



*J. Serb. Chem. Soc.* 77 (11) 1589–1597 (2012)  
JSCS–4373

Journal of  
the Serbian  
Chemical Society

JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

UDC 66.094.941+542.9+547.571+  
547.551:541.8:542.913:535.371

Original scientific paper

## Solvent-dependent synthesis and mono-hydrolysis of the di-Schiff base of ( $\pm$ )*trans*-1,2-cyclohexanediamine and 2-pyridinecarboxaldehyde in Cu(II), Co(II) and Zn(II) complexes

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(Received 3 December 2011, revised 24 March 2012)

**Abstract:** The Schiff base ligand *trans*-*N,N'*-bis(2-pyridinylmethylene)-1,2-cyclohexanediamine (L) was synthesized. This ligand when stirred with 1 equivalent of  $MCl_2 \cdot xH_2O$  ( $M = Cu, Co$  or  $Zn$ ) in ethanol, undergoes partial hydrolysis of the imino bond and the resultant tridentate ligand (L') immediately forms complexes with an  $N_3$  coordination sphere. The reactions of L with  $MCl_2 \cdot xH_2O$  ( $M = Cu, Co$  or  $Zn$ ) in THF gave the complexes  $[ML]Cl_2$ . The ligand (L) and the complexes  $[M(L')Cl]Cl$  and  $[ML]Cl_2$  were characterized by elemental analysis, UV–Vis, FT-IR,  $^1H$ -NMR spectroscopy, GC/MS and their luminescence properties. The  $^1H$ -NMR spectra of the ligand and its diamagnetic complexes were recorded in  $CDCl_3$  and DMSO solvents, respectively. The obtained data confirmed that the donor N atoms in the ligand coordinated to the metal ions. The luminescence studies show ligands and their complexes display intraligand ( $\pi$ – $\pi^*$ ) fluorescence in MeOH solution and the solid state at room temperature.

**Keywords:** mono-hydrolysis; Schiff base; solvent effect; fluorescence.

### INTRODUCTION

Schiff base ligands have been in the chemistry catalogues for decades and have played a key role as chelating ligands in main group and transition metal coordination chemistry. This is due to their ease of synthesis and stability under a variety of oxidative and reductive conditions.<sup>1–5</sup> Not only have they played an influential role in the development of modern co-ordination chemistry,<sup>6</sup> but they can also be found at key points in the development of inorganic biochemistry,<sup>7</sup> catalysis,<sup>8,9</sup> medical imaging,<sup>10</sup> optical materials<sup>11</sup> and thin films.<sup>12,13</sup> The formation of a Schiff base by condensation of diamine and carbonyl compounds is

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doi: 10.2298/JSC111203035L

well known.<sup>14–17</sup> The reverse process, *i.e.*, the hydrolysis of Schiff bases in the presence of a metal ion was observed by Ghosh and coworkers.<sup>18</sup> It was observed that the hydrolysis is dependent on several factors, such as the pH of the reaction medium,<sup>19</sup> the size of the chelate rings formed by the diamine fragment of the Schiff base,<sup>20,21</sup> the coordinating ability of the counter anions,<sup>22,23</sup> the nature of the metal ions,<sup>20,21</sup> the effect of carbonyl compounds,<sup>24</sup> *etc.* In order to investigate this type of reaction, the Schiff base *trans-N,N'*-bis(2-pyridinylmethylene)-1,2-cyclohexanediamine was synthesized by condensation of ( $\pm$ )*trans*-1,2-cyclohexanediamine with 2-pyridinecarboxaldehyde in a 1:2 mole ratio, respectively. The reaction of this ligand with a metal chloride in ethanol resulted in the hydrolysis of one of the imine bonds. On the other hand, reaction of this ligand with a metal chloride in THF solvent resulted in the coordination of two imino bonds to the metal. The details of the synthesis, structure, mass spectrum and luminescence behaviours are described herein.

## EXPERIMENTAL

### Materials

All starting materials and solvents except ( $\pm$ )*trans*-1,2-cyclohexanediamine (Alfa Aesar), were purchased from Merck and were used without further purification. The synthetic reactions and work-up were realized in open air.

### Physical measurements

The IR spectra (KBr discs, 500–4000  $\text{cm}^{-1}$ ) were recorded using a Bruker FTIR model Tensor 27 spectrometer. The elemental analysis was performed in a 2400 Series II CHN analyzer, Perkin-Elmer, USA. The UV–Vis absorption spectra and fluorescence measurements were recorded on a Perkin-Elmer Lambda 35 spectrophotometer and a Varian Cary Eclipse 1.1 spectrofluorometer, respectively. The  $^1\text{H-NMR}$  spectra were recorded on a Bruker 500 MHz model DRX spectrometer in  $\text{CDCl}_3$  and  $\text{DMSO-}d_6$  with TMS as the internal reference. The mass spectrum of the ligand (L) was studied with a GC/MS Quadrupole Agilent 5973 MSD spectrometer.

### Preparation of ligand (L)

A diethyl ether solution (5 ml) of 2-pyridinecarboxaldehyde (0.214 g, 2.00 mmol) was added to diethyl ether solution (5 ml) of ( $\pm$ )*trans*-1,2-cyclohexanediamine (0.114 g, 1.00 mmol). The mixture was stirred for 10 min and then kept in air to allow the solvent to evaporate, whereby yellowish crystals of the ligand L were obtained in 90% yield.

### Preparation of $[M(L')Cl]Cl$ (1–3)

$[\text{Cu}(L')\text{Cl}]Cl$  (**1**) was prepared by adding an ethanolic solution (10 ml) of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.170 g, 1.00 mmol) to an ethanolic solution (10 ml) of L (0.292 g, 1.00 mmol). The resulting mixture was stirred around 1 h. Finally, the precipitate of complex **1** was recovered by filtration, and washed several times with absolute ethanol and dried under vacuum at 65 °C for 1 h. Yield: 44 %.

$[\text{Co}(L')\text{Cl}]Cl$  (**2**) was prepared in a similar manner to **1** but using  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.237 g, 1.00 mmol). Yield: 31 %.

$[\text{Zn}(L')\text{Cl}]Cl$  (**3**) was prepared in a similar manner to **1** but using  $\text{ZnCl}_2$  (0.136 g, 1.00 mmol). Yield: 60 %.

### Preparation of $[ML]Cl_2$ (4–6)

$[CuL]Cl_2$  (**4**) was prepared by adding a THF solution (20 ml) of L (0.292 g, 1 mmol) to a THF solution (10 ml) of  $CuCl_2 \cdot 2H_2O$  (0.170 g, 1.00 mmol). After stirring the resulting mixture for around 1 h, the precipitated complex was recovered by filtration, washed with THF and  $Et_2O$  and finally dried under vacuum at  $65^\circ C$  for 1 h. Yield: 41 %.

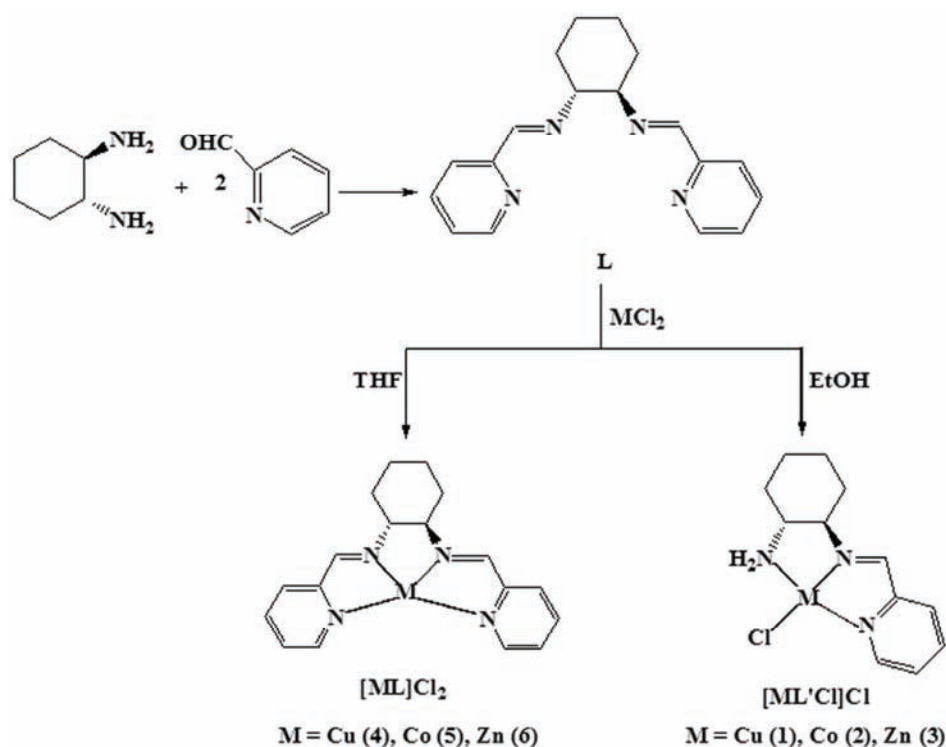
$[CoL]Cl_2$  (**5**) was prepared in a similar manner to **4** but using  $CoCl_2 \cdot 6H_2O$  (0.237 g, 1.00 mmol). Yield: 78 %.

$[ZnL]Cl_2$  (**6**) was prepared in a similar manner to **4** but using  $ZnCl_2$  (0.136 g, 1.00 mmol). Yield 53 %.

## RESULTS AND DISCUSSION

### Synthesis and formulation

The ligand L (Scheme 1) was synthesized by condensation of a 1:2 mole ratio of ( $\pm$ )*trans*-1,2-cyclohexanediamine with 2-pyridinecarboxaldehyde. When L reacts with  $MCl_2 \cdot H_2O$  ( $M = Cu, Co$  or  $Zn$ ) in ethanol, it undergoes partial hydrolytic cleavage to form an  $N_3$  coordination sphere of copper(II) (**1**), cobalt(II) (**2**) and zinc(II) (**3**) complexes. When L reacts with  $MCl_2 \cdot H_2O$  in THF,  $[ML]Cl_2$  ( $M = Cu$  (**4**),  $Co$  (**5**) or  $Zn$  (**6**)) complexes with  $N_4$  coordination sphere are formed.



Scheme 1. Synthetic routes to the ligand (L) and complexes 1–6.

*Some analytic and spectral data of the ligand and complexes 1–6*

*Ligand (L)*. Yield: 90 %; m.p.: 126 °C; IR (KBr,  $\text{cm}^{-1}$ ): 2931, 2853 ( $\text{CH}_2/\text{CH}$  stretching of cyclohexane ring), 1643 ( $\text{C}=\text{N}$  stretching of azomethine group), 772 (out-of-plane  $\text{C}-\text{H}$  deformation);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 1.51–1.91 (8H, *m*,  $\text{CH}_2$ ), 3.55–3.57 (2H, *m*, CH), 7.22–7.91 (8H, *m*, aromatic), 8.55–8.57 (2H, *d*,  $J = 7.1$  Hz,  $\text{CH}=\text{N}$ ); MS ( $m/z$ , (relative abundance, %)): 292 ( $\text{M}^+$ , 100); UV–Vis (MeOH) ( $\lambda_{\text{max}}$  / nm ( $\epsilon$  /  $\text{L mol}^{-1} \text{cm}^{-1}$ )): 203 (16595), 236 (20417), 274 (11481).

*[Cu(L)Cl]Cl (1)*. Yield: 44 %; m.p.: 230 °C; IR (KBr,  $\text{cm}^{-1}$ ): 3267, 3217 ( $-\text{NH}$  stretching of primary amine), 2862, 2929 ( $\text{CH}_2/\text{CH}$  stretching of cyclohexane ring), 1655 ( $\text{C}=\text{N}$  stretching of azomethine group), 776 (out-of-plane  $\text{C}-\text{H}$  deformation); UV–Vis (MeOH) ( $\lambda_{\text{max}}$  / nm ( $\epsilon$  /  $\text{L mol}^{-1} \text{cm}^{-1}$ )): 203 (12589), 235 (*sh*), 293 (6456), 304 (*sh*), 693 (*b*).

*[Co(L)Cl]Cl (2)*. Yield: 31 %; m.p.: 190 °C; IR (KBr,  $\text{cm}^{-1}$ ): 3289, 3240 ( $-\text{NH}$  stretching of primary amine), 2862, 2929 ( $\text{CH}_2/\text{CH}$  stretching of cyclohexane ring), 1634 ( $\text{C}=\text{N}$  stretching of azomethine group), 777 (out-of-plane  $\text{C}-\text{H}$  deformation); UV–Vis (MeOH) ( $\lambda_{\text{max}}$  / nm ( $\epsilon$  /  $\text{L mol}^{-1} \text{cm}^{-1}$ )): 206 (24547), 283 (*sh*), 451 (*sh*), 537 (*sh*).

*[Zn(L)Cl]Cl (3)*. Yield: 60 %; m.p.: 270 °C; Anal. Calcd. for:  $\text{C}_{12}\text{H}_{17}\text{N}_3\text{ZnCl}_2$ : C, 42.44; H, 5.05; N, 12.37 %. Found: C, 42.54; H, 5.06; N, 12.24 %; IR (KBr,  $\text{cm}^{-1}$ ): 3293, 3248 ( $-\text{NH}$  stretching of primary amine), 2929, 2859 ( $\text{CH}_2/\text{CH}$  stretching of cyclohexane ring), 1663 ( $\text{C}=\text{N}$  stretching of azomethine group), 776 (out-of-plane  $\text{C}-\text{H}$  deformation);  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO}-d_6$ ,  $\delta$  / ppm): 1.05–1.96 (8H, *m*,  $\text{CH}_2$ ), 3.32–3.62 (2H, *m*, CH), 7.48–8.83 (5H, *m*, aromatic,  $\text{HC}=\text{N}$ ); UV–Vis (MeOH) ( $\lambda_{\text{max}}$  / nm ( $\epsilon$  /  $\text{L mol}^{-1} \text{cm}^{-1}$ )): 204 (13803), 240 (7413), 283 (7585), 392 (*sh*).

*[CuL]Cl<sub>2</sub> (4)*. Yield: 41 %; m.p.: 220 °C; IR (KBr,  $\text{cm}^{-1}$ ): 2926, 2867 ( $\text{CH}_2/\text{CH}$  stretching of cyclohexane ring), 1653 ( $\text{C}=\text{N}$  stretching of azomethine group), 782 (out-of-plane  $\text{C}-\text{H}$  deformation); UV–Vis (MeOH) ( $\lambda_{\text{max}}$  / nm ( $\epsilon$  /  $\text{L mol}^{-1} \text{cm}^{-1}$ )): 208 (17782), 234 (*sh*), 290 (9332), 469 (323), 683 (*b*).

*[CoL]Cl<sub>2</sub> (5)*. Yield: 78 %; m.p.: 330 °C; IR (KBr,  $\text{cm}^{-1}$ ): 2931, 2868 ( $\text{CH}_2/\text{CH}$  stretching of cyclohexane ring), 1635 ( $\text{C}=\text{N}$  stretching of azomethine group), 775 (out-of-plane  $\text{C}-\text{H}$  deformation); UV–Vis (MeOH) ( $\lambda_{\text{max}}$  / nm ( $\epsilon$  /  $\text{L mol}^{-1} \text{cm}^{-1}$ )): 205 (22908), 264 (*sh*), 566 (457).

*[ZnL]Cl<sub>2</sub> (6)*. Yield: 53 %; m.p.: 290 °C; IR (KBr,  $\text{cm}^{-1}$ ): 2932, 2862 ( $\text{CH}_2/\text{CH}$  stretching of cyclohexane ring), 1639 ( $\text{C}=\text{N}$  stretching of azomethine group), 768 (out-of-plane  $\text{C}-\text{H}$  deformation);  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO}-d_6$ ,  $\delta$  / ppm): 1.42–1.89 (8H, *m*,  $\text{CH}_2$ ), 3.32–3.69 (2H, *m*, CH), 7.56–8.66 (10H, *m*, aromatic,  $\text{HC}=\text{N}$ ); UV–Vis (MeOH) ( $\lambda_{\text{max}}$  / nm ( $\epsilon$  /  $\text{L mol}^{-1} \text{cm}^{-1}$ )): 249 (7079), 258 (*sh*).

*IR and UV-Vis spectra of the ligand and complexes*

In the IR spectrum of ligand L, a strong and sharp band due to the azomethine  $\nu(\text{C}=\text{N})$  appears at  $1643\text{ cm}^{-1}$ . The bands at  $2853$  and  $2931\text{ cm}^{-1}$  are indicative of the presence of 1,2-cyclohexanediamine.

In the IR spectra of **1–3**, the two primary  $\text{NH}_2$  stretching modes are seen at around  $3267\text{--}3293$  and  $3217\text{--}3248\text{ cm}^{-1}$  as sharp bands (doublet) for the asymmetric and symmetric vibrations, respectively (Fig. 1). A strong absorption band at  $2929\text{--}2862\text{ cm}^{-1}$  corroborates the presence of the 1,2-cyclohexanediamine group in the complexes.<sup>25</sup> The band due to azomethine  $\nu(\text{C}=\text{N})$  appears at  $1655$ ,  $1634$  and  $1663\text{ cm}^{-1}$  for complexes **1–3**, respectively. In the IR spectra of complexes **4–6**, the strong absorption bands at  $2932\text{--}2857\text{ cm}^{-1}$  corroborate the presence of the 1,2-cyclohexanediamine group in the complexes. The band due to azomethine  $\nu(\text{C}=\text{N})$  appears at  $1653$ ,  $1635$  and  $1639\text{ cm}^{-1}$ , respectively. A comparison of the IR spectra of **1–3** with **4–6** provides clear evidence of the hydrolytic cleavage that had occurred in one imine bond of L. The IR spectra of complexes **4–6** exhibit bands typical of 2-substituted pyridines.<sup>26</sup> These pyridine bands are the four rings stretching vibrations ( $1604\text{--}1445\text{ cm}^{-1}$ ), the ring breathing vibration at around  $1026\text{--}1024\text{ cm}^{-1}$  and the out-of-plane C–H deformation

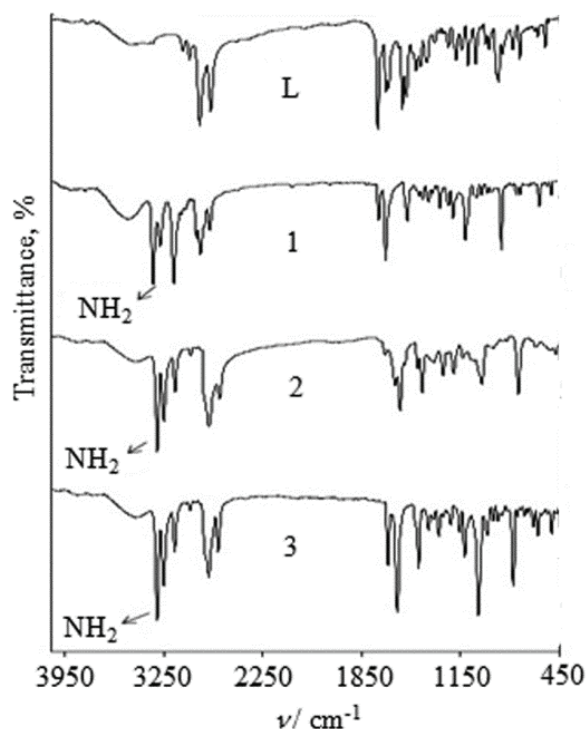


Fig. 1. IR spectra of ligand (L) and complexes **1–3**.

at around 782–768  $\text{cm}^{-1}$ . These compounds also show a strong band at around 1653–1635  $\text{cm}^{-1}$ , assigned<sup>27</sup> to the azomethine stretching vibration, which confirms the Schiff base nature of the coordinated L molecule.

The electronic spectra of complex **1** consist of one broad d–d transition band at 693 nm, as is usual for four coordinated Cu(II).<sup>28,29</sup> The higher energy bands are due to  $\pi$ – $\pi^*$  or n– $\pi^*$  transition. Complex **2** shows one band at 531 nm and the other at 451 nm indicating four coordinated geometry of the Co(II) complexes.<sup>30</sup> The electronic absorption spectra of **4** and **5** show absorption band at 683 and 566 nm, respectively. The bands are typical of d–d transition in a four coordinated environment around Cu(II) and Co(II).<sup>31</sup> The electronic absorption spectra of **3** and **6** show absorption bands at 204, 240, 283 and 392 nm and 249 and 258 nm, respectively. The bands are typical of intraligand transition.

#### *<sup>1</sup>H-NMR spectra of the ligand and complexes 3 and 6*

The <sup>1</sup>H-NMR spectra of the ligand (L) and complexes **3** and **6** were recorded using  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$  as solvent, respectively. Hydrogen atoms of the azomethine groups of L appeared at  $\delta$  8.55–8.57 ppm as a doublet. The aromatic protons are found in the range  $\delta$  7.22–7.91 ppm as a multiplet. The hydrogen atoms of the  $\text{CH}_2/\text{CH}$  groups in the cyclohexane ring are observed in the  $\delta$  1.51–3.57 ppm range.<sup>12</sup> In **3** and **6**, a slight downfield shift of 0.2–0.3 ppm in the resonance peaks corresponding to the aromatic and the azomethine protons is noticeable. This fact confirms that the nitrogen atoms were coordinated to the Zn(II) ion.<sup>32–34</sup>

#### *Luminescence studies*

The photophysical data for the ligand and complexes **1–6** are listed in Table I. The luminescence studies showed that complexes **1–3** exhibited an emission band at 413, 426 and 411 nm, respectively, in methanol solution and in the solid an emission band at 397, 385 and 387 nm, respectively, which may be assigned to an intraligand  $\pi$ – $\pi^*$  transition (Fig. 2). The fluorescence spectra of complexes **4–6** and the free ligand in the solid state at room temperature are presented in Fig. 3. The free ligand (L) showed an intensive emission band at 440 nm when excited

TABLE I. Photophysical data for L and complexes **1–6**

Sample	Absorption $\lambda$ / nm	Fluorescence at room temperature, $\lambda$ / nm	
		Solution in MeOH	Solid state
<b>L</b>	274	–	440
<b>1</b>	292	413	397
<b>2</b>	283	426	385
<b>3</b>	283	411	387
<b>4</b>	290	–	395
<b>5</b>	264	–	440
<b>6</b>	249	–	442

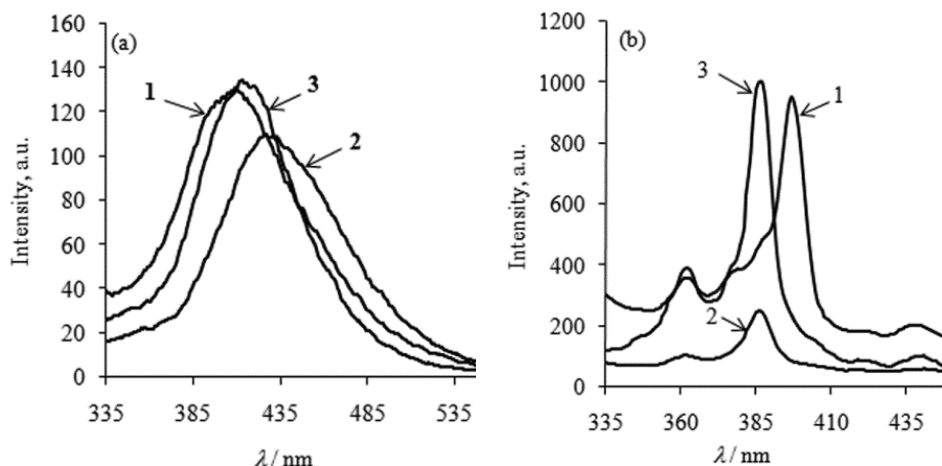


Fig. 2. Emission spectra of complexes 1–3: a) MeOH solution; b) solid state.

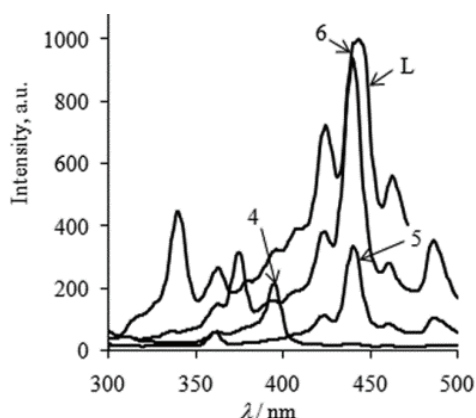


Fig. 3. Solid state emission spectra of ligand (L) and complexes 4–6.

with light of 274 nm which might be assigned to intraligand ( $\pi-\pi^*$ ) transition or ( $n-\pi^*$ ) charge transfer. It is interesting that the Zn(II) complex (6) exhibited a higher intensity than that of the free ligand L. In this case the coordination of the ligand to the zinc ion increased the rigidity of the molecular complex and reduced the loss of energy by radiationless thermal vibrations and hence the emission intensity of the complex was increased. However, the emission intensities for complex 4 at 395 nm and complex 5 at 440 nm were reduced, which, according to previous studies, could be assigned to the emission of ligand to metal charge transfer.<sup>35,36</sup> The quenching of fluorescence of a ligand by transition metal ions upon complexation, a rather common phenomenon, can be explained by processes such as magnetic perturbation, redox activity, and electrons.<sup>37,38</sup> The emission bands of the free ligand showed a reduction in intensity upon complexation and the phenomenon could be attributed to ( $n-\pi^*$ ) transitions



rather than ( $\pi-\pi^*$ ) transitions.<sup>39</sup> This is due to the pairs of electrons on the free ligand that are donated to the metal centre in the complex. The ( $n-\pi^*$ ) emission intensities were therefore reduced in complexes **4** and **5**.

#### CONCLUSIONS

When the reaction between  $MCl_2 \cdot H_2O$  ( $M = Zn, Cu$  or  $Co$ ) and **L** was performed in THF, complexes  $[ML]Cl_2$  (**4–6**) were obtained. In these complexes, **L** acts as a tetradentate ligand leading most probably to tetrahedral stereochemistry. In contrast to the complexes of **L** obtained in THF, the investigation of the reactions between  $MCl_2 \cdot xH_2O$  and **L** in ethanol led to the novel complexes  $[M(L')Cl]Cl$  (**1–3**). In each of these three complexes, one of the two imine bands in the parent ligand was hydrolysed on reaction with  $MCl_2 \cdot xH_2O$  ( $M = Zn, Cu$  or  $Co$ ) and the resultant primary amine nitrogen coordinated to the metal ions in a (possibly) pseudo-tetrahedral geometry. Work is also in progress in which this behaviour for other similar ligands is being investigated.

*Acknowledgement.* Financial assistance from Alzahra University is acknowledged.

#### ИЗВОД

#### СИНТЕЗА И МОНО-ХИДРОЛИЗА ДИШИФОВЕ БАЗЕ ( $\pm$ )*trans*-1,2-ЦИКЛОХЕКСАНДИАМИНА И 2-ПИРИДИНКАРБОКСАЛДЕХИДА У $Cu(II)$ , $Co(II)$ И $Zn(II)$ КОМПЛЕКСИМА ИНДУКОВАНА РАСТВОРАЧЕМ

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Синтетисана је Шифова база *trans*- $N,N'$ -бис(2-пиридинилметил)-1,2-циклохександиамин (**L**). Еквимоларна смеша овог лиганда и одговарајуће  $MCl_2 \cdot xH_2O$  соли ( $M = Cu, Co$  или  $Zn$ ) у етанолу као растварачу уз мешање подлеже парцијалној хидролози имино везе, при чему настаје тридентатни лиганд  $L'$  који истовремено гради комплексе  $N_3$  координационе сфере. У реакцијама лиганда **L** са  $MCl_2 \cdot xH_2O$  ( $M = Cu, Co$  или  $Zn$ ) у THF настају  $[ML]Cl_2$  комплекси. Лиганд **L** и комплекси  $[M(L')Cl]Cl$  и  $[ML]Cl_2$  су окарактерисани помоћу елементалне анализе, UV-Vis, FT-IR и  $^1H$ -NMR спектроскопије и GC/MS луминисцентних својстава.  $^1H$ -NMR спектри лиганда су снимани у  $CDCl_3$ , а спектри одговарајућих дијамагнетичних комплекса у DMSO растварачима. На основу ових спектроскопских података потврђено је да је лиганд преко донорских атома азота координован за јон метала. На основу луминисцентних испитивања лиганда и одговарајућих комплекса утврђено је да ова једињења показују интралигандну ( $\pi-\pi^*$ ) флуоресценцију у метанолу као растварачу, као и у чврстом стању на собној температури.

(Примљено 3. децембра 2011, прихваћено 24. марта 2012)

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