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Syntheses, characterizations and structures of NO donor Schiff base ligands and nickel(II) and copper(II) complexes

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1. Introduction

Schiff base ligands have played an important role in the development of coordination chemistry, especially their metal complexes exhibit wide applications in biological and industrial systems [1–6]. Furthermore, the Schiff bases are very important tools for the inorganic chemists as these are widely used to design molecular ferromagnets, in catalysis, in biological modeling applications, as liquid crystals and as heterogeneous catalysts [7–9]. Schiff base ligands containing various donor atoms (like N, O, S, etc.) show broad biological activity and are of special interest because of the variety of ways in which they are bonded to the transition metal ions [10,11]. Schiff base nickel(II) complexes have been regarded as models for enzymes such as urease [12]. Vanilline and furfurylamine Schiff base derivatives are very useful biochemical materials having biological activities [13,14]. Although the oxygen atom of the furan ring could not coordinate to the transition metals, the special tendency of the oxygen atom will be effective on the crystal structures of the complexes [15,16].

In the previous works, we reported the syntheses and crystal structures of different Schiff base compounds and their metal complexes [17–20]. In this article, we have succeeded in the syntheses of new Schiff base compounds (L^1 and L^2) and complexes [Ni(L^1)₂], [Cu(L^1)₂] and their characterizations by elemental analyses, FT-IR,

ABSTRACT

New Schiff base derivatives (L^1 and L^2) were prepared by the condensation of 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin) and 3-hydroxy-4-methoxybenzaldehyde (*iso*-vanillin) with 5-methylfurfurylamine. Two new complexes [Ni(L^1)₂] and [Cu(L^1)₂] have been synthesized with bidentate NO donor Schiff base ligand (L^1). The Ni(II) and Cu(II) atoms in each complex are four coordinated in a square planar geometry. Schiff bases (L^1 and L^2) and complexes [Ni(L^1)₂] and [Cu(L^1)₂] were characterized by elemental analyses, FT-IR, UV-vis, mass and ¹H, ¹³C NMR spectroscopies. The crystal structures of the ligand (L^2) and complexes [Ni(L^1)₂] and [Cu(L^1)₂] have also been determined by using X-ray crystallographic technique. © 2011 Elsevier B.V. All rights reserved.

mass, ¹H and ¹³C NMR, UV-vis and X-ray single crystal diffraction (Scheme 1).

2. Experimental

2.1. Reagents

2-Hydroxy-3-methoxybenzaldehyde (*o*-vanillin) and 3-hydroxy-4-methoxybenzaldehyde (*iso*-vanillin) were purchased from Aldrich, and used without further purification. Solvents were dried and distilled before use according to the standard procedure.

2.2. Physical measurements

Melting points were measured on a Thomas-Hoover apparatus using a capillary tube. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury, High Performance Digital FT-NMR (400 MHz) spectrometer (SiMe₄ as a internal standard). Chemical shifts for proton and carbon resonances were reported in ppm (δ) (¹H and ¹³C NMR chemical shifts are given according to the numbering scheme). IR spectra were obtained from PEL-DATA spectrum 100 series spectrometer. Carbon, nitrogen and hydrogen analyses were performed on LECO CHNS-932 elemental analyzer. Mass spectrometric analyses were performed on the Waters 2695 Allonce ZQ LC/MS spectrometer. Magnetic Susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MKI) at room temperature (300 K). UV-vis spectra were recorded using a Unicam UV2–100 series spectrometer.



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 $[Ni(L^1)_2] [Cu(L^1)_2]$

Scheme 1. Preparation of Schiff bases and complexes [Ni(L¹)₂] [Cu(L¹)₂].

2.3. X-ray data collection and structure refinement

Experimental data for L^2 , $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$ are listed in Table 1, selected bond lengths and angles and hydrogen-bond geometries are given in Tables 2 and 3, respectively. Crystallographic data were recorded on a Bruker Kappa APEXII CCD areadetector diffractometer using Mo K α radiation (λ = 0.71073 Å) at T = 100(2) K (for L^2) and T = 294 K (for $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$). Absorption corrections by multi-scan [21] were applied. Structures were solved by direct methods [22] and refined by full-matrix least squares against F² using all data [22]. All non-H atoms were refined anisotropically. All H atoms (for L^2) and only H7 atoms for $[Ni(L^1)_2]$ and [Cu(L¹)₂]) were located in difference syntheses and refined isotropically. The remaining H atoms were positioned geometrically at distances of 0.93 Å (CH), 0.97 Å (CH₂) and 0.96 Å (CH₃) from the parent C atoms; a riding model was used during the refinement process and the Uiso(H) values were constrained to be 1.2Ueq(carrier atom) for CH and CH₂ and 1.5U_{eq}(carrier atom) for CH₃. Computer programs: SHELXS97 [22], SHELXL97 [22], ORTEP-3 [23]. Source of atomic scattering Factor: Int. Table for X-ray Cryst. vol. IV, 1974 [24].

2.4. Syntheses of the Schiff bases and complexes

2.4.1. 2-Methoxy-6-((E){[(5-methyl-2furyl)methyl]imino}methyl)phenol (L¹)

5-Methylfurfurylamine (0.25 g, 2.24 mmol) was added to a stirred solution of 2-hydroxy-3-methoxybenzaldehyde (0.34 g, 2.24 mmol) in EtOH (50 mL). The mixture was refluxed and stirred for 3 h and then allowed to cool to ambient temperature. The yellow micro crystals were filtered off and re-crystallization has been performed in n-heptane solution. m.p.: 55 °C. Yield 83% (0.45 g, 1.85 mmol). Anal. Calcd. For C₁₄H₁₅NO₃; C, 68.56; H, 6.16; N, 5.71. Found: C, 68.37; H, 6.33; N, 5.46%. IR (KBr, cm⁻¹): $v_{C=N} = 1633, v_{C-H} = 2960; 2826, v_{C-O} = 1189.$

Table 1

Crystallographic data, details of data collection and structure refinement parameters for L^2 , $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$.

	L ²	[Ni(L ¹) ₂]	$[Cu(L^1)_2]$
Empirical formula Colour/shape Formula weight Temperature (K)	C ₁₄ H ₁₅ NO ₃ Yellow/block 245.27 100(2)	C ₂₈ H ₂₈ N ₂ NiO ₆ Brown/block 547.21 294(2)	C ₂₈ H ₂₈ N ₂ CuO ₆ Red/block 552.06 294(2)
Radiation used, graphite monochr. Crystal system Space group a, b, c (Å) β (°) V (Å ³) Z Absorption coefficient (mm ⁻¹) D_{calc} (Mg m ³) Max. Crystal dimen. (mm) θ (max) (°) Reflections measured	Mo K α (λ = 0.71073 Å) Monoclinic P2 ₁ /n 13.6380(3) 5.5151(1) 16.5592(3) 101.150(2) 1221.99(4) 4 0.094 1.333 0.19 × 0.26 × 0.28 28.29 3041	$\begin{array}{l} P2_1/n\\ 9.6382(4)\\ 7.2529(3)\\ 18.3790(5)\\ 102.050(5)\\ 1256.47(8)\\ 2\\ 0.819\\ 1.446\\ 0.20\times0.28\times0.30\\ 28.40\\ 3142\end{array}$	$\begin{array}{c} P2_1/c\\ 13.091(5)\\ 10.479(4),\\ 9.920(4)\\ 68.595(6)\\ 1267.0(9)\\ 2\\ 0.908\\ 1.447\\ 0.12\times0.25\times0.46\\ 28.60\\ 3209 \end{array}$
Range of <i>h</i> , <i>k</i> , <i>l</i> No. of refl. with $l > 2\sigma(l)$	-18 < h < 18 -7 < k < 7 -22 < l < 20 2142	-12 < h < 12 -9 < k < 9 -24 < l < 24 2602	-17 < h < 17 -14 < k < 14 -12 < l < 13 1711
Corrections applied Structure solution Treatment of H atoms No. of parameters var. GOF $R = F_0 - F_c / F_0 $ R_w $(\Delta/\rho) \max (eA^{-3})$ $(\Delta/\rho) \min (eA^{-3})$	Lorentz-polarization Direct methods Diff. Map. 223 1.009 0.0394 0.0980 0.220 –0.203	Geom. Calc. 175 1.029 0.0293 0.0778 0.225 -0.358	Geom. Calc. & Diff. Map. 175 0.971 0.0522 0.0885 0.381 -0.519

Table 2

Selected bond lenghts (Å) and angles (°) for L^2 , [Ni(L^1)₂] and [Cu(L^1)₂].

L ²		$[Ni(L^1)_2]$		$[Cu(L^1)_2]$	
N1-C7	1.2742(18)	Ni1—N1	1.9152(12)	Cu1—N1	2.0088(19)
N1-C8	1.4647(18)	Ni1-01	1.8263(10)	Cu1-01	1.8758(16)
01–C2	1.3564(16)	N1-C7	1.2924(19)	N1-C7	1.286(3)
02–C3	1.3623(17)	N1-C8	1.4968(19)	N1-C8	1.473(3)
02–C14	1.4276(18)	01–C1	1.2996(17)	01–C1	1.296(3)
C6–C7	1.462(2)	02—C2	1.365(2)	02–C2	1.362(3)
C8–C9	1.493(2)	C8–C9	1.483(2)	C8–C9	1.471(4)
C3-02-C14	116.73(12)	01-Ni1-N1	86.92(5)	01-Cu1-N1	91.32(7)
C9-03-C12	106.47(10)	01-Ni1-N1'	93.08(5)	01-Cu1-N1'	88.68(7)
C7-N1-C8	116.97(12)	Ni1-01-C1	130.53(10)	Cu1-01-C1	129.82(15)
C6-C7-N1	124.54(13)	Ni1-N1-C7	124.70(11)	Cu1-N1-C7	123.26(16)
C9-C8-N1	108.47(12)	Ni1-N1-C8	121.84(9)	Cu1-N1-C8	119.89(14)
C8–C9–C10	133.69(13)	C7-N1-C8	113.36(13)	C7—N1—C8	116.80(19)
C8–C9–O3	116.04(12)	N1-C7-C6	127.09(15)	N1-C7-C6	127.5(2)
O3-C9-C10	110.26(12)	N1-C8-C9	110.43(12)	N1-C8-C9	111.6(2)

Table 3

Hydrogen-bond geometries (, °) for L², [Ni(L¹)₂] and [Cu(L¹)₂].

	D—H···A	D—H	$H{\cdot}\cdot{\cdot}A$	$D{\cdots}A$	$D -\!\!\!\!- H \!\cdot \!\cdot \!\cdot A$
L ²	01—H1A…N1 ⁱ	0.94(2)	1.82(2)	2.7478(16)	173.2(19)
[Ni(L ¹) ₂]	C8—H8B…01	0.97	2.13	2.671(2)	114
[Cu(L ¹) ₂]	C8—H8A…01	0.97	2.28	2.778(3)	111

Symmetry code: (i) $\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$.

2.4.2. 2-Methoxy-5-((E){[(5-methyl-2-

furyl)*methyl*]*imino*}*methyl*)*phenol* (**L**²)

This Schiff base was prepared by a procedure similar to L^1 using 3-hydroxy-4-methoxybenzaldehyde (0.34 g, 2.24 mmol). The yellow solid was recrystallized from n-hexane/CH₂Cl₂ (2:1 v/v). Single

crystals of ligand (**L**²) suitable for X-ray analyses were obtained by slow evaporation of n-hexane/CH₂Cl₂ solution. m.p.: 64 °C. Yield 69% (0.38 g, 1.54 mmol). Anal. Calcd. For C₁₄H₁₅NO₃; C, 68.56; H, 6.16; N, 5.71. Found: C, 68.66; H, 6.39; N, 5.49%. IR (KBr, cm⁻¹): $v_{C=N} = 1635$, $v_{C-H} = 2964$; 2835, $v_{C-O} = 1175$.

2.4.3. Nickel (II) complex $[Ni(L^1)_2]$

To $[Ni(CH_3COO)_2]$. $4H_2O$ (0.24 g, 1 mmol) dissolved in 15 mL EtOH was added Schiff base (L^1) (0.49 g, 2 mmol) dissolved in 15 mL hot EtOH with stirring at reflux temperature for 3 h and then allowed to cool to ambient temperature. The brown crystals were filtered off and recrystallized from acetone. Single crystals of nickel (II) complex suitable for X-ray analyses were obtained by slow evaporation of acetone. m.p.: 183 °C. Yield 72% (0.35 g, 0.89 mmol).

Anal. Calcd. For $C_{28}H_{28}N_2O_6Ni$: C, 61.46; H, 5.12; N, 5.12. Found: C, 61.56; H, 5.49; N, 5.22%. IR (KBr, cm⁻¹): $v_{C=N}$ = 1609, v_{C-H} = 2918; 2833, v_{C-O} = 1167.

2.4.4. Copper (II) complex **[Cu(L¹)₂]**

Cu(II) complex was synthesized by similar method as described for **[Ni(L¹)₂]**, with [Ni(CH₃COO)₂]. 4H₂O replaced by [Cu(CH₃CO O)₂]. H₂O (0.20 g, 1 mmol). Crude product was filtered off and recrystallized from THF. The red single crystals of Cu(II) complex suitable for X-ray analyses were obtained by slow evaporation of THF. m.p.: 204 °C. Yield 63% (0.30 g, 0.88 mmol). Anal. Calcd. For C₂₈H₂₈N₂O₆Cu: C, 60.92; H, 5.07; N, 5.07. Found: C, 61.27; H, 4.78; N, 5.39%. IR (KBr, cm⁻¹): v_{C=N} = 1612, v_{C-H} = 2912; 2832,. v_{C-O} = 1165.

3. Results and discussion

3.1. Syntheses

The reactions between 5-methylfurfurylamine with appropriate aldehyde in EtOH yield Schiff base ligands (L^1 and L^2). The ligands (L^1 and L^2) were successfully synthesized with yields in the range 83% and 69%. Schiff bases (L^1 and L^2) are soluble in EtOH, CHCl₃, THF, acetone, DMSO, CH₃CN, n-hexane and n-heptane. Schiff base ligands (L^1 and L^2) were characterized by elemental analyses, IR, ¹H, ¹³C NMR, mass and UV-vis spectra. Single crystals of ligand (L^2) suitable for X-ray analyses were obtained by slow evaporation of n-hexane/CH₂Cl₂ solution.

The Schiff base L¹ readily formed complexes $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$, treating two equivalents of ligand with one equivalent of $[Ni(CH_3COO)_2]$. $4H_2O$ or $[Cu(CH_3COO)_2]$. H_2O in EtOH. The synthesis of various mononuclear complexes of copper(II) containing Schiff base ligands obtained in situ from appropriate amine and aldehyde [15,25]. The stoichiometries of the complexes derived from elemental analysis correspond to the general formula $[M(L^1)_2]$ which are confirmed by determining the X-ray crystal structures of $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$. The purity of the complexes were checked by C, H, N elemental analyses, mass and IR spectra. ¹H NMR and ¹³C NMR spectra were detected for $[Ni(L^1)_2]$, because $[Ni(L^1)_2]$ is diamagnetic and NMR active.

The magnetic susceptibility results of the complexes give indications of the geometries of the ligands around the central transition metal ions. Cu(II) complex shows room temperature magnetic susceptibility value as expected for an isolated d⁹ transition metal center. The effective magnetic susceptibility (μ_{eff}) value is found to be 1.74 B. M. at 300 K, which is very consistent with the expected spin only magnetic moment of a S = 1/2, d⁹ copper(II) configuration. Copper(II) complex [**Cu(L**¹)₂] was characterised by single crystal X-ray structure determination which shows that the copper(II) ion is in a square planar N₂O₂ environment.

The nickel(II) complex **[Ni(L¹)₂]** was diamagnetic as expected for a d⁸ electronic configuration and was found to be square planar geometry as indicated by X-ray crystallographic data.

3.2. Description of the structures of (L^2) , $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$

The X-ray structural determinations of L^2 , $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$ confirm the assignments of their structures from spectroscopic data. The molecular structures along with the atomnumbering schemes are depicted in Figs. 1a–c, respectively. The asymmetric units of $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$ contain one-halves of the molecules (Figs. 1b and c). The Ni1 and Cu1 atoms are located on the inversion centers and surrounded by the two N and the two O atoms of the symmetry related 2-methoxy-5-((E){[(5-methyl-2furyl)methyl]imino}methyl)phenol (L^2) ligands. The four atoms in



Fig. 1. ORTEP-3 drawings with the atom-numbering schemes of $L^2(a)$, $[Ni(L^1)_2]$ (b), and $[Cu(L^1)_2]$ (c). Displacement ellipsoids are drawn at 50% probability level. Hydrogen bonds are shown as dashed lines.

the equatorial planes around the Ni1 and Cu1 atoms form slightly distorted square-planar arrangements (Table 2). The Ni–O [1.8263(10) Å], Ni–N [1.9152(12) Å] and Cu–O [1.8758(16) Å],

Cu—N [2.0088(19) Å] bonds are in good agreement with the corresponding values [1.833(2) and 1.902(2)Å] in $(C_{26}H_{24}O_6N_2N_i)$ and [1.8932(2) and 2.006(2) Å] in $(C_{26}H_{24}O_6N_2Cu)$ [18], [1.896(1) and 2.000(2)Å] in (C₂₄H₂₀O₄N₂Cu) and [1.867(2) and 1.976(2)Å] in $(C_{26}H_{24}O_4N_2Cu)$ [25], [1.826(2) and 1.913(2) Å] in [Ni $(C_{14}H_{14}NO_2)_2$] [26] and [1.819(2), 1.922(2) and 1.823(2), 1.914(3)Å] in [Ni(C₁₆H₁₈NO₂)₂] [27]. The rings A (C1-C6) and B (O3/C9-C12) are, of course, planar and they are oriented at dihedral angles of $A/B = 79.04(4)^{\circ}$ (for L^2), 75.20(5)° (for $[Ni(L^1)_2]$) and 82.07(11)° (for [Cu(L¹)₂]). The ring C (Cu1/O1/N1/C1/C6/C7) (for [Cu(L¹)₂]) adopts envelope conformation with Cu1 atom displaced by -0.2738(4) Å from the plane of the other ring atoms, while ring C(Ni1/O1/N1/C1/C6/C7) (for $[Ni(L^1)_2]$) is planar. The intramolecular C—H···O hydrogen bonds (Table 3) result in the formations of the five membered rings D ((Ni1/O1/N1/C8/H8B) (for [Ni(L¹)₂]) and D (Cu1/O1/N1/C8/H8A) (for [Cu(L¹)₂]) having envelope conformations with H8B and H8A atoms displaced by 0.3097(1) and -0.3880(4) Å, respectively, from the planes of the other ring atoms. In the crystal structures, the intermolecular O-H···N hydrogen bonds link the molecules into double chains through the bifurcated hydrogen bonds (Table 3) along the *b*-axis for L^2 (Fig. 2a), while the Ni1 and Cu1 (for $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$, respectively) atoms are located at the corners of the unit cells (Figs. 2b and c). The molecules are alongated along the *a*-axis (for [Ni(L¹)₂]) and *c*-axis (for [**Cu**(**L**¹)₂]) and stacked along the *b*-axes.

3.3. IR spectra

The IR spectra of the Schiff base free ligands (L^1 and L^2) show strong bands at 1633 and 1635 cm⁻¹ due to $v_{C=N}$ of imine, which indicate that the Schiff base ligands have been obtained. The IR spectra of the ligand (L^1) and the corresponding complexes Ni(II) and Cu(II) are very similar. In metal complexes [Ni(L^1)₂] and [Cu(L^1)₂], azomethine band ($v_{C=N}$) was shifted to lower frequencies (1609 and 1612 cm⁻¹) after complexation. This lower shift could be attributed to a weakening of the C=N bonds on adduct formation and this can be explained by the donation of electrons from nitrogen to the empty d-orbitals of the transition metal ions [28–32]. The strong bands at 1189 and 1175 cm⁻¹ in the free Schiff base ligands (L^1 and L^2) are due to the phenolic C–O stretchings. On complex formation, these bands are shifted to lower frequencies (1167 and 1165 cm⁻¹) indicating coordinations through the phenolic oxygens.

3.3.1. ¹H and ¹³C NMR spectra

The ¹H NMR spectral data of the Schiff base ligands (L^1 and L^2) and complex [Ni(L^1)₂] are listed in Tables 4. In the ¹H NMR spectra of the Schiff bases (L^1 and L^2), the phenolic OH proton was detected as a broad singlet in the offset region at 13.70 and 13.67 ppm. The characteristic signals at 8.38 and 8.22 ppm are assigned to -HC=Nfor compounds L^1 and L^2 . The ¹H NMR spectra of the Schiff bases indicate the presence of the aliphatic protons (such as $-CH_3$, $-OCH_3$ and $-CH_2$ protons) in the range of 2.26, 3.90 and 4.72 ppm (for compound L^1) and 2.27, 3.90 and 4.70 ppm (for compound L^2) as singlets. The aromatic protons of the free ligands (L^1 and L^2) were observed as multiplets in the aromatic region.

The absence of the OH proton peak in the spectrum and the upfield shift (8.56 ppm) of the azomethine proton (HC=N) peak in complex $[Ni(L^1)_2]$ with respect to the corresponding free ligand, indicate the complexation with Ni(II). The aliphatic protons (--CH₃, --OCH₃ and --CH₂ for ligands L^1 and L^2) were detected in the expected regions.

The ¹³C NMR spectral data of the Schiff bases and Ni(II) complex is listed in Table 5. The free ligand Schiff bases show the azomethine carbon peaks at 166.06 and 162.35 ppm, respectively. The aliphatic $-CH_3$, $-OCH_3$ and $-CH_2$ carbon peaks for ligands L¹



Fig. 2. Partial packing diagrams of L^2 (a), (b) [**Ni**(L^1)₂] viewed down the *b*-axis, where *c*-axis is horizontal and *a*-axis is vertical, and (c) [**Cu**(L^1)₂] viewed down the *b*-axis, where *a*-axis is horizontal and *c*-axis is vertical. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

and L^2 are detected at 13.56, 56.15, 54.90 ppm and 13.62, 57.15, 56.10 ppm, respectively. The aromatic and four furyl ring carbons are observed in the expected regions. In the ¹³C NMR spectra for the Ni(II) complex, all the carbon peaks are slightly shifted upfield and downfield. The signals of carbons are equal to the number in the proposed structures of the Schiff bases and Ni(II) complex.

Table 4

Comp.	ОН	N=CH	-CH ₃	-0CH ₃	-CH ₂₍₅₎	H ₍₂₎	H ₍₃₎	H ₍₈₎	H _(10,11,12)	
L1	13.70	8.38	2.26	3.90	4.72	5.94	6.147	-	6.82-6.99	
[Ni(L ¹) ₂]	(bs, 1H) -	(s, 1H) 8.56 (s, 2H)	(s, 3H) 2.29 (s, 6H)	(s, 3H) 3.87 (s, 6H)	(s, 2H) 4.71 (s, 4H)	(d, 1H) <i>J</i> = 2.8 6.02 (d, 2H)	(d, 1H) <i>J</i> = 2.9 6.18 (d, 2H)	-	(m, 3H) 7.03–7.17 (m, 6H) H ₍₁₁₎	H ₍₁₂₎
L ²	13.67 (bs, 1H)	8.22 (s, 1H)	2.27 (s, 3H)	3.90 (s, 3H)	4.70 (s, 2H)	5.92 (d, 1H) <i>J</i> = 1.9	6.14 (d, 1H) <i>J</i> = 2.8	7.39 (d, 1H) <i>J</i> = 1.5	6.87 (d, 1H) <i>J</i> = 8.3	7.27 (q, 1H) <i>J</i> = 8.2, <i>J</i> = 1.5
	H 6 N 8 OH	5 CH ₂ 4 3		43	12 11 10 0 0 0 9 0 H	H 7 6 N 8		H₃ H₃C~ H₃C~		6 4 1 CH ₃ 0 CH ₃
(L ¹)					(L ²)			[Ni(L ¹)2]	~

¹H NMR spectral data of the Schiff bases (L^1 and L^2) and complex [Ni(L^1)₂] (in CDCl₃); δ in ppm; s, singlet; bs, broad singlet; d, doublet; m, multiplet; q, quartet; J = Hz.

Table 5 ¹³C NMR spectral data of the Schiff bases (L^1 and L^2) and complex [Ni(L^1)₂] (in CDCl₃); δ in ppm.

Comp.	$N = C_{(6)}H$	$-CH_3$	-0CH3	$-C_{(5)}H_2$	C _(1-4, 7-12)
L1	166.06	13.56	56.15	54.90	106.29; 108.79; 114.22; 118.00; 118.69; 123.13; 148.47; 149.07; 151.61; 152.24
L ²	162.35	13.62	57.15	56.10	106.23; 108.28; 110.31; 113.98; 121.37; 129.73; 145.89; 149.09; 150.63; 151.79
[Ni(L ¹) ₂]	166.18	13.59	56.13	54.96	106.37; 108.93; 113.96; 117.67; 118.18; 123.17; 148.01; 148.96; 151.03; 151.79

3.4. UV-vis spectra

The UV-vis spectra were recorded in EtOH solutions in the range of 210–450 nm for the Schiff bases and the complexes (Table 6). The molar absorbtivities (for ligands L^1 and L^2) at 328 and 314 nm may be assigned to an $n-\pi^*$ transition between lone-pair electrons of the p orbitals of the N atoms in the azomethine (HC=N) groups and the π bonds of the aromatic rings [32,33]. The peaks at 262 and 279 nm are assigned to the π - π^* transitions of the Schiff bases (L^1 and L^2).

In the electronic spectra of the complexes $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$, the LMCT band in the UV region (412 nm) can be assigned to N \rightarrow Ni charge transfer, while the other bands at 374 and 376 nm are also due to LMCT arising out of O \rightarrow Ni charge transfer [34]. Similar nickel(II) and copper(II) complexes with an asymmetric bidentate Schiff base ligand derived from furfuryl-

Table 6
UV-vis spectral data of the ligands and complexes.

Comp.	^a λ , nm (log ε)
L ¹	220 (3.73); 262 (3.35); 328 (2.53)
L ²	216 (3.75); 279 (3.57); 314 (3.40)
[Ni(L ¹) ₂]	224 (3.68); 266 (3.47); 374 (2.66); 412 (2.86)
[Cu(L ¹) ₂]	234 (3.75); 280 (3.51); 376 (2.89); 412 (2.93)

^a EtOH solutions 5×10^{-4} at 300 K.

amine, only one d-d transition is observed in the visible region at approximately 625 nm [35].

3.5. Mass spectra

The mass spectral data of the Schiff bases and complexes are given in Table 7. The mass spectra fragmentation patterns of the compounds were in good agreement with the suggested structures. The mass spectra of Schiff bases (\mathbf{L}^1 and \mathbf{L}^2) were characterized by an intense peak m/z [M + 1]⁺ 246 (100%) corresponding to the molecular ion peak (calculated value 245). The mass spectral data of the complexes [**Ni**(\mathbf{L}^1)₂] and [**Cu**(\mathbf{L}^1)₂] show molecular ion peaks (m/z); 547 and 552 corresponding to C₂₈H₂₈N₂O₆Ni and C₂₈H₂₈N₂O₆Cu, respectively. The important fragments of the ligands and complexes at m/z 246, 152 and 95 are attributed to the Schiff base molecular ion peak [M + H⁺], loss of methylfuran ring (C₈H₈NO₂+2H) and methylfuran ring (C₆H₇O⁺), respectively.

Table 7 Mass spectral data of the Schiff bases $(L^1 \mbox{ and } L^2)$ and complexes $[Ni(L^1)_2]$ and $[Cu(L^1)_2].$

Comp.	m/z	Relative intensity (%)	Fragment
L1	246 214 152 149 95 80	100 12.3 86.3 38.6 21.7 23.2	$\begin{array}{l} \left[C_{14}H_{15}NO_3+H\right]^{*}\\ C_{13}H_{12}NO_{2}^{+}\\ C_{8}H_{8}NO_{2}+2H\\ C_{8}H_{8}NO_{2}-H\\ C_{6}H_{7}O^{*}\\ C_{6}H_{5}O+H\\ \end{array}$
L ²	246 214 152 149 95 80	100 15.7 85.6 33.5 20.3 23.7	$\begin{array}{l} \left[C_{14}H_{15}NO_3+H\right]^{*}\\ C_{13}H_{12}NO_2^{*}\\ C_8H_8NO_2+2H\\ C_8H_8NO_2-H\\ C_6H_7O^{*}\\ C_6H_5O+H \end{array}$
[Ni(L ¹) ₂]	547 246 152 95	20.7 100 55.9 26.3	$[C_{28}H_{28}N_2O_6Ni]$ $C_{14}H_{14}NO_3 + 2H$ $C_8H_7NO_2 + 3H$ $C_6H_7O^+$
[Cu(L ¹) ₂]	552 246 152 95	22.4 100 57.1 25.3	$[C_{28}H_{28}N_2O_6Cu]$ $C_{14}H_{14}NO_3 + 2H$ $C_8H_7NO_2 + 3H$ $C_6H_7O^+$

4. Conclusion

In conclusion, we have prepared new Schiff bases $(L^1 \text{ and } L^2)$ and transition metal complexes $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$. The Ni(II) and Cu(II) ions are coordinated by two phenolic-O atoms and two azomethine (HC=N) atoms. Spectroscopic, structural and magnetic data show that $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$ are four-coordinate metal complexes owing to the ligation of two bidentate Schiff base moieties.

The molecular structures of the synthesized compounds were identified by IR, ¹H NMR and ¹³C NMR spectra, mass spectra and elemental analyses and their results showed that all the reactions were succesfully completed. The solid state structures of the ligand (L^2) and the complexes $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$ were determined by single crystal X-ray crystallography.

Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic data Centre as the supplementary publication Nos: CCDC 814578 (for compound **[Cu(L¹)₂]**), CCDC 814579 (for compound **[Ni(L¹)₂]**) and CCDC 814580 (for ligand L²). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44–1223-336033 or e-mail: deposit@ccdc.cam.ac. uk).

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