

Synthesis and characterization of ruthenium (II) complexes with new Schiff base ligand from the reaction of 4-(aminomethyl)phenol with picolinaldehyde

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ABSTRACT: The Schiff base ligand containing N,N donor atoms, (*E*)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol (*L*¹*H*) (Fig. 1), and its Ru(II) complex have been prepared. The ligand and its complex have been characterized by elemental analyses, IR spectra, UV-Visible spectroscopy, ¹H and ¹³C NMR spectra and magnetic susceptibility measurements. The analytical data show that the metal to ligand ratio in the *L*¹*H* complexes is 1:1.

Keywords: Schiff Base; Ru(II) complexes, characterization

4-(aminometil)fenol ve pikolinaldehitten sentezlenen Schiff bazı ligandı ve Ru(II) kompleksinin sentez ve karakterizasyonu

ÖZET: N,N donör atomlu Schiff bazı ligandı ve onun rutenyum (II) kompleksi sentezlenmiştir. Ligand ve kompleksin yapıları IR, UV-Visible spektroskopisi, ¹H ve ¹³C NMR spektroskopisi, elementel analiz magnetik süsebtibilite yöntemleri ile karakterize edilmiştir. Analitik veriler kompleks yapısında metal ligand oranının 1:1 olduğunu göstermiştir.

Anahtar Kelimeler: Schiff bazı, Ru(II) kompleksleri, karakterizasyon

1. INTRODUCTION

Among the various ligands, Schiff base ligands have significant importance because Schiff base ligands are potentially capable of forming stable complexes with metal ions [1]. By attaching donor atoms of Schiff bases, they can coordinate various metals and stabilize them in different oxidation states; such complexes are used as catalysts in many important processes [2, 3]. Schiff base complexes containing different central metal atoms such as Cu, Ni, Co and Pd have been studied in great detail for their various crystallographic features, enzymatic reactions, steric effects, structure-redox relationships, mesogenic characteristics, catalysis, magnetic properties and their important role in the understanding of the coordination chemistry of transition metal ions. In some Schiff base metal chelates, it has been show that minor changes in the structure of the ligands containing hard/soft donor atoms, *e.g.*, nitrogen, sulfur and/or oxygen markedly affected the activity of these compounds [4-5]. Metal complexes of Schiff bases have been extensively

studied at scientific applications as catalysts due to their attractive chemical and physical properties.

Complex formation studies of ruthenium with azo/azoimine ligands and their usage at transfer hydrogenation reaction, metal-carbon bond formation and catalytic transformations have been ongoing [6]. The ruthenium complexes formed by different types of ligands have significant importance. To design the new types of ruthenium (II) Schiff base complexes bearing oxygen and nitrogen donor atoms have importance due to their potential catalytic activities [7]. During recent years, half-sandwich (η^6 -arene)ruthenium (II) complexes draw attention very much and proceed to be the subject of intense research in the field of organometallic chemistry emphatically [8-9].

Due to the importance of the various properties of Schiff base metal complexes, we herein reported the synthesis and characterization of *L*¹*H* and its Ru(II) metal complex.

Ligand and complex structures were confirmed by, elemental analysis, FTIR, ¹H-, ¹³C- NMR, UV-Visible spectroscopy and elemental analyses. The

analytical data shows that the ratio of metal to ligand in the mononuclear Schiff Base complexes is 1:1.

2. EXPERIMENTAL

2.1. Materials and measurements

Reagents and solvents were purchased from chemical suppliers and purified to match the reported physical and spectroscopic data. The solvents were carefully dried using standard methods. Melting points were determined with an Electrothermal 9200 apparatus. Elemental analyses (C, H, N) were performed using a Carlo Erba 1106 elemental analyser. Infrared spectra were obtained using KBr discs ($4000\text{--}400\text{ cm}^{-1}$) on a Shimadzu 8300 FTIR spectrophotometer. The electronic spectra in the 200–900 nm range were obtained using DMF on a Hithachi U-3900 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian AS-400 MHz instrument. TMS was used as internal standard and deuterated DMSO as solvent. Magnetic measurements were carried out by the Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant.

2.2. Synthesis of (E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol (L¹H)

(E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol **1** (L¹H) (Figure 1) was synthesized as follow; 10 mmol (1.23 g) 4-(aminomethyl)phenol and 10 mmol (1.07 g) of picolinaldehyde were condensed by refluxing in 70 cm³ of absolute ethanol for 3 h. The solution was left at room temperature. (E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol was obtained as brown micro crystals; the micro crystals were filtered off, washed with 10 cm³ of absolute ethanol and then recrystallized from DMF. Mp: 130°C. ^1H NMR (400 MHz, CDCl_3) δ 10.02 (s, 1H), 8.64 (d, $J = 64.7$ Hz, 1H), 8.35 (s, 1H), 7.99 (s, 1H), 7.69 (s, 1H), 7.28 (s, 1H), 6.98 (s, 2H), 6.60 (s, 2H), 4.71 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.92, 155.84, 153.96, 148.89, 137.07, 129.84, 128.70, 125.00, 121.48, 115.58, 63.81. FT-IR (KBr, cm^{-1}): 3027, 2876–2789, 1639. Anal. Cald. For: $[\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}]$, C: 73.56, H: 5.70, N: 13.20. Found: C: 73.29, H: 5.59, N: 13.01. UV-Vis. (λ_{max} , nm) in MetOH: 255, 273, 280, 391.

2.3. General procedure for the synthesis of Ru(II) metal complex

Dichloro(*p*-cymene)ruthenium(II) dimer (0.28 g, 0.47 mmol) was added to the solution of (E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol **2** (0.2 g, 0.94 mmol) in methanol (10 ml) in one portion and refluxed for 6 h at nitrogen atmosphere in a schlenk

tube. The precipitate was filtered and rinsed petroleum ether (20 mL) and diethyl ether (20 mL). The complex **2** was obtained as brown solid. The Ru(II) complex is soluble in solvents such as EtOH and MetOH. Mp: 190°C. ^1H NMR (300 MHz, DMSO) δ 9.95 (s, 1H), 9.60 (d, $J = 4.5$ Hz, 1H), 8.37 (s, 1H), 8.23 (s, 2H), 7.78 (s, 2H), 7.28 (d, $J = 7.8$ Hz, 1H), 6.91 (d, $J = 7.8$ Hz, 2H), 6.31 (d, $J = 5.7$ Hz, 2H), 6.08 (d, $J = 5.7$ Hz, 1H), 5.92 (dd, $J = 12.0, 5.8$ Hz, 1H), 5.65 (d, $J = 16.1$ Hz, 2H), 5.30 (d, $J = 16.1$ Hz, 1H), 2.56 (m, 1H), 2.14 (s, 1H), 1.01 (d, $J = 6.5$ Hz, 3H), 0.91 (d, $J = 6.5$ Hz, 6H). FT-IR (KBr, cm^{-1}): 3037, 2866–2785, 1626. Anal. Cald. For: $[\text{C}_{23}\text{H}_{26}\text{Cl}_2\text{N}_2\text{ORu}]$, C: 53.28, H: 5.05, N: 5.40. Found: C: 53.16, H: 5.09, N: 5.31. UV-Vis. (λ_{max} , nm) in DMF: 274, 328, 363, 396, 404. μ_{eff} , BM: Diamagnetic.

3. RESULT and DISCUSSION

3.1. Synthesis of the compounds

The L¹H ligand, was prepared by the reaction of 4-(aminomethyl)phenol with picolinaldehyde, (1:1 molar ratio) in EtOH as shown in Figure 1. The level of the purity of the ligand was checked by T.L.C. on silica gel-coated plates. Beside this the Ruthenium (II) complex of L¹H was prepared. The ligand is stable at room temperature and soluble in common organic solvents such as EtOH, MeOH, DMF and CH_2Cl_2 . The complex is also stable at room temperature.

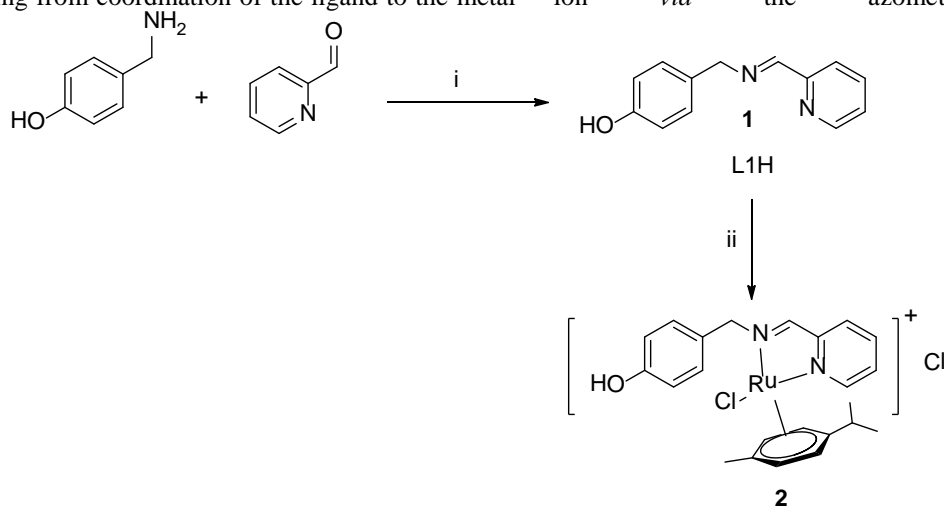
In the ligand FTIR spectra, L¹H exhibit OH band at 3420 cm^{-1} that are assignable to $\nu(\text{OH})$. The bands at $2876\text{--}2789\text{ cm}^{-1}$ can be assigned to $\nu(\text{Ar-CH})$ [10–11]. The band at 1639 cm^{-1} is due to the vibration of the azomethine group in the ligand.

The electronic absorption spectral data for L¹H ligand was obtained in MetOH solution at room temperature. There are absorption bands between 404 and 255 nm for the ligand and its metal complex at the UV–visible spectra. The band at λ_{max} 390 nm was assigned to $n \rightarrow \pi^*$ transitions of the azomethine groups in the L¹H ligand. In the spectra of the complex, the bands of the azomethine $n \rightarrow \pi^*$ transitions shifted to lower frequencies indicating the involvement of the imine nitrogen atom with the metal ion.

In order to better understand the structure of the ligand, ^1H and ^{13}C NMR spectral data in CDCl_3 as solvent are given in Figure 2 and exhibit all expected signals.

The ^1H NMR spectra of the ligand exhibit singlet signals in the 10.02 ppm and 8.64 ppm which are attributed to the OH and azomethine group protons, respectively [1]. In the spectra of the Ru(II) complex, the singlets which are attributed to the OH and azomethine groups, are seen in the 9.95 and 9.60 ppm as singlet signals. The difference at these signals can be

originating from coordination of the ligand to the metal ion via the azomethine nitrogen.



(i) Ethanol, reflux, 3 h; (ii) $[\text{RuCl}_2(\text{p-cymene})]_2$, MeOH, 50 °C, 12 h;

Figure 1. General synthesis of L¹H ligand and its Ru(II) complex.

In the L¹H spectrum, singlet signal at 4.71 and signals at 8.35-6.60 ppm may be assigned to aliphatic CH₂ protons and aromatic ring protons respectively. The ¹H NMR spectrum of L¹H is taken as a representative example and shown in Figure 2. Unlike the ligand, in the Ru(II) complex spectrum, the doublet signals at 1.01

and 0.91 ppm can be attributed to the CH₃ protons that originated from *p*-cymene molecule.

The ¹³C NMR spectra of the ligands exhibit singlet signals at 161.92 ppm which can be assigned to the azomethine group carbon atoms [12]. The signals due to the carbon atoms of aromatic ring are observed in the 115.58-155.84 ppm range.

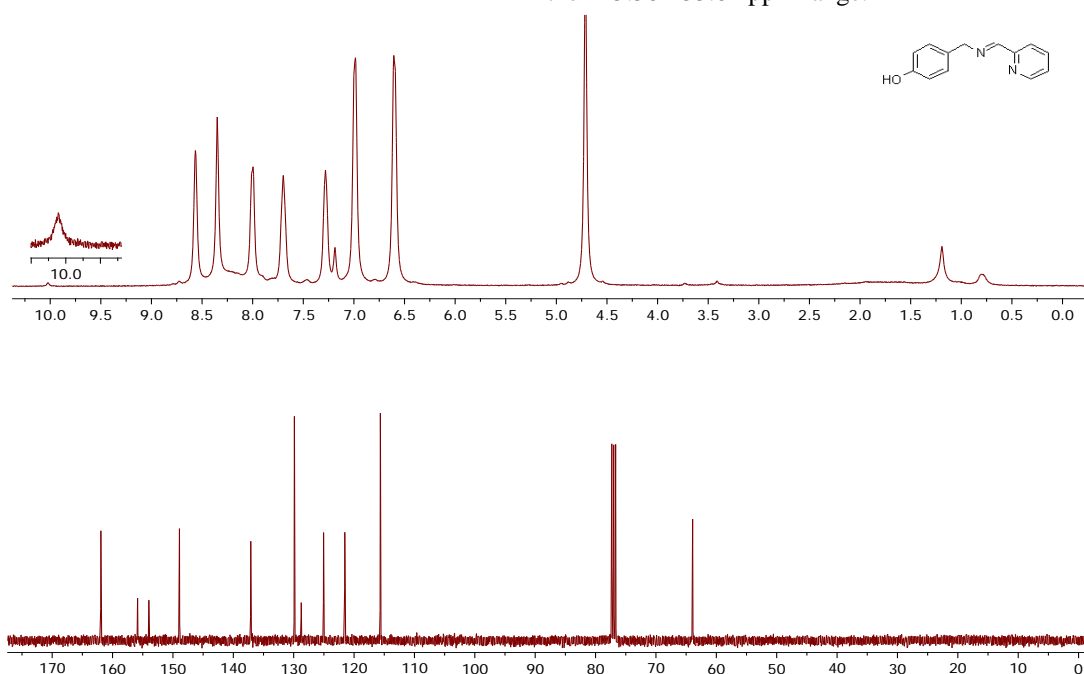


Figure 2. ¹H and ¹³C NMR spectra of L¹H ligand.

4. CONCLUSIONS

The Schiff base ligand containing N,N donor atoms, *(E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol (L¹H)* (Fig. 1) and its Ru(II) complex have been prepared in good yields. The ligand and their complex have been characterized by elemental analyses, IR spectra, UV-Visible spectroscopy, ¹H and ¹³C NMR spectra and magnetic susceptibility measurements. The analytical data show that the metal to ligand ratio in the L¹H complexes is 1:1.

5. ACKNOWLEDGEMENTS

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