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Lakhdar Sibous, Embarek Bentouhami, Mustayeen Ahmed Khan. Synthesis, Characterization, and Electrochemical Behaviour of Cobalt(II) and Nickel(II) Complexes with N₂O₂ Chelating Ligand 4,4'-(Biphenyl-4,4'-diyldinitrilo)dipentan-2-one. European Journal of Inorganic Chemistry, 2013, 2013, pp.1 - 11. 10.1155/2013/104979 . hal-03258132

HAL Id: hal-03258132

<https://univ-angers.hal.science/hal-03258132>

Submitted on 11 Jun 2021

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Research Article

Synthesis, Characterization, and Electrochemical Behaviour of Cobalt(II) and Nickel(II) Complexes with N_2O_2 Chelating Ligand 4,4'-(Biphenyl-4,4'-diylidinitrilo)dipentan-2-one

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Received 14 April 2013; Revised 30 June 2013; Accepted 1 July 2013

Academic Editor: Guido Crisponi

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4,4'-Diaminobiphenyl reacts with 2,4-pentanedione in absolute ethanol in a molar ratio 1 : 2 to form mainly the product of [1 + 2] condensation, 4,4'-(biphenyl-4,4'-diylidinitrilo)dipentan-2-one (H_2L). The Schiff base was used as tetradentate chelating ligand to coordinate Co^{II} and Ni^{II} chlorides leading to complexes where the ratio of metal ligand was found to be 2 : 1 or 2 : 2. All the synthesized products were characterized by elemental analysis, infrared, electronic, and mass spectroscopy, 1H NMR, and DSC. The electrochemical behaviour of the ligand and its complexes in DMF is also investigated.

1. Introduction

Aromatic Schiff base compounds have significant importance in the fields of coordination chemistry and material sciences because they are potentially capable to form stable complexes with different metal ions [1–3]. Schiff base ligands that have solvent dependent UV-vis spectra (solvatochromicity) can be suitable nonlinear optical (NLO) active materials [4]. They can be useful materials in solid phase extraction and synthesis of ion-selective electrodes for the determination of anions in analytical samples [5–7]. Schiff base ligands can also be used in enantioselective [8] and regioselective [9] ring opening of epoxides, enantioselective epoxidation of alkenes [10], and asymmetric oxidation of methyl phenyl sulphide [11].

Transition metal complexes with oxygen and nitrogen donor Schiff base ligands are of particular interest [12] because of their ability to possess unusual configuration, being structurally labile and their sensitivity to molecular environment [13]. Schiff base ligands can accommodate different metal centres involving various coordination modes thereby allowing successful synthesis of homo- and heterometallic complexes with varied stereochemistry [14]. This feature is employed for modelling active sites in biological systems [15].

Additionally, these complexes have wide applications such as antibacterial and antifungal agents [16].

Recently, much research on macrocyclic complexes have been focused on species containing the first-row transition metal ions and tetradentate ligands [17]. The formation of macrocyclic complexes depends significantly on the dimension of internal cavity, on the rigidity of the macrocycles, on the nature of its donor atoms, and on the complexing properties of the anion involved in the coordination [18]. The interest in such species stems from the application of these complexes ranging from modelling the active sites of many metalloenzymes [19] to hosting and carrying small molecules [20] or catalysts [21, 22].

In continuation of our investigation on the ligating properties of N_2O_2 Schiff base ligands [23], we report herein the synthesis and characterization of 4,4'-(biphenyl-4,4'-diylidinitrilo)dipentan-2-one (H_2L) derived from the condensation of 4,4'-diaminobiphenyl with 2,4-pentanedione in a molar ratio 1 : 2 and its two types of binuclear $Co(II)$ and $Ni(II)$ complexes. These products were characterized by elemental analysis, IR, UV-vis spectroscopy, and MS, 1H NMR, and DSC as well as cyclic voltammetry.

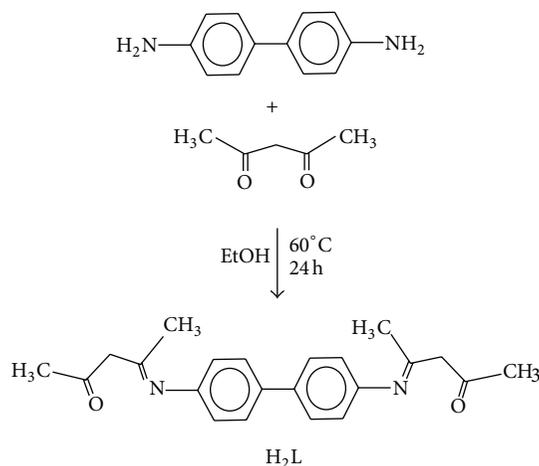


FIGURE 1: Synthetic route of the Schiff base ligand H_2L .

2. Experimental

2.1. Materials and Methods. All materials and solvents were analytical reagent grade. The compounds 4,4'-diaminobiphenyl and 2,4-pentanedione were commercial samples from Aldrich and purified by standard procedures. Their purity was determined by thin layer chromatography (TLC) or dry column "flash" chromatography (DCFC) (SiO_2 , Merck-Kieselgel 60 H). All metals were hydrated chlorides and used as received. Reactions of 4,4'-diaminobiphenyl with 2,4-pentanedione were carried out using ethyl alcohol-reactants in sealed Rotafluo-tapped Pyrex ampoules (50 cm^3). Crude reaction product mixture was examined by TLC, and individual components were separated by filtration. Further purification, where necessary, was achieved by TLC or repeated DCFC.

2.2. Measurements. Products were examined by IR and recorded with a Perkin-Elmer 1000 series FT-IR spectrophotometer using KBr disks. UV-vis spectra were obtained in DMF with a UNICAM UV-300 spectrophotometer. ^1H NMR spectra of the ligand and the diamagnetic complexes were recorded on a Jeol GSX WB spectrometer instrument operating at 270 MHz, and the chemical shifts to low field of the reference are designated positive and given in ppm, using tetramethylsilane (TMS) as external reference. NMR samples were run as solutions in $\text{DMSO}-d_6$. Mass spectra were recorded on a Bruker Daltonics Data Analysis 3.1 spectrometer using electron impact (EI) conditions. Elemental analysis was carried out with an EL III-ELEMENTAR. Melting points were determined with a Kofler bench and are uncorrected. Differential scanning calorimetry (DSC) diagrams were recorded in the $25\text{--}400^\circ\text{C}$ range with a Mettler DSC 822^e unit, with the help of Mettler Toledo STAR^c SW 8.10 System software; the heating rate was 10°C per minute; all measurements were made in 40 mm^3 closed Al crucibles.

Electrochemical measurements were recorded on a Radiometer VOLTALAB 32 (DEA 332 type): the working electrode was a 2 mm diameter Pt rotating disk and the auxiliary electrode a Pt wire. A saturated calomel electrode

was used as the reference electrode, and measurements were carried out at room temperature. DMF was used as solvent and the ionic strength maintained at 0.1 mol L^{-1} , with Bu_4NClO_4 (TBAP) as supporting electrolyte. The concentrations of species were in the $2.5 \cdot 10^{-3}$ to $5 \cdot 10^{-3}\text{ mol L}^{-1}$ range. The sweep speed was 100 mV s^{-1} unless otherwise indicated.

2.3. Preparation of the Ligand 4,4'-(Biphenyl-4,4'-diyl)dinitrilo)dipentan-2-one. The Schiff base ligand (shown in Figure 1) has already been synthesized [24]. In our work, however, the same product is prepared using a different procedure compared to either the previous one or that of literature [25], which reported the NMR characterization of β -diketone Schiff bases in CDCl_3 . Here, 4,4'-Diaminobiphenyl and 2,4-pentanedione were mixed in absolute ethanol and sealed *in vacuo* in a dry Rotafluo-tapped Pyrex tube (ca. 50 cm^3) as follows: to a solution of 4,4'-diaminobiphenyl (0.75 g , 0.81 mol L^{-1}) was added a solution of 2,4-pentanedione (0.82 g , 1.63 mol L^{-1}) in a 1:2 molar ratio. The mixture was heated *in vacuo* at 60°C during 24 h to give yellow solution and pale yellow precipitate. The volatile material was removed *in vacuo* by condensation into a trap cooled to -196°C and identified as ethanol by IR spectroscopy. The residue (1.17 g) which remained in the tube was washed out using fresh ethanol and then extracted with the same solvent ($3 \times 10\text{ mL}$) to give, after removal of the solvent from the filtrate under reduced pressure, the ligand H_2L that is formed from the [1+2] condensation. This product was furthermore subjected to dry column "flash" chromatography (DCFC) using ethanol as eluent, and its yield was almost quantitative (83%).

2.4. Preparation of the Co(II) and Ni(II) Complexes. All the complexes were prepared using the same synthetic pathway described in literature [26, 27] by mixing in absolute EtOH amounts of ligand H_2L (0.2 g , 0.1 mol L^{-1}) and hydrated cobalt and nickel chlorides in 1:1 or 1:2 molar ratio. After standing under reflux conditions for 16 h, the mixture was kept overnight at room temperature. The complex, which precipitated, was removed by filtration, washed several times

TABLE 1: Main analytical data for the ligand and its complexes in the solid state.

Compound	Color	Yield (%)	M.p. (°C)	M ⁺	Elemental analysis found (calcd.) (%)		
					C	H	N
H ₂ L	Yellow	83	134	348.2	75.68 (75.83)	7.14 (6.94)	7.75 (8.04)
[[Co(H ₂ L)] ⁴⁺] ₂	Blue	65	>260	814.7	64.78 (64.86)	6.21 (5.93)	6.99 (6.87)
[[Ni(H ₂ L)] ⁴⁺] ₂	Yellow	79	>260	814.2	64.64 (64.90)	6.16 (5.94)	7.04 (6.88)
[(CoCl ₂) ₂ (H ₂ L)] ⁴⁺	Green	60	>260	608.1	43.72 (43.45)	4.25 (3.97)	4.75 (4.60)
[(NiCl ₂) ₂ (H ₂ L)] ⁴⁺ ·2H ₂ O	Yellow	58	>260	—	41.01 (41.18)	4.30 (4.08)	4.65 (4.36)

TABLE 2: Mass spectrometry data of H₂L, [[Co(H₂L)]⁴⁺]₂, [(CoCl₂)₂(H₂L)]⁴⁺, and [[Ni(H₂L)]⁴⁺]₂ in the solid state.

Compound	<i>m/z</i>	Assignment	Abundance (%)
H ₂ L	348.2	M ⁺	78
	305.3	(C ₂₀ H ₂₁ N ₂ O) ⁺	20
	248.2	(C ₁₇ H ₁₆ N ₂) ⁺	10
[[Co(H ₂ L)] ⁴⁺] ₂	814.7	M ⁺	10
	686.4	(C ₃₇ H ₃₄ N ₃ O ₃ Co ₂) ⁷⁺	27
	392.2	(C ₂₁ H ₂₁ N ₂ O ₂ Co) ⁵⁺	91
	241.1	(C ₉ H ₁₄ N ₂ O ₂ Co) ⁵⁺	17
	608.1	M ⁺	10
[(CoCl ₂) ₂ (H ₂ L)] ⁴⁺	501.7	(C ₂₂ H ₂₄ N ₂ O ₂ Co ₂ Cl) ⁵⁺	18
	380.1	(C ₁₇ H ₁₆ NOC ₂ Cl) ³⁺	63
	233.1	(C ₁₁ H ₁₂ NOC ₂) ³⁺	84
[[Ni(H ₂ L)] ⁴⁺] ₂	814.2	M ⁺	13
	599.3	(C ₃₆ H ₃₄ N ₃ O ₂ Ni) ⁵⁺	16
	393.1	(C ₂₁ H ₂₂ N ₂ O ₂ Ni) ⁵⁺	93
	316.1	(C ₁₅ H ₁₇ N ₂ O ₂ Ni) ⁵⁺	15

with EtOH (3 × 10 mL), and dried under vacuum. Their purity was verified using thin layer chromatography (TLC) and CH₂Cl₂/EtOH (3 : 7, v/v) as eluent and were shown, in any case, to contain only one component (*R_f* 0.52). These products were again subjected to (DCFC) to afford the 1:1 or 1:2-complexes in good yields (58–79%) (Table 1).

3. Results and Discussion

3.1. Synthesis and Characterization. The synthesized Schiff base H₂L (Figure 1) was used as tetradentate ligand to form the four complexes reported in this account. This compound employs two imine nitrogen and two oxygen atoms to bind the metals. All complexes were synthesized in good yield by reacting H₂L with hydrated metal chlorides Co^{II} and Ni^{II} in a molar ratio 1:1 or 1:2, using ethyl alcohol as solvent at 60°C. Analytically pure solid compounds were obtained in all cases as indicated by mass spectrometry and elemental analysis. They are air stable and are of higher melting points than the parent ligand. The higher melting points of these complexes (>260°C) compared to those of the ligand (134°C) can be taken as an evidence for the bonding to the cobalt(II) or nickel(II) ions with chelate rings formation [28]. This

last information together with the presence of the parent ion peaks (M⁺) in the mass spectra of three complexes in the solid state are consistent with the proposed molecular formulae, and the (metal-ligand) ratio is compatible with the 2:1 or 2:2 form depending on the molar ratio of the mixed reactants used during the preparation. The main analytical data obtained for the ligand and its complexes at the solid state is collected in Table 1.

3.2. Mass Spectra of the Ligand and Its Complexes. The information about the (metal-ligand) ratio was obtained from mass spectrometry of the three complexes examined in the solid state which reveal that the complexes are binuclear compounds. The molecular weights of these products were determined using electron impact (EI) conditions which gave the parent ion peaks M⁺ at *m/z* 814.7, 608.1, and 814.2. These values are assigned, respectively, to the species [[Co(H₂L)]⁴⁺]₂⁺, [(CoCl₂)₂(H₂L)]⁴⁺, and [[Ni(H₂L)]⁴⁺]₂⁺ (Figures 2(b), 2(c) and 2(d)). All MS data of the metal complexes which are compiled in Table 2 show similar fragmentation pattern and exhibit ion peaks attributed to (M⁺ + 1) and (M⁺ + 2). Furthermore, prominent breakdown peaks corresponding to loss of chlorine atoms were also observed in case of [(CoCl₂)₂(H₂L)]⁴⁺ and [(NiCl₂)₂(H₂L)]⁴⁺·2H₂O complexes. In addition, the ligand H₂L was also examined, and its mass spectrum gave the molecular ion at *m/z* 348.2 as shown in Figure 2(a) and Table 2. These results agree with the proposed structures and are mentioned in Table 1 as well as in Table 2.

3.3. Infrared Spectra of the Ligand and the Complexes. A comparative study of the IR spectral data of the reported complexes with that of the uncomplexed ligand gives meaningful information regarding bonding sites of the ligand molecule with metal cations. In fact, the Schiff bases such as H₂L contain a proton adjacent to the carbonyl group and consequently can undergo, in solution, an equilibrium between three tautomers as indicated in Figure 3. Structural studies about this type of Schiff base ligands have indicated that they exist predominantly as the ketoamine tautomer III. This determination is first based upon IR spectra using bands in the 3200–3500 cm⁻¹ region assigned to the ν(N–H) stretching vibration. However, infrared spectroscopy may not be a sufficient tool because it is difficult to distinguish between a ν(O–H) of a coordinated enolimine tautomer II and a ν(N–H) of a coordinated ketoamine tautomer III [29]. The second way is ¹H NMR by using the chemical shifts in the δ 8.4–12.6 p.p.m. range [24, 30].

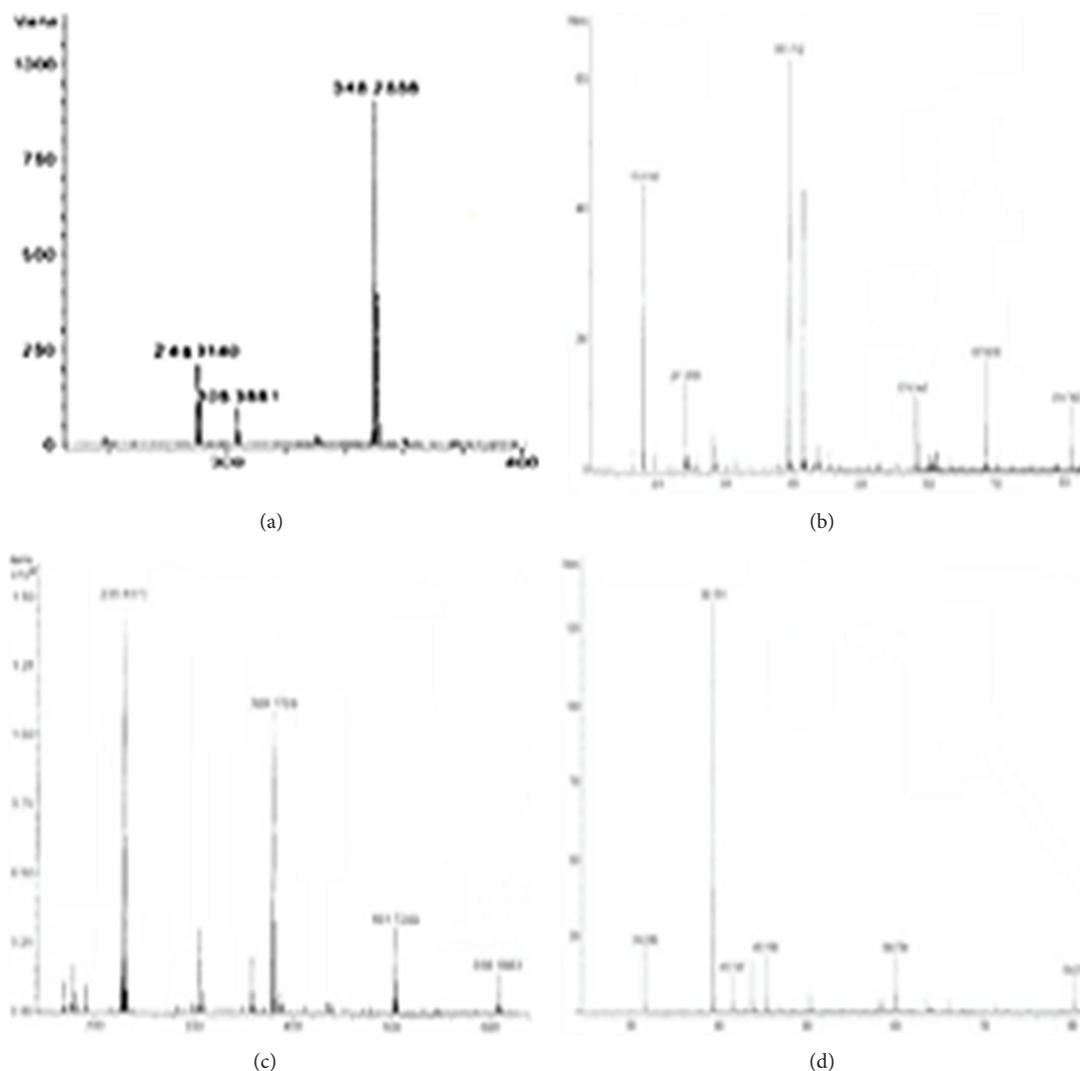


FIGURE 2: Mass spectra of H₂L (a), ([Co(H₂L)]⁴⁺)₂ (b), [(CoCl₂)₂(H₂L)]⁴⁺ (c), and ([Ni(H₂L)]⁴⁺)₂ (d).

TABLE 3: Main spectroscopic IR data for the ligand (solid state) and its complexes (CH₂Cl₂ solution). For UV-visible both in DMF solution.

Compound	Infrared (cm ⁻¹)					UV-vis (DMF solution)		
	$\nu(\text{N-H})$	$\nu(\text{O-H})$	$\nu(\text{C=N})$	$\nu(\text{C=O})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	λ_{max} (nm)
H ₂ L	—	—	1570 s	1610 vs	—	—	—	351
([Co(H ₂ L)] ⁴⁺) ₂	3296 b	—	1557 m	1626 s	—	516 w	473 w	299, 610, 678
([Ni(H ₂ L)] ⁴⁺) ₂	3293 m	—	1551 m	1619 s	—	514 w	437 w	302
[(CoCl ₂) ₂ (H ₂ L)] ⁴⁺	3289 m	—	1550 m	1625 s	—	515 w	435 w	303, 608, 674
[(NiCl ₂) ₂ L] ²⁺ ·2H ₂ O	—	3378 b	1548 m	—	1370 m	514 w	448 w	300

vs: very strong; m: medium; b: broad; w: weak.

The main IR bands for the free ligand H₂L recorded as KBr disks and its complexes in CH₂Cl₂ solution with their tentative assignments are given in Table 3. The free ligand exhibits bands at 1610 and 1570 cm⁻¹ regions due to the stretching vibrations $\nu(\text{C=O})$ and $\nu(\text{C=N})$, respectively. The wavenumber of the keto stretching vibration band is typical of the presence of hydrogen bonding between this oxygen

atom and the hydrogen atom from the imino functional group [31]. The low energy position of the $\nu(\text{C=N})$ band could be attributed to its involvement in conjugation with the aromatic system. The medium bands at 2991 and 3051 cm⁻¹ not mentioned in Table 3 are assigned to the aliphatic and the aromatic protons. These data indicate that the free ligand exists mainly in the ketonic form in the solid state. The

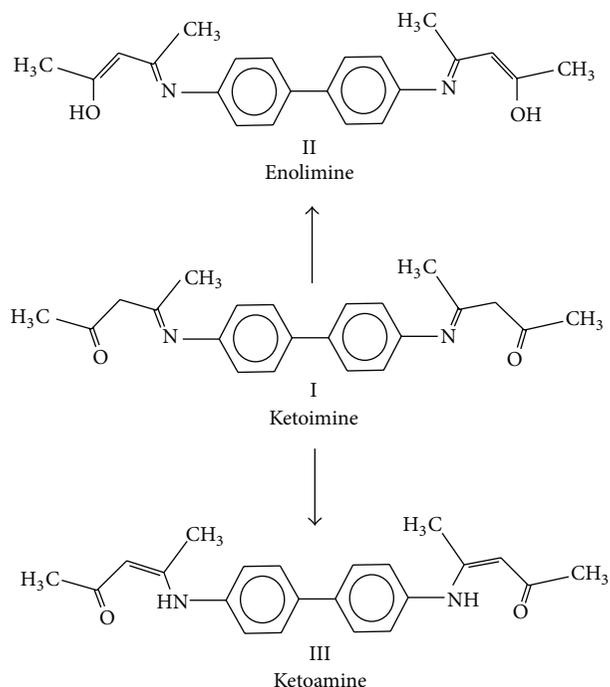


FIGURE 3: Ketoimine form of the Schiff base ligand H_2L in solid state and its ketoamine or enolimine tautomer form when dissolved in organic solvent.

appearance of only one band for each of the $C=O$ and $C=N$ groups indicates the symmetrical nature of the free ligand H_2L .

The IR spectra of $[(CoCl_2)_2(H_2L)]^{4+}$, $[(Co(H_2L)]^{4+}$, and $[(Ni(H_2L)]^{4+}$ complexes show the very strong band due to $\nu(C=O)$ shift to higher wavenumbers (1626, 1619, and 1625 cm^{-1} , resp.), but there was a new medium band instead, in case of $[(NiCl_2)_2L]^{2+} \cdot 2H_2O$ complex which loses 2H and two positive charges in solution. This band was observed at 1370 cm^{-1} and assignable to $\nu(C-O)$. On the other hand, the $\nu(C=N)$ bands were shifted to lower frequencies as compared to the position in the ligand and occur within $1548\text{--}1557\text{ cm}^{-1}$ range due to the conjugate system $-C=N-C=C-$ indicating the keto form of the ligand even in the presence of the metal ion [32, 33]. Additional evidence for coordination of nitrogen and oxygen atoms is the appearance of the new $\nu(M-N)$ and $\nu(M-O)$ bands in the $435\text{--}448\text{ cm}^{-1}$ and $514\text{--}516\text{ cm}^{-1}$ regions, respectively. These observations are in good agreement with earlier reported results [34–36].

Furthermore, the aliphatic and aromatic vibration protons are not greatly affected upon complexation. In the $3200\text{--}3500\text{ cm}^{-1}$ region, only the complex $[(NiCl_2)_2L]^{2+} \cdot 2H_2O$ presents a broad band around 3378 cm^{-1} , corresponding to the $O-H$ stretching vibration band of water molecules. In all other spectra, the shape of the band is similar, indicating the absence of hydrogen bonding. Accordingly, the ligand acts as a dibasic tetradentate ligand coordinating to the Co^{2+} or Ni^{2+} ions and producing the 2:2 (metal-ligand) complexes via the ketoxyoxygen and azomethine-nitrogen atoms. However, in case of the 2:1 compounds, the complexation to the Co^{2+}

was via the ketoxyoxygen and azomethine-nitrogen while to the Ni^{2+} was found to be via the enolatoxyoxygen and azomethine-nitrogen atoms.

3.4. Electronic Spectra of the Ligand and Its Co(II) and Ni(II) Complexes. Electronic spectra of the ligand and its metal complexes have been measured in DMF, and the numerical data of the band maxima (λ_{max}) are presented in Table 3. In general, the UV-visible region of the electronic spectra of all the products was dominated by intense band which is assigned to a $\pi-\pi^*$ transition associated with the azomethine linkage [37].

The ligand and the complexes exhibit intense bands in the high energy region in the $299\text{--}351\text{ nm}$ range ($\epsilon = 5518\text{--}32444\text{ L mol}^{-1}\text{ cm}^{-1}$) which can be assigned to LMCT (ligand-metal charge transfer) bands [38]. The electronic spectra show that absorption bands of the two nickel(II) complexes occur below 600 nm . A lack of any electronic transition at longer wavelengths is consistent with the square planar geometry of Ni(II) compounds. However, in the case of cobalt(II) complexes, the d-d transitions were observed in the $608\text{--}678\text{ nm}$ range. The bands located at 610 nm ($\epsilon = 240\text{ L mol}^{-1}\text{ cm}^{-1}$) and 678 nm ($\epsilon = 3671\text{ L mol}^{-1}\text{ cm}^{-1}$) are attributed to $[(Co(H_2L)]^{4+}$, while those at 608 nm ($\epsilon = 363\text{ L mol}^{-1}\text{ cm}^{-1}$) and 674 nm ($\epsilon = 6179\text{ L mol}^{-1}\text{ cm}^{-1}$) are assigned to $[(CoCl_2)_2(H_2L)]^{4+}$. These bands usually correspond to a tetrahedral environment around Co^{2+} ion [31].

The obtained values are of particular importance since they were highly dependent on the geometry of the molecule. It is known that the transitions from a square planar structure to a deformed tetrahedral one leads to a red shift of absorption in the electronic spectra [39].

Thus, the smaller value of the wavelength of the band corresponding to the transitions is resemblance between the geometry of the complex and that of square planar complex.

3.5. 1H NMR Spectra of the Ligand and Its Ni(II) Complexes. Comparison of 1H NMR spectral data of the ligand H_2L and the diamagnetic Ni(II) complexes recorded in $DMSO-D_6$ solution as indicated in Figure 4 further supplements the conclusion drawn from IR data.

The aromatic protons of the ligand (Figure 4(a)) showed a multiplet at $\delta 7.2\text{--}7.5\text{ p.p.m.}$, assigned to biphenyl protons and a singlet at $\delta 12.43\text{ p.p.m.}$ typical for hydrogen bonded $N-H$ or $O-H$ which disappeared in presence of D_2O . The spectrum exhibits also a singlet at $\delta 5.1\text{ p.p.m.}$ due to the ethylenic ($CH=C$) protons. In addition, the singlet at $\delta 1.95\text{ p.p.m.}$ was attributed to the methyl groups. These peaks are in good agreement with the presence of H_2L in solution either in its ketoamine form (tautomer III) or in its enolimine form (tautomer II) [29, 30, 40].

In case of the $[(Ni(H_2L)]^{4+}$ complex, no changes were observed in the 1H NMR spectrum (Figure 4(b)) concerning the absorption previously indicated at $\delta 12.43\text{ p.p.m.}$ in the ligand. In solution of $DMSO-D_6$, this proton resonates after complexation at $\delta 12.45\text{ p.p.m.}$ without any deprotonation which means that the ligand was in its ketoamine form (tautomer III). It should be noted that this peak cannot be

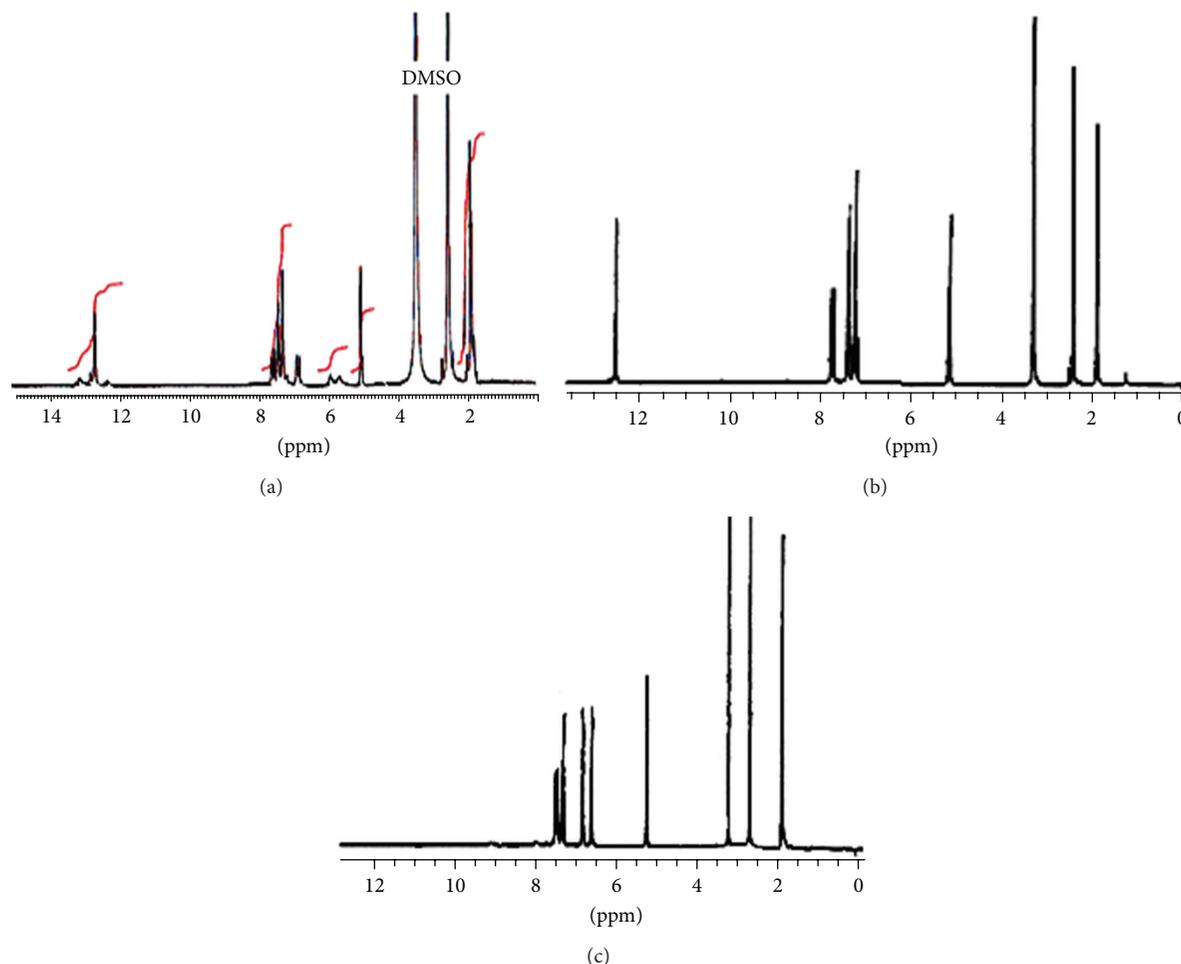


FIGURE 4: ^1H NMR spectra of H_2L (a), $[(\text{Ni}(\text{H}_2\text{L}))^{4+}]_2$ (b), and $[(\text{NiCl}_2)_2\text{L}]^{2+}$ (c) in DMSO-D_6 solution and in the δ 0–13 ppm range.

observed if the complex does not exist in a tautomeric form (case of the solid state). All other signals were very similar and no significant shifts were observed.

However, in case of the $[(\text{NiCl}_2)_2\text{L}]^{2+} \cdot 2\text{H}_2\text{O}$ complex in solution the difference becomes more important since the signal which appeared in the free ligand, at δ 12.43 p.p.m., completely disappeared in the spectrum (Figure 4(c)). This indicates that during complexation, the ligand H_2L in its eno-imine form (tautomer II) undergoes deprotonation followed by coordination to the Ni^{2+} ions. All the remaining signals in this complex were very similar to that of the ligand and appear nearly at the same positions.

Apparently, the single peak which is located in the δ 5.1–5.2 p.p.m. range in the spectra of the ligand H_2L and the two Ni(II) complexes and attributed to the ethylenic ($\text{CH}=\text{C}$) proton was found to be most useful, indicating that every product is present as individual isomer.

3.6. Thermal Analysis. In order to give more insight into the structure of the ligand and its complexes, the thermal studies of these compounds have been carried out using DSC technique where the diagrams of these products show significant differences between the ligand H_2L and its complexes. The

decomposition of all these species occurs at temperatures higher than 340°C and is generally followed by several exothermic peaks due to this phenomenon.

The DSC diagram of the ligand shows two endothermic peaks occurring at ca. 140 and 340°C . The first one either corresponds to the melting of the molecule or to the coordinated water, and the second one is followed by several exothermic peaks due to the chemical decomposition of the molecule.

The 2 : 1 and 2 : 2 (cobalt-ligand) complexes do not contain any hydrated or adsorbed water molecules. They are very thermally stable and show weak endothermic peaks at 360 – 390°C range. On the opposite side, the DSC diagram of the 2 : 1 (nickel-ligand) complex shows many peaks at the 110 – 130°C range and is due to loss of water molecules, while the 2 : 2 (nickel-ligand) compound shows a very weak endotherm at 190°C followed with a well-resolved endotherm at 380°C .

3.7. Proposed Structures for the Co(II) and Ni(II) Complexes.

Depending on the IR, ^1H NMR, and mass spectra, the suggested structures are given in Figures 5(a) and 5(b), showing how the complexes should be either in solution or in the solid states, respectively. The Schiff base H_2L acts as a tetradentate ligand via the ketoimine tautomer,

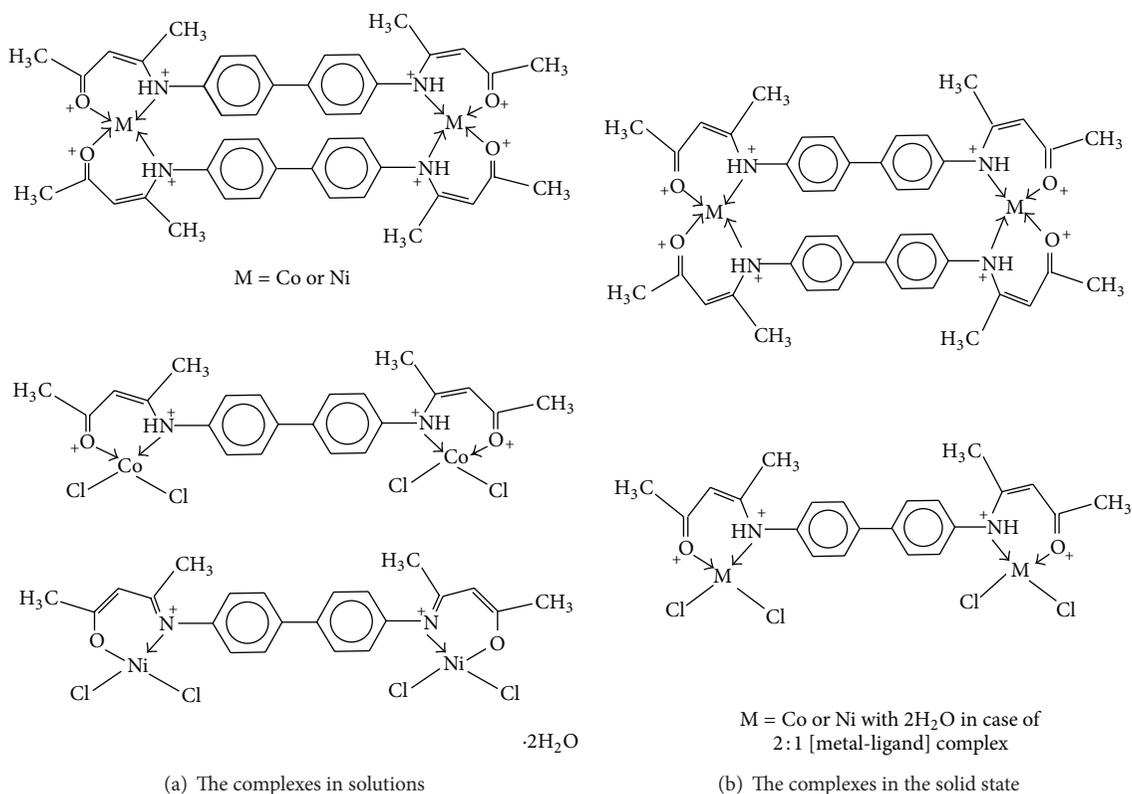


FIGURE 5: Proposed structures for Co^{II} and Ni^{II} complexes either in solution (a) or in solid state (b).

according to a symmetrical configuration. This geometry remains unchanged after complexation.

The cobalt(II) and nickel(II) complexes exhibit different structures. These species are binuclear complexes, and the coordination of the metal cation is linked through N(imino) and O(keto) atoms. The two cobalt(II) compounds present a distorted tetrahedral geometry while the two nickel(II) complexes exhibit a typical square planar surrounding [39, 40]. In addition, two water molecules appear in case of 2:1 [Ni(II)L] (as indicated by infrared spectroscopy and thermal analysis).

3.8. Electrochemical Behaviour of the Ligand and the Complexes. The main electrochemical results of the examined ligand as well as its complexes are summarised in Table 4, and some representative voltammograms are shown in Figure 6. The electrochemical behaviour in the whole range investigated (Figures 6(a)–6(e)) showed a pattern that could be considered as the sum of the individual responses.

The voltammetric response of the ligand H₂L in the –1.8 to +1.8 V range (Figure 6(a)) shows three waves in the anodic side with peak potential values of +0.56, +0.87 and +1.20 V which can be ascribed to the irreversible oxidations of the ligand and one cathodic peak at –0.97 V resulting from the reduction of the imino group [40]. During reduction sweep, the cyclic voltammogram shows only one quasireversible cathodic peak at +0.76 V associated with the reduction of the oxidised species of H₂L (oxidation of the azomethine moiety) [41].

When the speed sweep is varying (i.e., 500, 300, 200, 100 mVs^{–1}, resp.), the curve i_{pa} (at +0.76 V) as a function of speed square root is a curve line (not shown) and the curve $E_{pa} = f(\log \nu)$ is a straight line. These results show that this reduction peak corresponds to a diffusion controlled quasireversible system [42].

The cyclic voltammograms of the four complexes exhibit oxidation and reduction metal centred processes, as for complexes previously published [43]. On the cathodic side, the cyclic voltammograms of the 2:2 and 2:1 (cobalt-ligand) complexes (Figures 6(b) and 6(c)) show a similar reoxidation peak at –0.10 V and two cathodic peaks at –1.14 V and –1.17 V attributed to $[(Co(H_2L)]^{4+}]_2$ and $[(CoCl_2)_2(H_2L)]^{4+}$, respectively. The cathodic peaks at –1.14 and –1.17 V correspond to the reduction of complexed Co^{II} into Co⁰ [44]. Finally, Co⁰ is oxidised to give back coordinated Co^{II} (anodic peak at –0.10 V). When performing successive sweeps, the intensity of the peak at –1.14 V diminished, and in the meantime metallic cobalt was formed.

In case of nickel(II) complexes, these products in addition to the ligand peaks undergo reduction processes located at –1.54 V and –1.18 V (Figures 6(d) and 6(e)) and attributed to the 2:2 and 2:1 [nickel-ligand] complexes, respectively. These peaks correspond in fact to the reduction of Ni^{II} into Ni⁰, and the reoxidation of Ni⁰, in case of the 2:2 compound, is observed at –0.11 V while that of 2:1 complex is located at +0.11 V. These values agree with those previously described for nickel complexes in the same solvent [45].

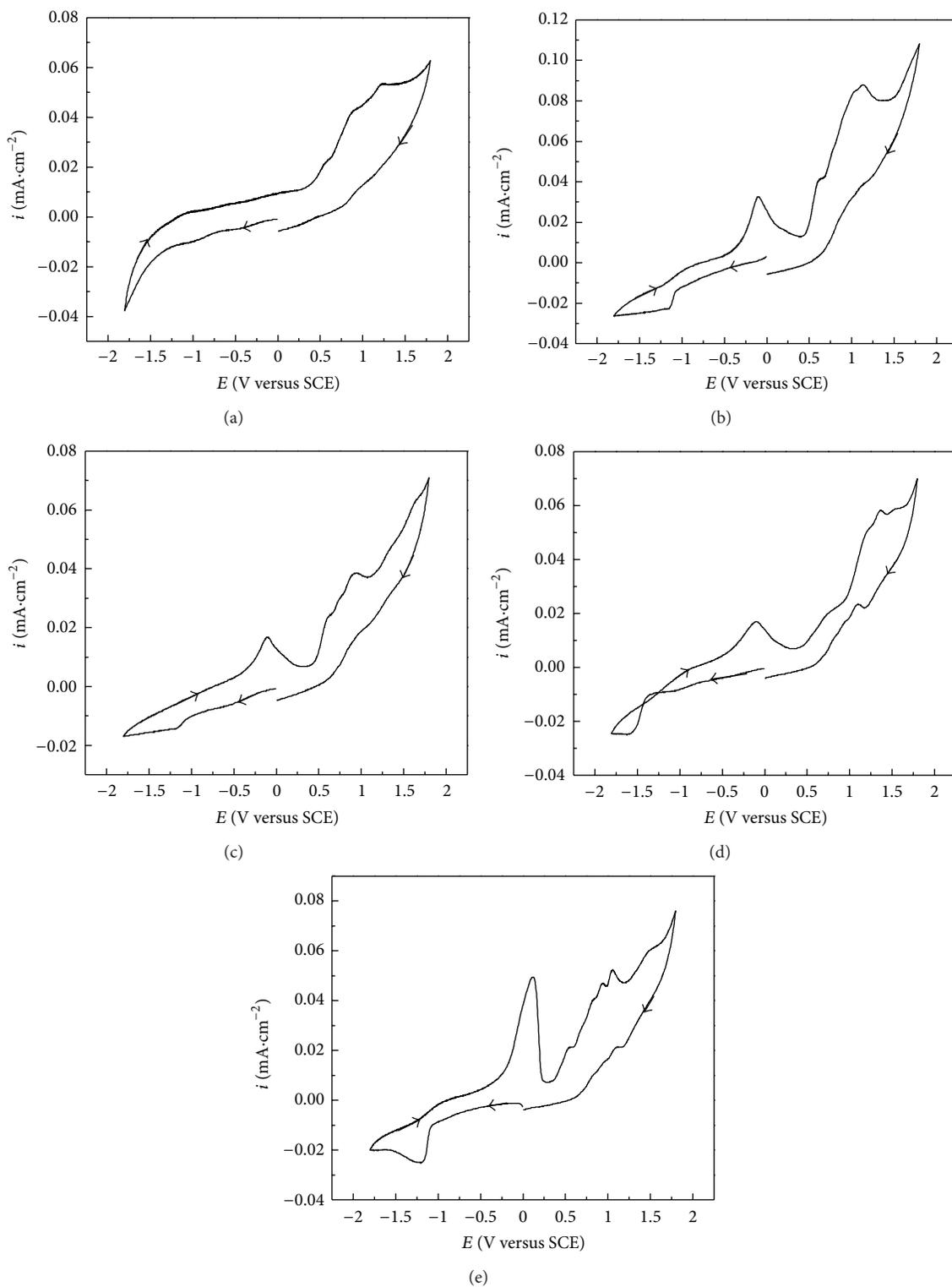


FIGURE 6: Representative cyclic voltammograms in DMF at room temperature (ionic strength: 0.1 mol L^{-1} , Bu_4NClO_4 , i in mA, $\nu = 100 \text{ mVs}^{-1}$) of H_2L (a), $[\text{Co}(\text{H}_2\text{L})]^{4+}_2$ (b), $[(\text{CoCl}_2)_2(\text{H}_2\text{L})]^{4+}$ (c), $[\text{Ni}(\text{H}_2\text{L})]^{4+}_2$ (d), and $[(\text{NiCl}_2)_2\text{L}]^{2+}$ (e) in the -1.80 to $+1.80$ range.

TABLE 4: Voltammetric results at room temperature ($26 \pm 1^\circ\text{C}$) in DME, ionic strength 0.1 mol L^{-1} (TBAP), results in V versus SCE, sweep speed: 100 mVs^{-1} , E_{pa} : anodic; E_{pc} : cathodic.

Compound	E_{pa1}	E_{pa2}	E_{pa3}	E_{pa4}	E_{pc1}	E_{pc3}	E_{pc4}	$\Delta E_{\text{p}}^{\text{a}}$	$E_{1/2}^{\text{b}}$
H_2L	—	+0.56	+0.87	+1.20	-0.97	+0.76	—	0.11	0.925
$([\text{Co}(\text{H}_2\text{L})]^{4+})_2$	-0.10	+0.62	+1.05	+1.12	-1.14	+0.68	+1.25	0.37	1.235
$([\text{Ni}(\text{H}_2\text{L})]^{4+})_2$	-0.11	+0.73	+1.17	+1.35	-1.54	+0.65	+1.20	0.52	1.430
$([\text{CoCl}_2]_2(\text{H}_2\text{L}))^{4+}$	-0.10	+0.59	+0.92	+1.31	-1.17	+0.68	+1.17	0.24	1.040
$([\text{NiCl}_2]_2\text{L})^{2+} \cdot 2\text{H}_2\text{O}$	+0.11	+0.54	+0.94	+1.47	-1.18	+0.66	+1.19	0.28	1.080

$$^{\text{a}}\Delta E_{\text{p}} = E_{\text{pc}} - E_{\text{pa}}$$

$$^{\text{b}}E_{1/2} = 0.5\Delta E_{\text{p}} + E_{\text{pa}}$$

Furthermore, a linear dependence which was observed between E_{p} and i_{p} as the voltage scan rate (ν) increased (i.e., 100, 200, 300, 500 mVs^{-1} , resp.) indicates a diffusion controlled quasireversible electrode exchange reaction. The curve E_{pa} for the oxidation peak potential at -0.11 V or $+0.11 \text{ V}$ of the 2:2 or the 2:1 [nickel-ligand] complex, respectively, as a function of $\log \nu$ (not shown) gave a straight line parallel to the horizontal x -axis and does not depend upon the sweep speed. In addition, the ratio $i_{\text{pc}}/i_{\text{pa}}$ was independent of scan rate and equal to unity for scan rates changing from 100 mVs^{-1} to 1 Vs^{-1} .

These results are in good agreement with the above proposed structures.

4. Conclusion

In summary, the Co(II) and Ni(II) complexes were synthesized using the binucleating tetradentate chelating agent formed by the condensation of 4,4'-diaminobiphenyl with 2,4-pentanedione. IR, ^1H NMR, mass spectral data, and elemental analysis are used to confirm the structure of the Schiff base H_2L . The mass spectra are also used to proof the stoichiometry and formulation of the complexes. Based on the UV-vis spectral data, a square planar geometry is assumed for Ni(II) complexes, while the Co(II) compounds present a distorted tetrahedral geometry. In addition, they are more easily oxidizable in the cyclic voltammetry and also show a quasireversible behavior. Finally, these products could be investigated in the near future in the fields of microbiology and electrocatalysis.

Acknowledgment

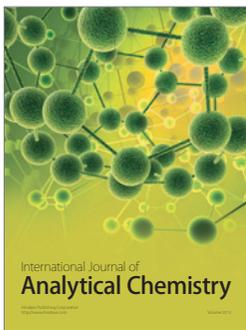
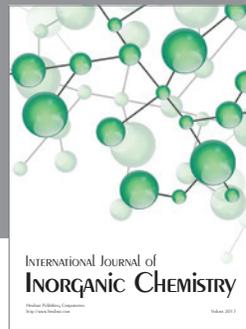
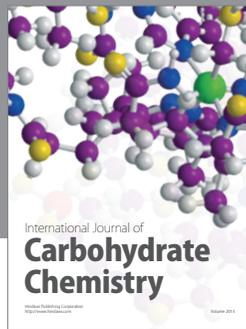
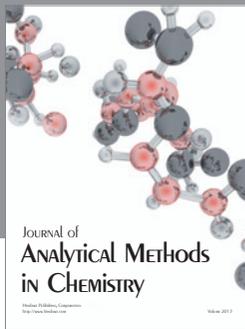
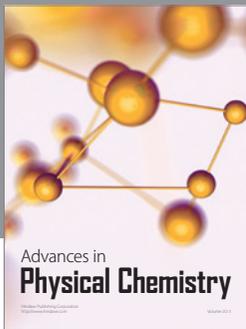
The authors are indebted to and thank the Pharmacy Department (U. F. A. Sétif) for the general facility projects and financial support.

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