Transition Metal Chemistry
https://doi.org/10.1007/s11243-017-0195-z

Cobalt(II), nickel(II) and copper(II) complexes of a Schiff base ligand: synthesis, structural characterization and luminescence properties

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Received: 6 September 2017 / Accepted: 29 November 2017

Abstract
A Schiff base ligand (HL), 2,4-dimethoxy-*N*-(5-chloro-2-hydroxybenzylidene)-benzenamine, derived from 5-chloro-2-hydroxybenzaldehyde and 2,4-dimethoxyaniline, and its metal complexes $[Co(L)_2]\cdot CH_3OH$ (**1**), $[Ni(L)_2]$ (**2**), $[Cu(L)_2]$ (**3**) have been synthesized. The compounds were characterized by analytical and spectroscopic methods. In addition, the structures of the Schiff base HL and its Co(II) complex were determined by single-crystal X-ray analysis. The Co(II) center is six-coordinate, being coordinated to two imine nitrogen, two phenolate oxygen and two methoxy oxygen atoms of two crystallographically independent Schiff base ligands. Luminescence properties of HL and its complexes were investigated both in solution and in the solid state.

Introduction

Schiff bases have an important role as ligands in coordination chemistry, being readily obtained by condensation of aromatic aldehydes or ketones with amines. Transition metal complexes of Schiff bases are of interest for a wide variety of applications and structural aspects. It has been suggested that the imine bond is responsible for the biological activities of Schiff bases which can include antitumor, anticancer, antioxidant and other biological properties [1, 2]. On the other hand, they are also utilized in organic synthesis, dyes, pigments, polymer stabilizers, corrosion inhibitors, fungicidal, agrochemical ion exchange, nonlinear optics and industrial catalysis [3–5]. Additionally, Schiff base compounds can show photoluminescence properties depending on the electron-donating groups and π-electrons in different parts of the structure (such as imine bonds, methoxy and ethyl groups, ethylene and aromatic rings, involving mesomeric and inductive effects) [6, 7].

In the present study, a new Schiff base (HL), namely 2,4-dimethoxy-*N*-(5-chloro-2-hydroxybenzylidene)-benzenamine, and its cobalt(II), nickel(II) and copper(II) complexes were synthesized. The compounds were characterized by elemental analysis, ^{1}H and ^{13}C NMR, FTIR, TGA, ICP, Q-TOF LC/MS, magnetic susceptibility, melting point and single-crystal X-ray diffraction techniques (for HL and $[Co(L)_2]\cdot CH_3OH$). The luminescence and thermal properties of the compounds were also investigated.

Experimental

Materials and methods

All chemicals were purchased from commercial sources and used without further purification. $Co(OAc)_2\cdot 4H_2O$, $Ni(OAc)_2\cdot 4H_2O$, $Cu(OAc)_2$, 2,4-methoxy aniline and 5-chloro-2-hydroxybenzaldehyde were purchased from Sigma-Aldrich. Infrared spectra were obtained on a PerkinElmer RX-1 (KBr disk 4000–400 cm^{-1}) FTIR spectrometer. Thermogravimetric analysis (TGA) was performed with a PerkinElmer Pyris Diamond TG/DTA N_2 (50–900 °C range) at a heating rate of 20 °C/min. A PerkinElmer Lambda 25 spectrometer was used for the UV–Vis spectrophotometric studies. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 600 MHz instrument using TMS as internal standard and

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11243-017-0195-z) contains supplementary material, which is available to authorized users.

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Published online: 06 December 2017

DMSO-d_6 as solvent. A Bruker APEX2 CCD diffractometer was used for the X-ray diffraction analysis of HL and the Co(II) complex. Data reduction was performed using Bruker SAINT. SHELXS97 was used to solve and SHELXL2014/6 to refine the structures [8]. A PerkinElmer LS55 luminescence spectrometer was used for the luminescence studies. All samples were prepared both in the solid state and in different solvents at constant concentration (1.10^{-5} M, DMSO, ethanol, methanol and chloroform solutions) and analyzed in a 1 cm optical path quartz cuvette. Mass analysis was performed on an Agilent 6545 Accurate Mass Q-TOF LC/MS.

Synthesis of HL

HL was prepared by refluxing 2,4-dimethoxy aniline (0.77 g, 5.0 mmol) with 5-chloro-2-hydroxybenzaldehyde (0.78 g, 5.0 mmol) in ethanol (20 mL) for 3 h. The dark orange solution was filtered, and the solvent was removed by rotary evaporation. Single crystals of HL suitable for X-ray diffraction were obtained from slow evaporation of a solution in methanol (Scheme 1) [9].

HL: Yield: 96%, Orange solid. Anal. Calcd.: For $C_{15}H_{14}NO_3Cl$: C, 61.76; H, 4.84; N,4.80%. Found: C, 61.71; H, 4.78; N, 4.64%. FTIR data (KBr pellet, cm^{-1}): 3851–3734 υ(O–H) aromatic or water, 2998–2836 υ(C–H) aliphatic, 1602 υ(CH=N), 1480 υ(C–C) aromatic, 1303–1205 υ(C–O) phenolic. ^{1}H NMR (600 MHz, DMSO-d_6) δ ppm: 14.21 (s, –NH–, 1H), 8.95 (s, =CH–N, 1H), 7.65 (d, J = 3 Hz, 1H), 7.43 (d, J_1 = 9 Hz, J_2 = 1.2 Hz, 1H), 7.37 (dd, J_1 = 12 Hz, J_2 = 3 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.70 (d, J = 2.4 Hz, 1H), 6.63 (dd, J_1=11.4 Hz, J_2=2.4 Hz, 1H), 3.86–3.82 (s, OCH_3, 6H). ^{13}C NMR(150 MHz, DMSO-d_6) δ ppm: 160.64 (C=O), 159.87 (C=N–), 158.78–99.75 (Ar–C), 56.39–55.99 (OCH_3). MS: m/z 292.08 [M^+].

Synthesis of the complexes

HL (0.58 g, 2.0 mmol) was dissolved in CH_3OH (20 mL), followed by addition of the required metal salt (0.25 g, 1.0 mmol) for $Co(OAc)_2{\cdot}4H_2O$; (0.25 g, 1.0 mmol) for $Ni(OAc)_2{\cdot}4H_2O$; (0.18 g, 1.0 mmol) for $Cu(OAc)_2$; in CH_3OH (20 mL). The solution was refluxed for about 3 h. After cooling to room temperature, dark brown single crystals of $[Co(L)_2]{\cdot}CH_3OH$ were obtained by slow evaporation of a methanol solution. The other compounds were obtained as powders (Scheme 2).

Complex (1): Yield: 95%, Red solid. Anal. Calcd.: For $C_{31}H_{30}N_2O_7Cl_2Co$: C, 56.27; H, 4,09; N, 4.37%; Found: C, 55.64; H, 4.22; N, 3.98%. FTIR (KBr pellet, cm^{-1}): 3393 methanol or water, 3008–2836 υ(C–H) aliphatic, 1613–1591 υ(CH=N), 1505 υ(C–C) aromatic, 1317–1266 υ(C–O) phenolic, 510 υ(Co–O), 455 υ(Co–N). MS: m/z 641.05 [M^+].

Complex (2): Yield: 94%, Dark yellow solid. Anal. Calcd.: For $C_{30}H_{26}N_2O_6Cl_2Ni$: C, 56.29; H, 4.09; N, 4.38%; Found: C, 56.04; H, 4.18; N, 4.10%. FTIR (KBr pellet, cm^{-1}): 2943, 2837 υ(C–H aliphatic, 1617 υ(CH=N), 1597 υ(C–C) aromatic, 1268 υ(C–O) phenolic, 512 υ(Ni–O), 457 υ(Ni–N). MS: m/z 641.06 [M^+].

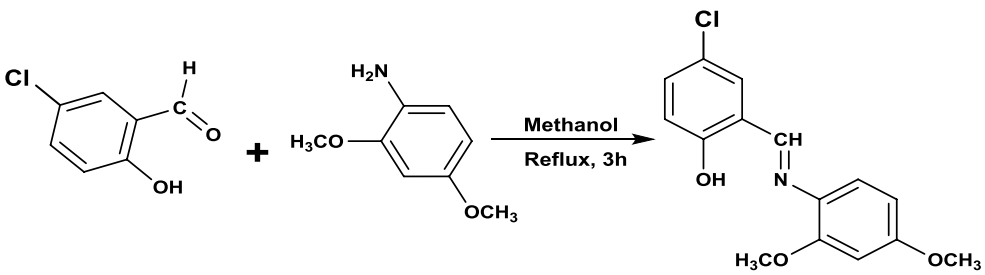
Complex (3): Yield: 96%, Brown solid. Anal. Calcd.: For $C_{30}H_{26}N_2O_6Cl_2Cu$: C, 55.87; H, 4.06; N, 4.34%; Found: C, 55.80; H, 3.93; N, 4.61%. FTIR (KBr pellet, cm^{-1}): 2967–2836 υ(C–H) aliphatic, 1619 and 1597 υ(CH=N), 1284 υ(C–O)phenolic, 510 υ(Cu–O), 463 υ(Cu–N). MS: m/z 646.05 [M^+].

X-ray structure determination

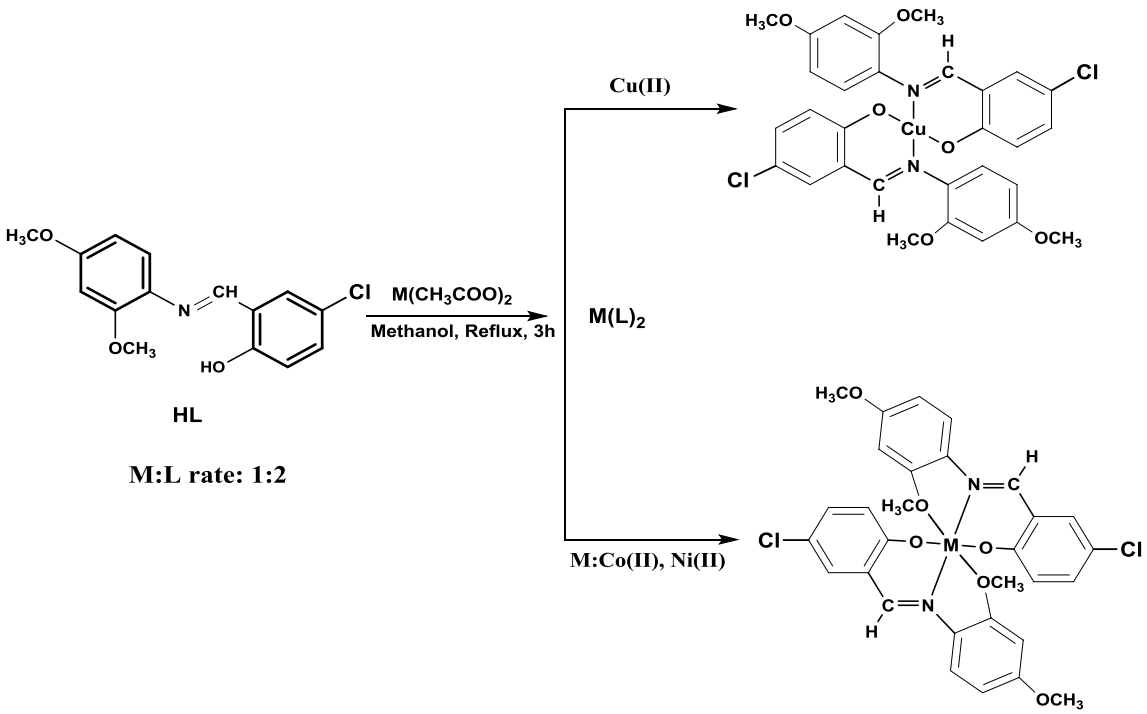
X-ray crystallographic data for both HL and $[Co(L)_2]{\cdot}CH_3OH$ were collected at room temperature on a Bruker ApexII CCD diffractometer (Mo–Kα radiation, λ = 0.71073 Å). Bruker SAINT was used for data reduction [10]. The structures were solved by direct methods and refined on F^2 using all the reflections. All the nonhydrogen atoms were refined using anisotropic atomic displacement parameters, and hydrogen atoms bonded to carbon and oxygen were inserted at calculated positions using a riding model and refined with temperature factors. The crystal and refinement data for the compounds are given in Table 1.

Results and discussion

The Schiff base (HL) and its metal complexes are stable in air and soluble in common organic solvents, as reported in Table S1. The compounds were characterized by elemental analysis, FTIR spectra, ICP, Q-TOF LC/MS, UV–Vis



Scheme 1 Synthesis of 2,4-dimethoxy-*N*-(5-chloro-2-hydroxybenzylidene)-benzenamine (HL)



Scheme 2 Synthesis of complexes of HL

Table 1 Crystal data and structure refinement for the HL and $[Co(L)_2]\cdot CH_3OH$

Identification code	HL	$[Co(L)_2]\cdot CH_3OH$
Empirical formula	$C_{15}H_{14}ClNO_3$	$C_{31}H_{30}Cl_2CoN_2O_7$
Formula weight	291.72	672.40
Temperature	293 (2) K	293 (2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
Unit cell dimensions a= 39.513 (9) Å	$\alpha = 90°$	$a = 11.4715$ (9), $\alpha = 115.650$ (2)°
$b = 3.9544$ (9) Å	$\beta = 107.090$ (7)°	$b = 11.6019$ (8), $\beta = 93.245$ (3)°
$c = 18.126$ (4) Å	$\gamma = 90°$	$c = 13.0508$ (10), $\gamma = 103.566$ (3)°
Volume (Å^3)	2707.1 (11)	1497.1 (2)
Z	8	2
Density (calculated) (Mg/m^3)	1.432	1.492
Absorption coefficient (mm^{-1})	0.289	0.803
Crystal size (mm)	$0.09 \times 0.06 \times 0.05$	$0.16 \times 0.12 \times 0.11$
Index ranges	$-48 \le h \le 48, -4 \le k \le 4, -22 \le l \le 22$	$-15 \le h \le 15, -15 \le k \le 15, -17 \le l \le 17$
Reflections collected	12,324	83,056
Independent reflections	2713 [R(int)= 0.1813]	7446 [R(int) = 0.0686]
Completeness to theta = 25.242°	99.8%	99.8%
Final R indices [I > 2sigma(I)]	$R_1 = 0.0738$, $wR_2 = 0.1199$	$R_1 = 0.0388$, $wR_2 = 0.0827$
R indices (all data)	$R_1 = 0.2069$, $wR_2 = 0.1532$	$R_1 = 0.0616$, $wR_2 = 0.0909$

absorption studies and X-ray diffraction studies. The characterization data are in good agreement with theoretical values. The physical and analytical data of the obtained compounds are shown in Table S2.

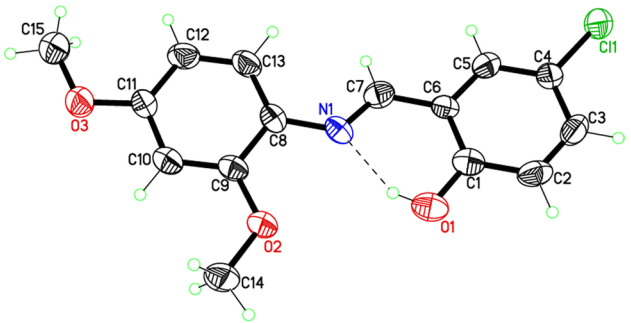


Fig. 1 Molecular structure of HL with thermal ellipsoids at 50% probability. The intramolecular hydrogen bonds are shown as dashed lines

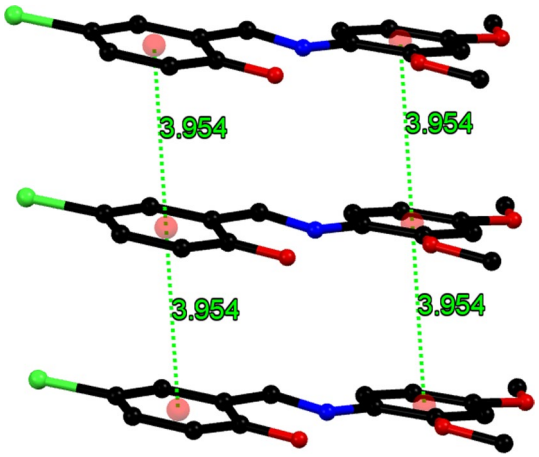


Fig. 2 π–π interactions in HL

X-ray crystal structure of HL

The molecular structure of the Schiff base ligand was determined by single-crystal X-ray diffraction. The structure was solved in monoclinic crystal system, C2/c space group, and is shown in Fig. 1. All bond lengths and angles are within the normal ranges and comparable with those of similar compounds in the literature [11]. The values are given in Table S3.

The azomethine (N1–C7) bond length is 1.269 (5) Å, which is in the range characteristic of C=N values. There is an expected phenol–imine intramolecular hydrogen bond in the structure (O1···N1). Hydrogen bond parameters are listed in Table S4. The aromatic rings (C1/C6 and C8/C13) are slightly twisted, and the dihedral angle between the two is 8.07 (20)°. Crystal packing of HL is stabilized by π–π interactions, CH···π and CH···Cl weak hydrogen bonding interactions. The phenol (C1/C6) and dimethoxy benzene (C8/C13) rings are stacked with the same section of an adjacent molecule. The centroid–centroid distance (C1/C6···C1/C6 and C8/C13···C8/C13) is 3.954 Å (Fig. 2), and a packing diagram of the compound is shown in Figure S1.

X-ray structure of $[Co(L)_2]\cdot CH_3OH$

The Co(II) complex of HL was crystallized from slow evaporation of a methanol solution. Its molecular structure is shown in Fig. 3. The asymmetric unit contains one complex molecule and a methanol solvate. The Co(II) center is six-coordinate, being coordinated by two imine nitrogens, two phenolate oxygens and two methoxy oxygens from two crystallographically independent Schiff base ligands. The phenolic group of each ligand is deprotonated such that the two anionic Schiff base ligands are charge-balanced by Co(II). As expected, the Co–O (methoxy) bond distances are longer than the Co-O and Co-N bond distances. The imine bond distances (N1–C7 and N2–C22) are 1.290 (2) and 1.292 (2) Å, respectively, which are within the normal

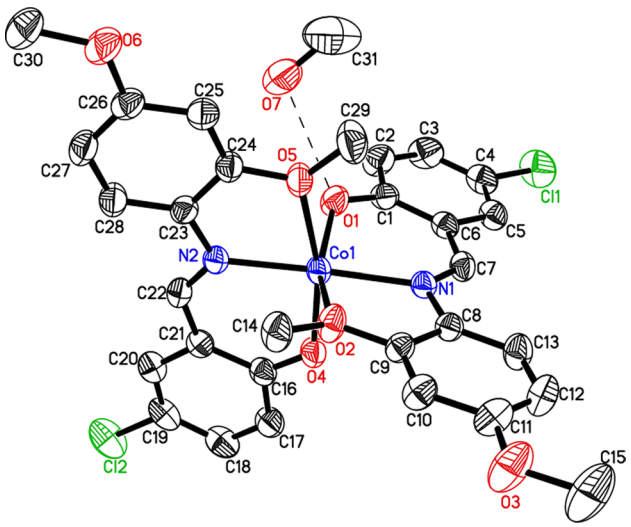


Fig. 3 Molecular structure of $[Co(L)_2]\cdot CH_3OH$ with thermal ellipsoids at the 50% probability level, hydrogen atoms are omitted for clarity

Table 2 Hydrogen bonds for $[Co(L)_2]\cdot MeOH$ [Å and °]

D–H···A	d(D–H)	d(H···A)	d(D···A)	< (DHA)
O(7)–H(7A)···O(1)	0.82	1.95	2.767 (2)	170.2

range of C=N double-bond distances. Selected bond lengths and angles are listed in Table S5.

The methanol solvate is involved in hydrogen bonding with one of the phenolate oxygen atoms. Hydrogen bond details are given in Table 2. The aromatic rings in the Schiff base ligands are slightly twisted. The dihedral angles between the aromatic rings in each ligand (C1/C6–C8/C13 and C16/C21–C23/C28) are 5.32 (11)° and 15.97 (12)°, respectively. The complex molecules are linked by π–π

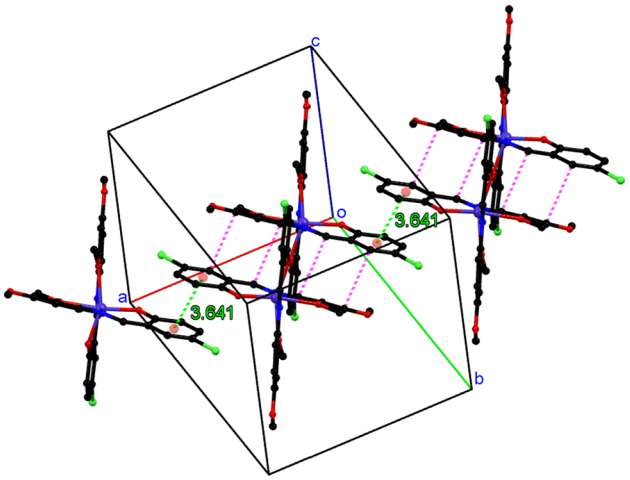


Fig. 4 Packing diagram of $[Co(L)_2]\cdot CH_3OH$, hydrogen atoms are omitted for clarity

interactions as shown in Fig. 4. The chlorobenzene ring (C16/C21) of one ligand stacks with the same section of an adjacent molecule, with a centroid–centroid distance of 3.641 Å. There are also edge to edge π–π interactions, further stabilizing the crystal structure.

It is informative to compare the crystal structure of $[Co(L)_2]\cdot CH_3OH$ with the Co(II) complex $[Co(HA)_2]$ of an analogous Schiff base ligand (HA) prepared from 5-bromosalicylaldehyde and 2-methoxyaniline. The $[Co(HA)_2]$ complex was synthesized and structurally characterized by Galini et al. [11]. In both $[Co(L)_2]\cdot CH_3OH$ and $[Co(HA)_2]$ (Fig. S2), the Co(II) centers are six-coordinate with similar Co-ligand distances. The coordination geometry around Co(II) centers in both complexes is a slightly distorted octahedron.

Mass spectra of the compounds

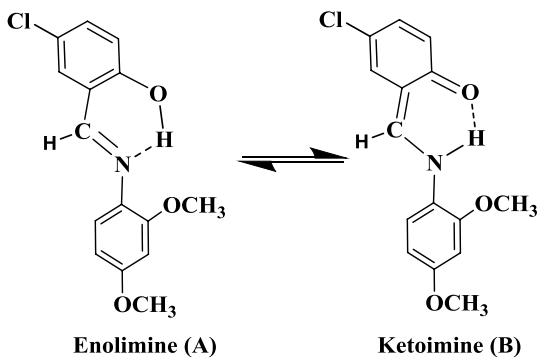
Both HL and its complexes were characterized by Q-TOF LC/MS analysis (Figs. S3–S6). The mass spectrum of HL indicated a molecular weight of 291.50 (m/z: 292.08 MH+ ion) which is consistent with the molecular weight of the compound. The mass spectra of the complexes indicated molecular weights of 640.14 for **1** (m/z: 641.05 MH+ ion), 640.38 for **2** (m/z: 641.06 MH+ ion), 644.99 for **3** (m/z: 646.05 MH+ ion), which are consistent with the formula weights.

FTIR spectra

The FTIR spectrum of free HL showed a strong band at 1602 cm^{-1} which is ascribed to the azomethine ν(HC=N) group. The equivalent ν(C=N) stretching frequencies for the complexes were shifted to 1613–1619 cm^{-1}, indicating coordination of azomethine nitrogen to the metal centers [12]. These results are further supported by the presence of new bands in the regions of 510–512 and 430–457 cm^{-1} assigned to ν(M-O) and ν(M–N) stretching frequencies, respectively. The band arising from the ν(Ar–OH) vibration was observed at 3851–3734 cm^{-1} in the spectrum of free HL. A band assigned to ν(O–H) of methanol present in the crystal lattice of the Co(II) complex was observed at 3393 cm^{-1}. The IR spectra of HL and its complexes are given in Figs. S7–S10 [13, 14].

^{1}H and ^{13}C NMR spectra

The ^{1}H NMR spectrum of free HL was recorded in DMSO-d_6 using TMS as internal standard. The aromatic protons of HL were observed at δ 6.63–7.65 (Ar–H, 6H). A peak at 8.95 (s, 1H) ppm is assigned to the azomethine proton (=CH–N) of HL and a peak at 14.21 (s, 1H) ppm to the N–H group [18]; signals at 3.86 (s, 3H)–3.82 (s, 3H) ppm are assigned to the methoxy protons of HL [15–17]. The ^{13}C NMR spectrum of HL showed signals between 99.75 and 158.78 ppm from the aromatic carbons. The azomethine carbon resonated at 159.87 ppm. A peak at 160.64 ppm can be assigned to the carbonyl double bonds (C=O) (see Scheme 3b) [18] arising from the tautomeric form. Signals at 56.39–55.99 ppm are assigned to the methoxy carbon [19]. The ^{1}H and ^{13}C NMR spectra data of HL are given in Figs. S11–S12. Free HL may exist in two tautomeric forms, an OH form (A) and an NH form (B) as shown in Scheme 3. From the NMR data, we have determined that HL exists as the NH tautomer in DMSO solution. Hence, the polar DMSO solvent causes reversible proton transfer from the OH to NH form in solution [20].



Scheme 3 Enol(A)–Keto(B) tautomerism of the Schiff base HL in solution

Electronic spectra

The electronic spectra of free HL and its complexes were recorded in ethanol and are shown in Fig. 5. The spectrum of the HL Schiff base showed two main bands. An intense peak at 258 nm (38,759 cm^{-1}) can be assigned to the $\pi \rightarrow \pi^*$ transitions of the aromatic rings. The second band at 372 nm (26,882 cm^{-1}) is assigned to $n \rightarrow \pi^*$ transition of the nitrogen lone pair to the aromatic ring. Three intense bands were observed in the electronic spectra of each of the complexes. They were observed around 279–434 nm (35,842–23,041 cm^{-1}) for Co(II), 277–450 nm (36,101–22,222 cm^{-1}) for Ni(II) and 276–423 nm (36,232–23,641 cm^{-1}) for Cu(II). In all three complexes, the $\pi \rightarrow \pi^*$ transitions of the azomethine groups were redshifted by about 20 nm, consistent with coordination through the nitrogen atoms of the C=N groups. The $n \rightarrow \pi^*$ transitions shifted to lower wavelengths, confirming coordination of the oxygen atoms of HL to the metal centers [21, 22]. In the electronic spectra of the complexes, charge transfer (CT) bands were also observed. Peaks assigned to metal → ligand charge transfers (MLCT) were observed at 434 nm (23,041 cm^{-1}) for Co(II), 450 nm (22,222 cm^{-1}) for Ni(II) and 423 nm (23,641 cm^{-1}) for Cu(II) [23, 24].

Magnetic susceptibilities

The magnetic susceptibilities of the complexes were determined using an Evans balance at room temperature in the solid state. Diamagnetic corrections for each complex were calculated using Pascal's constants. The magnetic moment data are shown in Table 3. The experimental μeff values for the complexes are within the ranges found for mononuclear complexes for $[Co(L)_2]\cdot CH_3OH$ (d^7); $[Ni(L)_2]$ (d^8); [25] and $[Cu(L)_2]$ (d^9). Also, the magnetic moments (μ_{eff}: 4.12, 2.93 and 1.58 B.M., respectively) provide additional evidence as reported in the literature of an octahedral geometry for the Co(II) and Ni(II) complexes and square planar geometry for the Cu(II) complex [26, 27].

Thermal analysis

Thermal analyses of all three complexes revealed that the water or methanol molecules are stepwise eliminated, namely the crystallization solvent up to 140 °C and coordinated water between 140 and 200 °C [28]. The TG curves show distinct mass losses; the curves are shown in Figs. S13–S16. The Schiff base HL decomposed in a single step, continuous up to 700 °C with complete mass

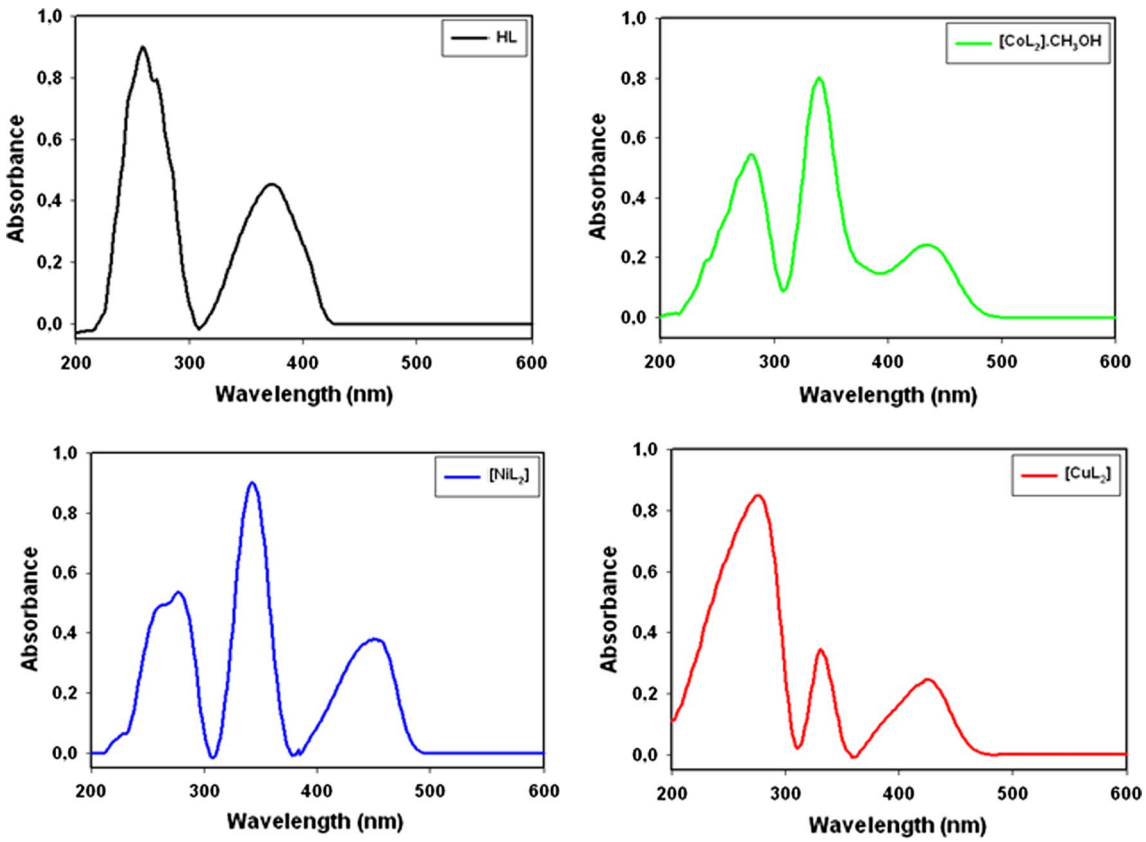


Fig. 5 UV–Vis spectra of the Schiff base and its complexes

Table 3 Selected FTIR bands (cm^{-1}) and magnetic moment values for the complexes

Compound	υ (OH)	υ (C=N)	υ (M–O)	υ (M–N)	μ_{eff} (B.M.) Exp./Lit.
HL	3851–3734	1602	–	–	–
$[Co(L)_2]\cdot CH_3OH$	3393	1613	510	455	4.12/4.25 [25]
$[Ni(L)_2]$	–	1617	512	457	2.93/3.20 [26]
$[Cu(L)_2]$	–	1619	510	430	1.58/1.73 [25]

Exp. experimental, *Lit.* literature

loss (Found: 99.25%, Calcd.: 100%). The decomposition of $[Co(L)_2]\cdot CH_3OH$ occurs in two steps. The first corresponds to the loss of a lattice methanol molecule in the temperature range 50–110 °C, with a mass loss of 3.87% (Calcd.: 4.75%). The second step is assigned to decomposition of the organic content, with a mass loss of 83.67% (Calcd.: 82.3%) in the temperature range 50–899 °C. The remaining weight of 12.47% is attributed to the final product of Co_2O_3 (Calcd.: 12.95%). The thermogram of $[Ni(L)_2]$ showed two weight loss steps. This complex is thermally stable up to 300 °C. Decomposition of the organic residue with a mass loss of 88.68% (Calcd.: 88.33%) occurs in the temperature range 300–900 °C. The remaining residue (11.32%) is attributed to NiO (Calcd.: 11.67%) [19]. $[Cu(L)_2]$ is thermally stable up to 290 °C. Decomposition of the organic components occurs with a mass loss of 87.38% (Calcd.: 87.67%) in the temperature range 290–900 °C. The residue is assigned to CuO, Found 12.62% (Calcd.: 12.33%) [29].

Luminescence properties

To determine the luminescence properties of the synthesized compounds and the effect of solvents, we performed luminescence measurements in the solid state and also in different solvents. The resulting UV–Vis spectra and maximum excitation–emission wavelengths are summarized in Table 4. As shown in Fig. 6, sharp and single emission bands were obtained in the solid state. The free Schiff base showed an emission band with a maximum at 615 nm upon excitation at 307 nm which is attributed to $\pi \rightarrow \pi^*$ transitions [30]. Compared to the free ligand, the maximum emission of the Co(II) complex showed a blueshift of about 45 nm. The emission spectrum of the Ni(II) complex was similarly 64 nm blueshifted compared to free HL, while the Cu(II) complex showed a blueshift of 50 nm. These blueshifts may arise from ligand to metal charge transfer (LMCT) [31].

The photoluminescence spectra of the Schiff base and its metal complexes were also recorded in various solvents

Table 4 Photophysical data of the HL ligand and its complexes

Compounds	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	CT	λ_{ex}	λ_{em}	Stoke shift
HL	258	372	–	307[s]	615[s]	308[s]
				287[a]	528[a]	241[a]
				398[b]	529[b]	131[b]
				309[c]	532[c]	223[c]
				403[d]	535[d]	132[d]
$[CoL_2]\cdot CH_3OH$	279	339	434	346[s]	570[s]	224[s]
				349[a]	486[a]	137[a]
				377[b]	485[b]	108[b]
				372[c]	485[c]	113[c]
				347[d]	529[d]	182[d]
$[NiL_2]$	277	342	450	372[s]	551[s]	179[s]
				367[a]	526[a]	159[a]
				368[b]	528[b]	160[b]
				311[c]	370[c]	59[c]
				372[d]	519[d]	147[d]
$[CuL_2]$	276	331	423	360[s]	565[s]	205[s]
				366[a]	521[a]	155[a]
				367[b]	518[b]	151[b]
				346[c]	514[c]	168[c]
				363[d]	471[d]	108[d]

s: solid state, a: CH_3OH, b: C_2H_5OH, c: $CHCl_3$, d: DMSO

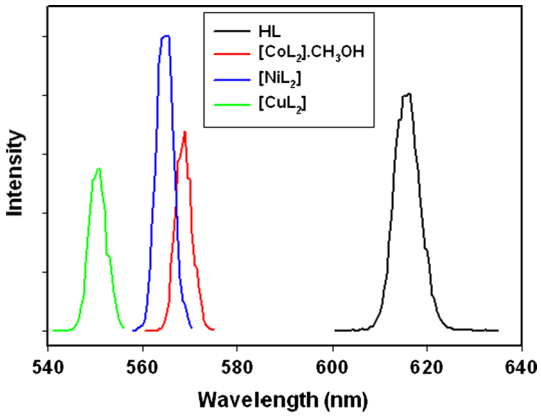


Fig. 6 Solid-state emission spectra of the compounds at room temperature

at room temperature (Fig. 7). In methanol solution, the free Schiff base showed a maximum emission centered at 528 nm upon excitation at 287 nm. The Co(II) complex showed an emission band at 486 nm upon excitation at 349 nm, while the Ni(II) (λ_{em}: 526 nm) and Cu(II) (λ_{em}: 521 nm) complexes showed similar emission maxima with higher intensities when excited at 367 and 366 nm, respectively. In ethanol, free HL gave two emission peaks. The complexes showed maxima at 529 nm for Ni(II) and 518 nm for Cu(II) upon excitation at 398, 377, 368 and 367 nm, respectively. These emission bands may be assigned to ligand-based $\pi \rightarrow \pi^*$ transitions [32, 33]. In DMSO solution, the complexes showed broad emission bands at 535 nm (HL), 529 nm (**1**), 519 nm (**2**) and 471 nm (**3**) when excited to their corresponding absorption bands (403, 347, 372 and 363 nm, respectively). In chloroform solution, HL and its complexes exhibited emissions with λ_{max} at 508–532 nm upon irradiation at 309–372 nm (see Table 4 and Fig. 7). The full version of photophysical data of the free ligand HL and its complexes is given in Table S6.

These results confirm an emission predominantly arising not only from $\pi \rightarrow \pi^*$ transitions, but also due to chelation-enhanced fluorescence by coordination of imine group to the metals [34]. It is interesting to note that the copper(II) complex gave very sharp and single emission bands in all solvents except DMSO. The λ_{em} of the compounds in different solvents were almost identical, showing that the solvent polarity has very little influence on the emission bands of these complexes. Significant Stoke shifts were observed for

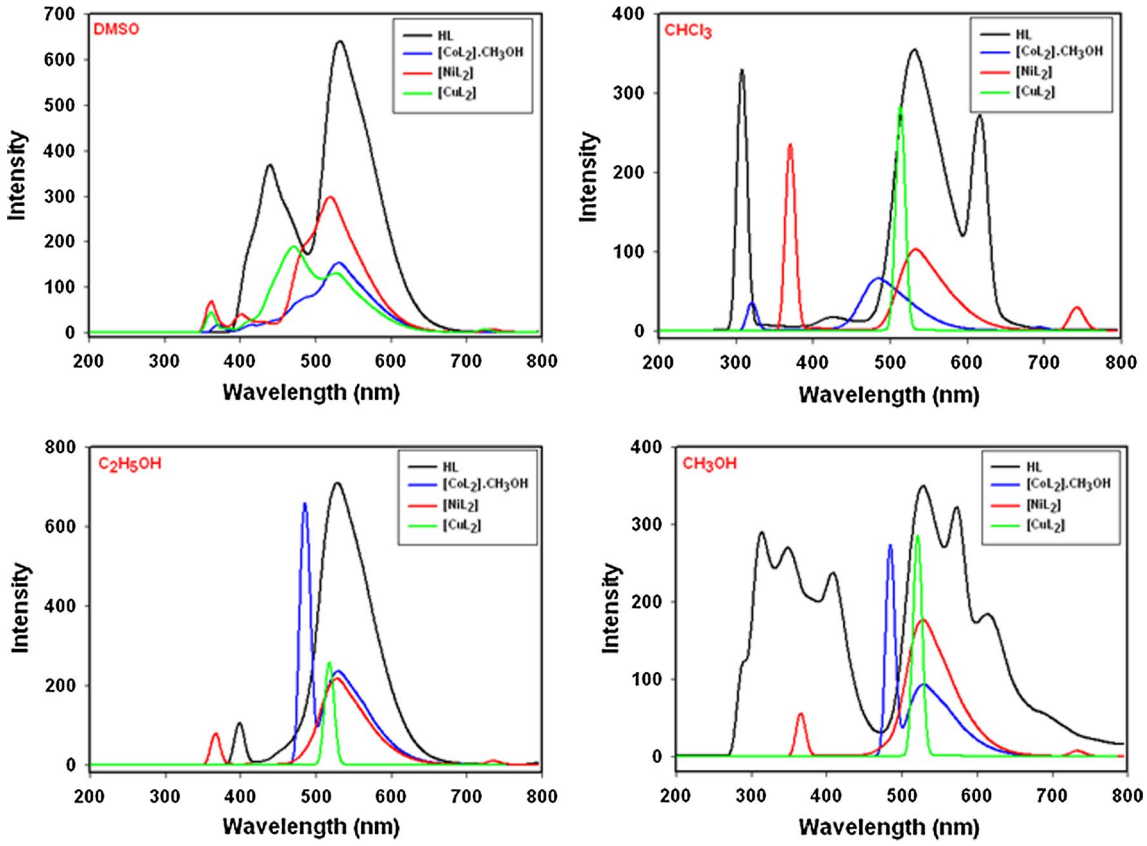


Fig. 7 Emission spectra of the compounds in different solvents: chloroform, dimethyl sulfoxide, ethanol and methanol with a concentration of 1.0×10^{-5} M

the compounds, as can be seen from the difference in the wavelengths of the excitation and emission peak maxima (Table 4). These large Stokes shifts confirm the existence of excited state intramolecular proton transfer, involving interconversion of the enol and keto forms of the ligand [35].

Conclusions

In this study, we have synthesized a new Schiff base and its metal complexes. All compounds were characterized by spectroscopic and analytical methods, and the molecular structures of HL and $[Co(L)_2]\cdot CH_3OH$ were determined by single-crystal X-ray diffraction studies. Studies of the photoluminescence properties showed that the solvent has very little influence on the emission bands of these complexes. Significant Stokes shifts were observed in all three cases, confirming the existence of excited state intramolecular proton transfer between the enol and keto forms of the ligand. The luminescence studies suggest that these compounds may have potential applications as luminescent blue light-emitting materials.

Appendix: Supplementary material

CCDC 1509986 and 1509987 contain the supplementary crystallographic data for the Schiff base HL and its complex $[Co(L)_2]\cdot$MeOH, respectively. The data can be obtained free of charge via www.ccdc.cam.ac.uk/datarequest/cif, by e-mailing data request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre 12 Union Road Cambridge CB2 1EZ, UK Fax: +44(0)1223-336033.

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