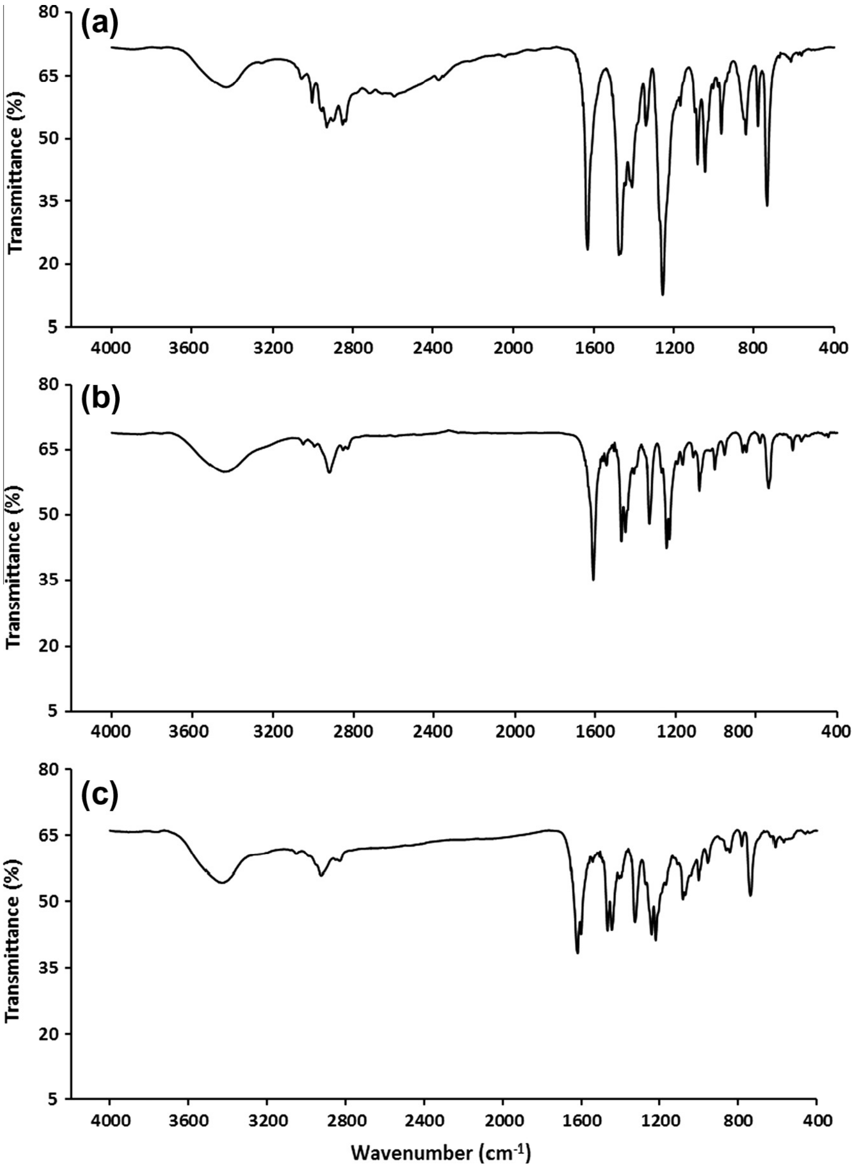


Fig. 1. Infrared spectra of (a) Schiff base, (b) nickel(II) and (c) palladium(II) complex.

3.04 ppm, respectively and also exhibited a triplet signal due to —N—CH_2— resonances at 3.74 and 3.85 ppm which showed a down field shift [47].

Electronic spectra

The electronic spectra of the Schiff base ligand and its complexes were investigated in DMSO solution (6×10^{-5} M). The Schiff base ligand and its complexes exhibit two absorption peaks at a lower energy region (>200 nm). The stronger and higher energy peak (Table 2) was attributed to the $\pi \rightarrow \pi^*$ transition of the azomethine chromophore and the benzene ring, while the weaker and less energetic peak is assigned to the $n \rightarrow \pi^*$ transition involving the promotion of the lone pair electron of azomethine nitrogen atom to the antibonding π orbital associated with the azomethine group [48]. The absorption spectra of the nickel and palladium complexes bands were observed at 390 and 419 nm which was a

Table 2
The electronic spectra data (nm) of Schiff base and relevant metal co mplexes.

Compounds	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$d \rightarrow d$
1	270	330	–
2	280	390	525
3	266	419	522

higher wavelength shifting of the azomethine band of $n \rightarrow \pi^*$ showing the coordination of the nickel and palladium with CH=N. Weak bands observed in the 525 nm ($\varepsilon = 1300\ M^{-1}\ cm^{-1}$) and 522 nm ($\varepsilon = 670\ M^{-1}\ cm^{-1}$) were due to d–d transition in nickel and palladium complexes, respectively [49].

Fluorescence spectral studies

The emission spectra of the Schiff base ligand and its nickel complex (**1** and **2**) were investigated at room temperature (298 K) in methanol solution (Fig. 2). The Schiff base ligand was characterized by emission band around 429 and 489 nm upon photo excitation at 424 nm. The emission observed in the Schiff base was assigned to the $\pi \rightarrow \pi^*$ intraligand fluorescence. The fluorescence of the ligand was probably quenched by the occurrence of a photoinduced electron transfer (PET) process due to the presence of a lone pairs of electrons of the donor atoms in the ligand (N and O) [50]. On the other hand, the Ni(II) complex was characterized by the emission band at 530 nm with a higher emission intensity than the Schiff base. Since, PET process is prevented by the complexation of the Schiff base ligand with metal ion; thus the fluorescence intensity can be greatly enhanced by the coordination of Ni(II). Moreover, the complex was coordinated with two Schiff base ligands and the $\pi \rightarrow \pi^*$ intramolecular electron transition was accordingly much higher [50,51] and the chelation of the ligands to metal ion increases their rigidity and thus reduces the loss of energy by thermal vibration decay [52].

Eelectrochemical studies of the Schiff base and its complexes

Cyclic voltammetry was performed with 2×10^{-3} M solutions of Schiff base and its complexes in CH_3CN with 0.2 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte and scan rates 100 mV/s within the potential range +2.0 to −2.0 V (Figs. 3–5). All solutions were nitrogen-purged prior to experiment. The obtained data from the cyclic voltammograms of the Schiff base ligand and its metal complexes were given in Table 3. A typical cyclic voltammogram of Schiff base ligand, **1**, was shown in Fig. 3. The cyclic voltammogram showed one quasi-reversible process at E_{pc} = +0.70 V and E_{pa} = +0.78 V due to the reduction of Schiff base ligand with i_{pa}/i_{pc} close to unity (i_{pa}/i_{pc} = 0.91). One anodic peak was also detected at E_{pa} = +0.96 V which can be attributed to the oxidation of —SH group in the ligand.

The cyclic voltammogram of Ni(II) complex (Fig. 4) showed a well-defined reversible reduction peak at E_{pc} = −1.26 V and E_{pa} = −1.17 V which correspond to Ni(II) $\rightleftharpoons$ Ni(I) [53–56]. The two other peaks at Fig. 4 were attributed to the Schiff base ligand which revealed a little potential shift due to the complexation. On the other hand, E_{pa} = +0.96 in the cyclic voltammetry of ligand was disappeared due to the S—S coupling in resulted complex and so no oxidation peak of —SH was observed in this region.

The cyclic voltammogram of the Pd(II) complex (Fig. 5) showed a well-defined redox process corresponding to the formation of Pd(II)/Pd(I) couple at E_{pc} = −0.09 V and E_{pa} = −0.41 V. This couple is found to be quasi-reversible process. The peaks of Schiff base

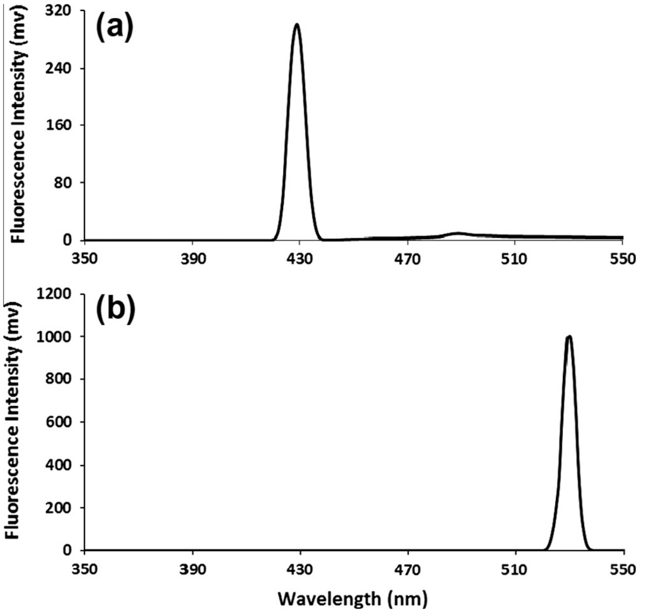


Fig. 2. Fluorescence spectra of (a) Schiff base ligand (λ_{exc} = 424 nm) and (b) nickel(II) complex (λ_{exc} = 524 nm) in methanol.

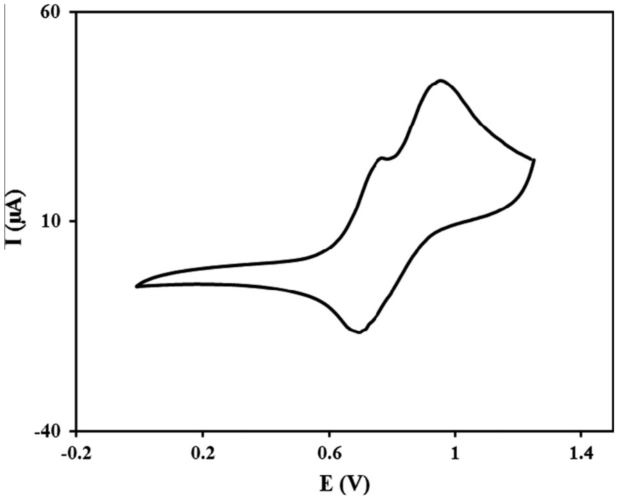


Fig. 3. Cyclic voltammetry of Schiff base (2.0 mM) in acetonitrile (0.20 M TBAP) at a stationary platinum-disk electrode (i.d. = 0.3 cm) with a scan rate of 0.1 V s^{-1}, at 25 °C.

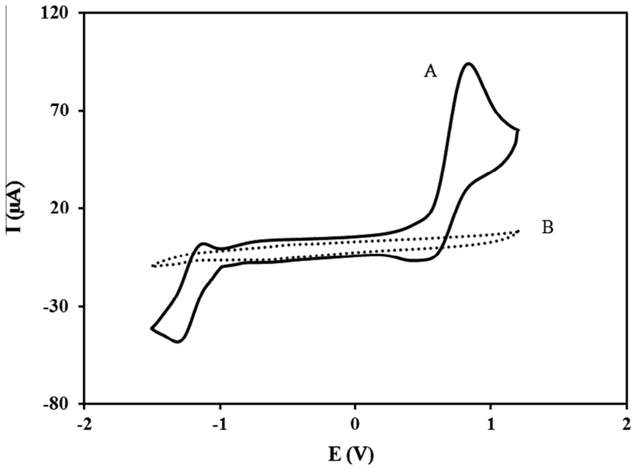


Fig. 4. Cyclic voltammetry of nickel(II) complex (2.0 mM) in acetonitrile (0.20 M TBAP) at a stationary platinum-disk electrode (i.d. = 0.3 cm) with a scan rate of 0.1 V s^{-1} at 25 °C: (A) nickel(II) complex (2.0 mM); (B) supporting electrolyte.

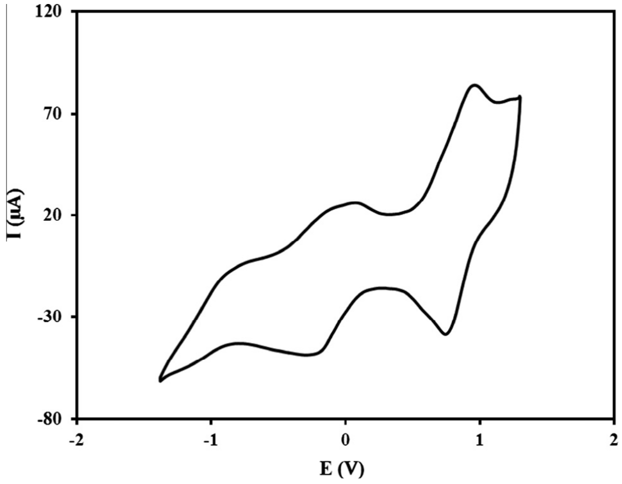


Fig. 5. Cyclic voltammetry of palladium(II) complex (2.0 mM) in acetonitrile (0.20 M TBAP) at a stationary platinum-disk electrode (i.d. = 0.3 cm) with a scan rate of 0.1 V s^{-1} at 25 °C.

ligand at +0.56 and +0.72 V were again observed in the voltammogram of palladium complex.

Molar conductivity measurements

The molar conductivity of 3×10^{-4} M complexes was measured in DMSO at room temperature. The molar conductivity values of both complexes were in the range of 1.68–3.21 $ohm^{-1}\ cm^2\ mol^{-1}$, indicating the non-electrolytic nature of these complexes [57]. The conductivity value of complex **2** in DMSO can be explained with respect to the crystal structure of this compound which showed it did not have any ionic structure.

Table 3

Electrochemical parameters[a] for the Schiff base, nickel(II) and palladium(II) complexes in acetonitrile solution containing TBAP (0.20 M).

Compound	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$	i_{pa}/i_{pc}
Schiff base	0.70	0.78	0.74	0.91
	–	0.96	–	–
Nickel(II) complex	0.60	0.81	0.71	2.24
	−1.26	−1.17	−1.22	0.98
Palladium(II) complex	0.56	0.72	0.64	0.76
	−0.41	−0.09	−0.25	1.94

[a] Measured at a stationary platinum-disk electrode (i.d. = 0.3 cm) with a scan rate of 0.1 V s^{-1} at 25 °C.

Description of the molecular structure of 2

Green crystals of **2** were obtained by slow diffusion of petroleum ether into a saturated CH_2Cl_2 solution during 7 days at room temperature. Crystallographic data and parameters for complex were summarized in Table 1. This Table reveals that complex **2** crystallize in the triclinic (space group, $P\bar{1}$) crystal system. The asymmetric unit of the complex consists of one crystallographically independent Ni(II) species. An ORTEP drawing of the complex **2** was presented in Fig. 6. The coordination geometry around nickel ion can be described as distorted octahedral geometry. The distorted octahedral geometry can rationalize the reduced effective magnetic moment value (1.82 B.M). As shown in Fig. 6, four coordination sites were occupied by doubly deprotonated Schiff base ligand and two other by two acetic acid molecules [58]. Nickel(II) has six-coordination number in which two deprotonated phenolic oxygen atoms occupy *trans* positions and two acetate and two imine nitrogen atoms are located in *cis* position relative to each other. Selected bond lengths and angles with their standard deviations for complex **2** were given in Table 4. Structural parameter

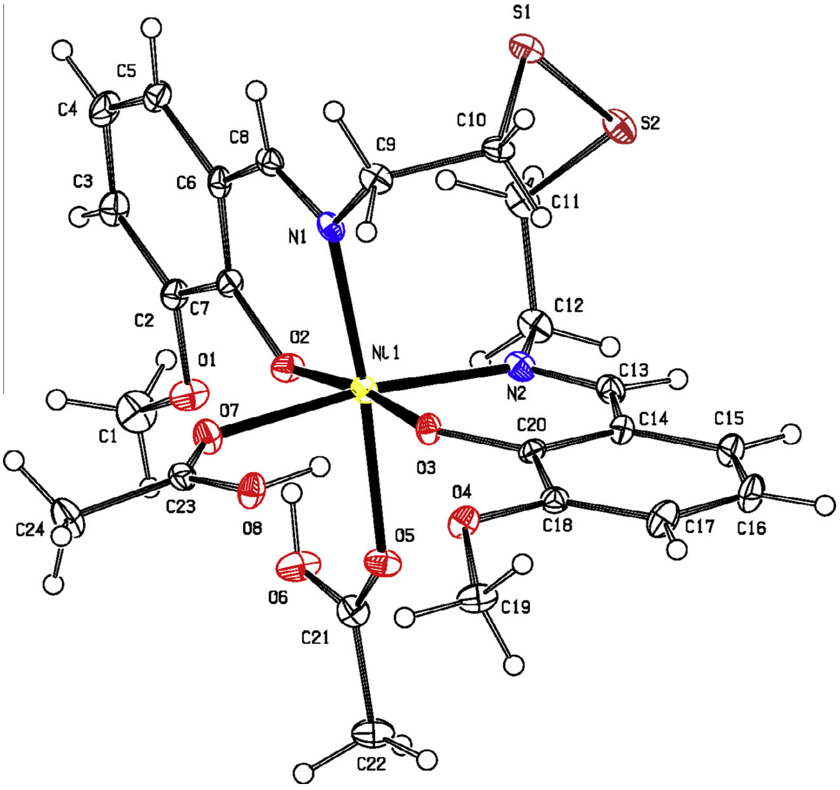


Fig. 6. The labeled diagram of complex **2** (thermal ellipsoids are at 30% probability level).

Table 4
Selected bond distances (Å) and bond angles (°) for **2**.

Ni(1)—O(2)	2.010(3)	Ni(1)—O(3)	2.012(3)
Ni(1)—N(1)	2.067(4)	Ni(1)—N(2)	2.049(4)
Ni(1)—O(5)	2.180(3)	Ni(1)—O(7)	2.131(3)
S(1)—C(10)	1.825(5)	S(2)—C(11)	1.820(5)
S(1)—S(2)	2.0335(19)	O(8)—C(23)	1.313(6)
N(1)—C(8)	1.290(6)	N(2)—C(13)	1.294(6)
O(2)—Ni(1)—O(3)	172.69(15)	N(2)—Ni(1)—N(1)	97.58(15)
O(7)—Ni(1)—O(5)	86.10(13)	O(3)—Ni(1)—O(7)	87.25(13)
N(2)—Ni(1)—O(7)	172.41(15)	N(1)—Ni(1)—O(7)	89.70(14)
O(3)—Ni(1)—O(5)	88.03(13)	N(2)—Ni(1)—O(5)	86.76(15)

which have shown in Table 4 are comparable with previously reported Ni(II) containing multidentate Schiff base ligands [59].

Conclusion

The Schiff base ligand and its nickel and palladium complexes were synthesized and characterized using microanalysis, ^{1}H NMR, IR, UV–Vis spectral data and conductometry. The Schiff base ligand was coordinated as a bidentate ligand through NO donor atoms of both phenolic and azomethine groups in nickel and palladium complexes. Due to using 1:2 Metal:Ligand stoichiometry, the S donor atoms in the Schiff bases were not coordinated to the metals and —S—S— coupling was occurred which stabilized the structure of the complexes. The elemental analysis and also X-ray structure of these compounds revealed the proposed molar ratio and the S–S coupling, respectively. The Schiff base ligand and its nickel complex display intraligand ($\pi \rightarrow \pi^*$) fluorescence. Electrochemical properties of the ligand and its metal complexes were investigated in the CH_3CN solvent and showed one reversible and quasi-reversible processes at 100 and mV s^{-1} scan rate.

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Appendix A. Supplementary material

CCDC 908058 contains the supplementary crystallographic data for complex **2**. 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. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.02.179.

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