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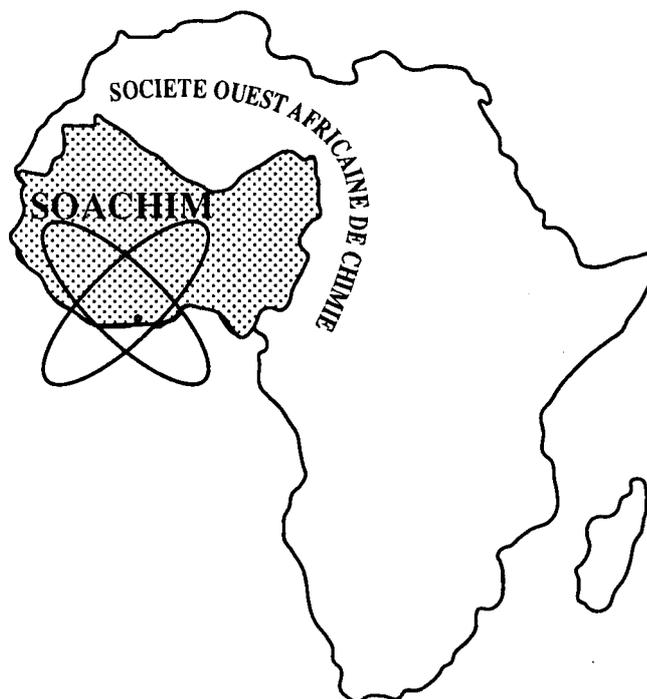
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*Journal de la Société Ouest-Africaine de Chimie*

*J. Soc. Ouest-Afr. Chim.(2016), 042 : 43 - 51*

21<sup>ème</sup> Année, Décembre 2016



ISSN 0796-6687

Code Chemical Abstracts : JSOCF2

Cote INIST (CNRS France) : <27680>

Site Web: <http://www.soachim.org>

## **Synthesis and characterization of two novel M(II) (M= Co or Cu ) complexes with a long flexible and neutral tetradentate dipyridyl ligand**

**Djiby Lo<sup>a</sup>, Papa Aly Gaye<sup>a</sup>, Ibrahima Elhadj Thiam<sup>a</sup>, Aliou Hamady Barry<sup>b</sup>, Abdou Salam Sall<sup>a</sup>, Mohamed Gaye<sup>a\*</sup>, Pascal Retailleau<sup>c</sup>**

<sup>a</sup>*Department of Chemistry, University Cheikh Anta Diop, Dakar, Senegal.*

<sup>b</sup>*Department of Chemistry, University de Nouakchott, Nouakchott, Mauritania.*

<sup>c</sup>*Centre de Recherche de Gif, Institut de Chimie des Substances Naturelles, CNRS-UPR2301, 1 Avenue la Terrasse, 91198 Gif sur Yvette, France.*

(Reçu le 13/12/2015 – Accepté après corrections le 03/01/ 2017)

**Abstract:** Cobalt(II) and copper(II) compounds,  $\{[\text{Co}(\text{L})(\text{H}_2\text{O})_2](\text{NO}_3)_2(\text{H}_2\text{O})\}$  (**1**) and  $[\text{CuCl}_2(\text{L}_{0.5})]_n$ , (**2**) (where L = *N*-(phenyl(pyridine-2-ylmethylene)-2-(2-(2-(phenyl(pyridine-2-yl)methyleneamino)ethoxy)ethoxy)ethanamine is potentially hexadentate Schiff-base ligand with two arms) have been prepared and characterized by elemental analysis, IR, UV-Vis spectroscopy and single-crystal X-ray diffraction. Compound **1** crystallizes in triclinic space group *P* $\bar{1}$  with cell dimensions  $a = 11.086(1)$ ,  $b = 12.106(1)$ ,  $c = 14.551(1)$ ,  $\alpha = 79.767(3)$ ,  $\beta = 69.599(3)$  and  $\gamma = 66.838(3)$ , whereas compound **2** crystallizes in monoclinic space group *C2/c* with cell dimensions of  $a = 13.854(1)$ ,  $b = 13.940(1)$ ,  $c = 15.934(1)$ ,  $\beta = 95.071(2)$ . The mononuclear cobalt complex **1** shows the metal ion Co(II) in an octahedral environment, being coordinated by the two arms of the ligand molecule in a  $\text{N}_4\text{O}_2$  core where the two O atoms are from two coordinated water molecules. Instead, in complex **2**, each of the metal centers is coordinated by one arm of the molecule ligand which acts as bridge between two metal centers. Two metal centers are bridged by two chloride anions leading a polymeric chains parallel to [101] direction. Each copper ion is bonded to a chloride atom in apical position leading a distorted  $\text{N}_2\text{Cl}_3$  square pyramidal environment around the metal center.

**Keywords:** Schiff base, Phenolate, Cobalt (II), Copper(II), mononuclear complexes, X-ray structure.

## **Synthèse et caractérisation de deux nouveaux complexes (M= Co ou Cu ) avec un ligand tétradentate flexible et neutre possédant des groupements pyridyles**

**Résumé :** Les composés de cobalt(II) et de cuivre(II),  $\{[\text{Co}(\text{L})(\text{H}_2\text{O})_2](\text{NO}_3)_2(\text{H}_2\text{O})\}$  (**1**) et  $[\text{CuCl}_2(\text{L}_{0.5})]_n$ , (**2**) (avec L = *N*-(phenyl(pyridine-2-ylmethylene)-2-(2-(2-(phenyl(pyridine-2-yl)methyleneamino)ethoxy)ethoxy)ethanamine qui est une base de Schiff potentiellement hexadentate possédant deux “bras” avec plusieurs sites de coordination) sont préparés et caractérisés par les techniques de l’analyse élémentaire, de la spectroscopie (UV et IR) et de la diffraction des rayons X sur des monocristaux. Le composé **1** cristallise dans le système triclinique dans une maille de paramètres  $a = 11.086(1)$ ,  $b = 12.106(1)$ ,  $c = 14.551(1)$ ,  $\alpha = 79.767(3)$ ,  $\beta = 69.599(3)$  et  $\gamma = 66.838(3)$ , avec comme groupe d’espace *P* $\bar{1}$ , alors que le composé **2** cristallise dans le système monoclinique dans le groupe d’espace *C2/c* avec comme paramètres de maille  $a = 13.854(1)$ ,  $b = 13.940(1)$ ,  $c = 15.934(1)$ ,  $\beta = 95.071(2)$ . La structure du composé mononucléaire **1** montre l’ion de Co(II) dans un environnement octaédrique  $\text{N}_4\text{O}_2$  avec les atomes d’azote provenant des deux bras du ligand et les deux atomes d’oxygène provenant de molécules d’eau coordonnées au métal. Par contre le complexe **2** est un polymère dans lequel chaque ion de  $\text{Cu}^{2+}$  est coordonné par un seul bras du ligand qui agit comme un pont entre deux atomes de cuivre. Deux atomes de cuivre de deux molécules sont pontés par deux atomes de chlore, tandis qu’un atome de chlore reste en position terminale sur chaque atome de cuivre. On observe des chaînes polymères parallèles à la direction [101] ainsi qu’un environnement pyramidal carré  $\text{N}_2\text{Cl}_3$  autour de l’ion Cu(II).

**Mots clés:** Base de Schiff, phénolate, Cobalt(II), Cuivre(II), mononucléaire, structure par diffraction des rayons X.

\* Correspondance : mohamedl.gaye@ucad.edu.sn

## 1. Introduction

The environment around metal center in coordination compound depends on both of the nature of the metal center and the behaviors of the organic ligands [1-4]. Synthesis and use of flexible multidentate organic ligands in the construction of coordination compounds, with different coordination styles are widely developed in these last years. Flexible organic molecules is known to coordinate metals ions in several modes [5-8]. Owing to its configuration the flexible organic molecule can encapsulated only one ion metal or acts as bridging ligand encapsulating one pair or more metals ions [9, 10]. Because of their versatility to adopt various modes, these kinds of ligand are able to generate stable framework [11-14]. The structures of metal complexes with ligand containing both amino and pyridyl nitrogen atoms are sufficiently well studied. These organic molecules can act as chelating multidentate or as bridging ligand, and the presence of pyridyl moieties in different positions allows these ligands to adopt different coordination modes through one or both nitrogen atoms, leading to mononuclear compound or homometallic polymeric compounds [15,16]. Studies using ligand containing pyridyl groups with spacers as bridging ligand in transition metal complexes showed the versatility of these kinds of ligand [17-20].

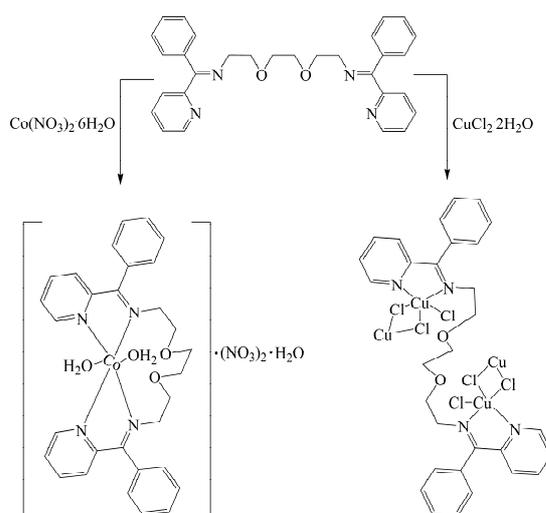
Herein we report the synthesis of the acyclic ligand derived from the 2-(2-(2-aminoethoxy)ethoxy)ethanamine precursor and benzoylpyridine. We have prepared the acyclic flexible neutral ligand L (Scheme 1), which has on

each of his two arms an N<sub>2</sub> receptor cavity suitably to coordinate metal ions. The complexation capacity of this acyclic ligand towards the first row transitional metal Co(II) and Cu(II) ion has been investigated producing complexes of formulae  $\{[Co(L)(H_2O)_2](NO_3)_2 \cdot (H_2O)\}$  and  $\{[CuCl_2L_{0.5}]\}_n$ .

## 2. Experimental

### 2.1. Materials and Measurements

2-Benzoylpyridine, 2-(2-(2-aminoethoxy)ethoxy)ethanamine and metal salts were commercial products of highest chemical grade (Aldrich). Solvents were purified according to standard procedures. Elemental analysis of C, H and N was performed by the analytical laboratory of the Department of Inorganic Chemistry (University of Padua, Italy). FTIR spectra were recorded with a Nicolet 55XC FT-IR spectrophotometer using KBr pellets. The UV-Vis spectra were run on a Jenway 6505 UV- Spectrophotometer (1100–200 nm) on 10<sup>-3</sup> M DMF solutions of the complexes. Molar conductance measurement was made using a WTW LF-330 conductivity meter with a WTW conductivity cell on about 1 mmol dm<sup>-3</sup> dimethylformamide solution at room temperature. Room temperature magnetic susceptibility measurements were made on solid complex using a Johnson-Mathey Gouy balance with Hg[Co(SCN)<sub>4</sub>] as the calibrator. X-ray data were collected using a ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) (Centre de Recherche de Gif., France).



Scheme 1

## 2.1. Synthesis of metal complexes

To 2-Benzoylpyridine (0.75 g, 4 mmol) in 20 mL of methanol was added dropwise a solution 2-(2-(2-aminoethoxy)ethoxy)ethanamine (0.3033 g, 2 mmol) in 10 mL of methanol. The mixture was refluxed for 5 hours yielding a yellow solution. On cooling a solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1.1641 g, 4 mmol) or  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.6819g, 4 mmol) was added. The solution was refluxed for two hours before cooling. After filtration, the solution was left a room temperature for three weeks. Appropriate crystals of  $\{[\text{Co}(\text{L})(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot (\text{H}_2\text{O})\}$  (red) and  $\{[\text{CuCl}_2\text{L}_{0.5}]\}_n$  (yellow) suitable to be studied by X-ray diffraction were obtained by slow evaporation of the methanol.

### 2.1.1. $\{[\text{Co}(\text{L})(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot (\text{H}_2\text{O})\}$ (1)

Yield : 76 %. Anal. Calc for  $\text{C}_{30}\text{H}_{36}\text{CoN}_6\text{O}_{11}$ : C, 50.35; H, 5.07; N, 11.74. Found: C, 50.67; H, 5.13; N, 11.53 %. IR (KBr,  $\text{cm}^{-1}$ ): 3442 [ $\nu_{\text{H}_2\text{O}}$ ]; 3220 [ $\nu_{\text{H}_2\text{O}}$ ]; 1625 [ $\nu_{\text{C}=\text{N}}$ ]; 1580, 1466 [ $\nu_{\text{C}=\text{N}}_{\text{py}}$  and  $\nu_{\text{C}=\text{C}}_{\text{ar}}$ ], 1380 [ $\nu_{\text{NO}_3}$ ], 1245 [ $\nu_{\text{C}-\text{O}}$ ]; 823 [ $\delta_{\text{H}_2\text{O}}$ ];  $\mu_{\text{eff}}$  ( $\mu_{\text{B}}$ ) 5.88.  $\Lambda_{\text{M}}$  (DMF,  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) = 145. UV-Vis ( $\lambda$ , nm) ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 291(3); 315(0.77); 465(0.22); 476(0.28); 530(0.16); 1046(0.11). Colour: red.

### 2.1.2. $[\text{CuCl}_2(\text{L}_{0.5})]_n$ (2)

Yield : 82 %. Anal. Calc for  $[\text{C}_{15}\text{H}_{15}\text{Cl}_2\text{CuN}_2\text{O}]_n$ : C, 59.49; H, 4.99; N, 9.25. Found: C, 59.19; H, 4.77; N, 9.01 %. IR (KBr,  $\text{cm}^{-1}$ ): 1623 [ $\nu_{\text{C}=\text{N}}$ ]; 1582, 1460 [ $\nu_{\text{C}=\text{N}}_{\text{py}}$  and  $\nu_{\text{C}=\text{C}}_{\text{ar}}$ ], 1244 [ $\nu_{\text{C}-\text{O}}$ ].  $\mu_{\text{eff}}$  ( $\mu_{\text{B}}$ ) 1.56.  $\Lambda_{\text{M}}$  (DMF,  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) = 4.2. UV-Vis ( $\lambda$ , nm) ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 293(3); 358(3); 461(3); 615(0.19); 811(0.09). Colour: yellow.

## 2.2. X-ray data collection, structure determination, and refinement

Slow evaporation of methanol solution gave X-ray quality crystals of the compound. The details of the X-ray crystal structure solution and refinement are given in Table I. Diffraction data were collected using a ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex

scattering factors were taken from the program package *SHELXTL* [21]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on  $F^2$  by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [21]. The hydrogen atoms were located in their calculated positions and refined using a riding model. Molecular graphics were generated using *ORTEP-3*[22].

## 3. Results and discussion

### 3.1. General studies

The coordination ability of the ligand **L**, towards hexahydrated nitrate  $\text{Co}(\text{II})$  and monohydrated chloride  $\text{Cu}(\text{II})$  compounds in 1:2, ligand: metal molar ratio was studied by adding methanol solutions of  $\text{Co}^{2+}$  or  $\text{Cu}^{2+}$  to a methanol solution of the ligand **L** prepared *in situ*. The complexes appear to be air stable and soluble in common organic solvents. These complexes were characterized by elemental analysis, IR and UV-Vis spectroscopy, molar conductivity, magnetic measurements and X-ray diffraction studies.

Elemental analysis is consistent with a mononuclear nature of the complex of Cobalt (II) in 1:1 ratio ligand:metal. While the complex of Copper (II) appears as polymeric in 1:2 ratio ligand:metal. In the IR spectra of the complexes, the band appearing near  $1620 \text{ cm}^{-1}$  is attributed to the  $\text{C}=\text{N}$  vibration. The  $\nu_{\text{C}=\text{N}}$  band is expected near  $1650 \text{ cm}^{-1}$  in uncoordinated form. This shifting to lower frequencies is indicative of interaction between the metal ion and the azomethine groups through the nitrogen atom. Both spectra show band at  $1580 \text{ cm}^{-1}$  as expected for the highest-energy pyridine ring vibration. In the spectrum of the cobalt (II) complex, band near  $3442 \text{ cm}^{-1}$  is assigned to the hydroxyl group of lattice water molecules [23]. The bands at *ca.*  $3220$  and  $823 \text{ cm}^{-1}$  are characteristic of coordinated water molecules [24]. The sharp and intense band appearing at  $1380 \text{ cm}^{-1}$  in the spectrum of the cobalt (II) is characteristic of the presence of a nitrate ion non-involved in coordination [25]. Magnetic moments determined for the cobalt (II) and copper(II) complexes at room temperature are 5.88 and 1.56 BM, respectively. The value of 5.88 BM is indicative of high-spin octahedral  $\text{Co}(\text{II})$  ( $d^7$ ) complex [26]. The value of 1.56 BM of the copper complex is close to the spin only value of 1.73 BM expected for one unpaired electron [27].

**Table I :** Crystal data and structure refinement for complexes  $C_{30}H_{34}CoN_4O_4 \cdot 2(NO_3) \cdot H_2O$  (**1**) and  $C_{15}H_{15}Cl_2CuN_2O$  (**2**).

Empirical formula	$C_{30}H_{34}CoN_4O_4 \cdot 2(NO_3) \cdot H_2O$ ( <b>1</b> )	$C_{15}H_{15}Cl_2CuN_2O$ ( <b>2</b> )
Formula weight	715.58	373.73
Crystal system	Triclinic	Monoclinic
space group	P1	C2/c
Temperature (K)	293	293
<i>a</i> (Å)	11.086 (1)	13.854 (1)
<i>b</i> (Å)	12.106 (1)	13.940 (1)
<i>c</i> (Å)	14.551 (1)	15.934 (1)
$\alpha$ (°)	79.767 (3)	90
$\beta$ (°)	69.599 (3)	95.071 (2)
$\gamma$ (°)	66.838 (3)	90
<i>V</i> (Å <sup>3</sup> )	1681.0 (2)	3065.2 (4)
<i>Z</i>	2	8
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.412	1.620
Radiation type	Mo K $\alpha$	Mo K $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.58	1.77
<i>F</i> (000)	744	1520
$\theta$ range (°)	2.93-25.44	2.92-25.39
Completeness to $\theta_{max}$ (%)	96.2	99.3
Crystal size (mm)	0.15 × 0.10 × 0.08	0.20 × 0.15 × 0.08
<i>hkl</i> ranges	-12, 13; -14, 14; -17, 17	-16, 16; -16, 16; -19, 19
Absorption correction	None	none
Measured reflections	10181	5380
Observed reflections, <i>I</i> > 2 $\sigma$ ( <i>I</i> )	6000	6000
<i>R</i> <sub>int</sub>	0.024	0.026
<i>R</i> , <i>wR</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0502, 0.1380	0.0406, 0.1294
<i>R</i> , <i>wR</i> (all data)	0.0640, 0.1521	0.0549, 0.1393
Data/restraints/parameters	6000/9/445	2804/0/190
Goodness-of-fit (Gof) on <i>F</i> <sup>2</sup>	1.035	1.093
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (eÅ <sup>-3</sup> )	0.760, -0.426	0.540, -0.604

Symmetry codes : (i) : -x, y, 1/2-z ; (ii) : 1/2+x, 1/2-y, -1/2+z ; (iii) : 1/2-x, 1/2-y, -z.

**Table II.** Selected bond distance (Å) and angle (°) for complexes (**1**) and (**2**).

(1)				(2)			
Co1—O1	2.082 (2)	O1—Co1—O2	85.46 (10)	Cu1—N2	2.037 (3)	N2—Cu1—N1	
Co1—O2	2.106 (2)	O1—Co1—N1	91.95 (10)	Cu1—N1	2.043 (3)	N2—Cu1—Cl2	
Co1—N1	2.122 (2)	O2—Co1—N1	95.11 (9)	Cu1—Cl2	2.2400 (11)	N1—Cu1—Cl2	
Co1—N3	2.123 (2)	O1—Co1—N3	166.01 (10)	Cu1—Cl1	2.3007 (9)	N2—Cu1—Cl1	
Co1—N4	2.124 (2)	O2—Co1—N3	85.61 (9)	Cu1—Cl1i	2.5820 (11)	N1—Cu1—Cl1	
Co1—N2	2.145 (2)	N1—Co1—N3	99.56 (9)	Cl1—Cu1i	2.5820 (11)	Cl2—Cu1—Cl1	
N1—C19	1.337 (4)	O1—Co1—N4	93.10 (10)	N1—C1	1.334 (4)	N2—Cu1—Cl1i	
N1—C23	1.349 (4)	O2—Co1—N4	90.44 (10)	N1—C5	1.352 (4)	N1—Cu1—Cl1i	
N2—C24	1.281 (4)	N1—Co1—N4	172.77 (9)	N2—C6	1.273 (4)	Cl2—Cu1—Cl1i	
N2—C18	1.471 (4)	N3—Co1—N4	76.22 (9)	N2—C13	1.468 (4)	Cl1—Cu1—Cl1i	

Symmetry code: (i) -x+3/2, -y+1/2, -z+1.

**Table III.** Hydrogen-bond geometry (Å, °) in the cobalt complex.

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1W1...O5i	0.821(18)	2.13(2)	2.892(5)	153(4)
O1—H2W1...O8	0.808(18)	2.05(2)	2.831(6)	162(4)
O1—H2W1...O6	0.808(18)	2.41(3)	3.115(6)	146(4)
O1—H2W1...N5	0.808(18)	2.62(2)	3.423(4)	173(4)
O2—H1W2...O5i	0.830(18)	1.922(19)	2.727(4)	163(4)
O2—H2W2...O10	0.819(18)	1.96(2)	2.766(4)	167(4)
O2—H2W2...N6	0.819(18)	2.68(2)	3.488(4)	167(4)
O5—H1W3...O7 <sup>ii</sup>	0.90	1.97	2.841(5)	163.4
O5—H2W3...O11 <sup>iii</sup>	0.96	2.12	3.018(5)	154.5
O5—H2W3...O9 <sup>iii</sup>	0.96	2.48	3.111(6)	123.0
O5—H2W3...N6 <sup>iii</sup>	0.96	2.68	3.507(5)	145.2

Symmetry codes: (i)  $x-1, y+1, z$ ; (ii)  $-x+2, -y, -z$ ; (iii)  $-x+2, -y, -z+1$ .

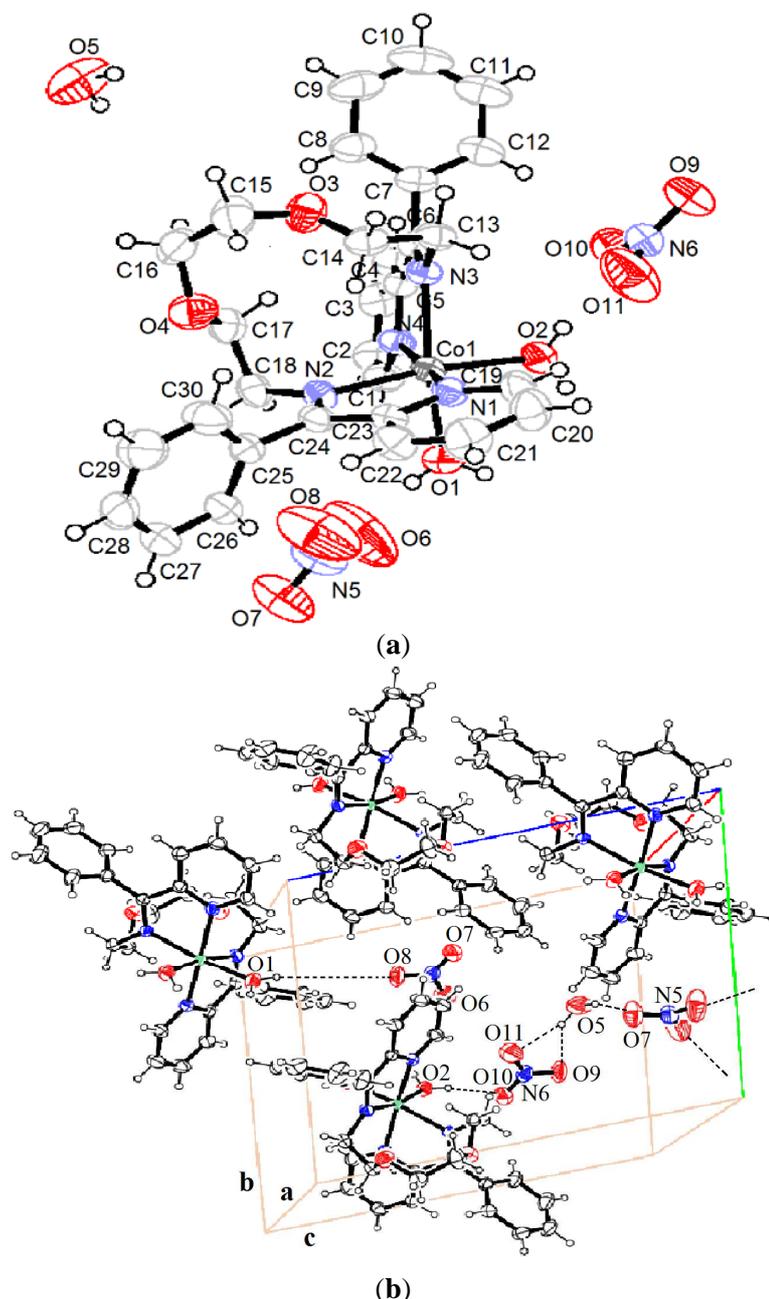
For octahedral high-spin cobalt (II) complexes, three spin permissible d-d transitions are expected:  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  ( $\nu_3$ ),  ${}^4T_{1g} \rightarrow {}^2A_{2g}$  ( $\nu_2$ ) and  ${}^4T_{1g} \rightarrow {}^4T_{2g}$  ( $\nu_1$ )<sup>[28]</sup>. The electronic spectrum of the synthesized cobalt (II) complex exhibits in DMF solvent absorption bands at *ca.* 476 ( $\nu_3$ ), 530 ( $\nu_2$ ) and 1046 ( $\nu_1$ ) nm which are in accordance with distorted octahedral geometry of Co<sup>II</sup> complex<sup>[29]</sup>. For the copper complex, the electronic spectrum shows a band in the region 600–620 nm followed by a band in the region 800–815 nm assigned to the d–d transition assuming a square-pyramidal geometry around the copper ion<sup>[30]</sup>. In both spectrum, a moderately intense band at 465 nm characteristic of the pyridine-to-metal charge transfer and a more intense band in the region 220–320 nm assigned to the  $\pi \rightarrow \pi^*$  transition of the phenyl and pyridyl rings and C=N moieties are observed.

Molar conductivities were measured for freshly prepared solutions in DMF and after standing for two weeks. The conductivities increased very slightly with time in dmf for the two complexes. The conductance value of  $\{[Co(L)(H_2O)_2](NO_3)_2 \cdot (H_2O)\}$  complex is  $145 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ . This value which lies in the range ( $130\text{--}170 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ ) which is indicative of a 2:1 electrolyte and thus  $[Co(L)(H_2O)_2]^{2+}$  species are present in DMF solution. For the polymeric Cu(II) complex the conductance is  $4.2 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$  indicative of a neutral complex in DMF solution<sup>[31]</sup>. The formulations obtained from the spectroscopic studies for these complexes are in accordance with the measured molar conductivities.

## 3.2. X-ray diffraction analysis

### 3.2.1. $\{[Co(L)(H_2O)_2](NO_3)_2 \cdot (H_2O)\}$ (1)

The crystal structure of the complex  $\{[Co(L)(H_2O)_2](NO_3)_2 \cdot (H_2O)\}$  (1) is illustrated in Figure 1a and the crystallographic data are summarized in **Table I**. The compound crystallizes in the centrosymmetric space group  $P\bar{1}$ . The asymmetric unit contains one Co(II) mononuclear complex. The cobalt ion is bounded by two symmetrically related moieties of the same ligand molecule where each arm coordinates the Co(II) ion through the secondary amine nitrogen atoms and the pyridyl nitrogen atom resulting in five membered-rings. The N1–Co1–N2 and N3–Co1–N4 angles are respectively  $76.51(9)^\circ$  and  $76.22(9)^\circ$  and are significantly smaller than the ideal value of  $90^\circ$  presumably due to the constraint imposed by the five membered chelate rings<sup>[32]</sup>. Two water molecules complete the coordination sphere around the Co(II) center. The cobalt center has a slightly distorted  $N_4O_2$  octahedral geometry. The basal plane of the octahedral polyhedron is formed by the two imino nitrogen (N3 and N2) of the ligand and the two oxygen atoms of the ligated water molecules. The apical positions are occupied by the two pyridine nitrogen atoms (N1 and N4) of the organic ligand molecule. The bond angles N2–Co–N3  $101.99(9)$ , O1–Co–N2  $88.35(10)$ , O2–Co–N3  $85.61(9)$  and O1–Co–O2  $85.46(10)$  (**Table II**) indicate distortion from an ideal octahedral geometry. The Co–N distances are similar for both arms of the molecule ligand, varying from 2.122(2) to 2.145(2) Å. These distances are slightly longer than those found in the corresponding nitrate complex<sup>[33]</sup>, and shorter to that corresponded to the complex  $[CoLCl_2] \cdot CH_3OH \cdot 0.5H_2O$  (where L is: (E)-N-(pyridin-2-ylmethylene)-2-(3-(2-((E)-pyridin-2-ylmethylamino)phenoxy)naphthalen-2-ylloxy)benzenimine)<sup>[34]</sup>. The Co–O<sub>water</sub> bond lengths are 2.082(2) for Co–O1 and 2.106(2) Å for Co–O2 and are comparable to those found in a diaqua octahedral complex<sup>[35]</sup>. The packing of the structure consists of an arrangement of discrete molecules, between which lie the solvation water molecules and the nitrate counter-ions. These entities establish different types of Hydrogen bonds O–H...O–NO<sub>2</sub> and O–H...O<sub>wligated</sub> (**Table III**) which contribute to the stabilization and expansion of a 3D frameworks **Figure 1b**.



**Figure 1:** Molecular representation of the compound with atom-numbering showing mononuclear Co complex and isolated water molecule and nitrate ions (a). Hydrogen bonds are showed (b).

### 3.2.1. $[\text{CuCl}_2(\text{L}_{0.5})]_n$ (2)

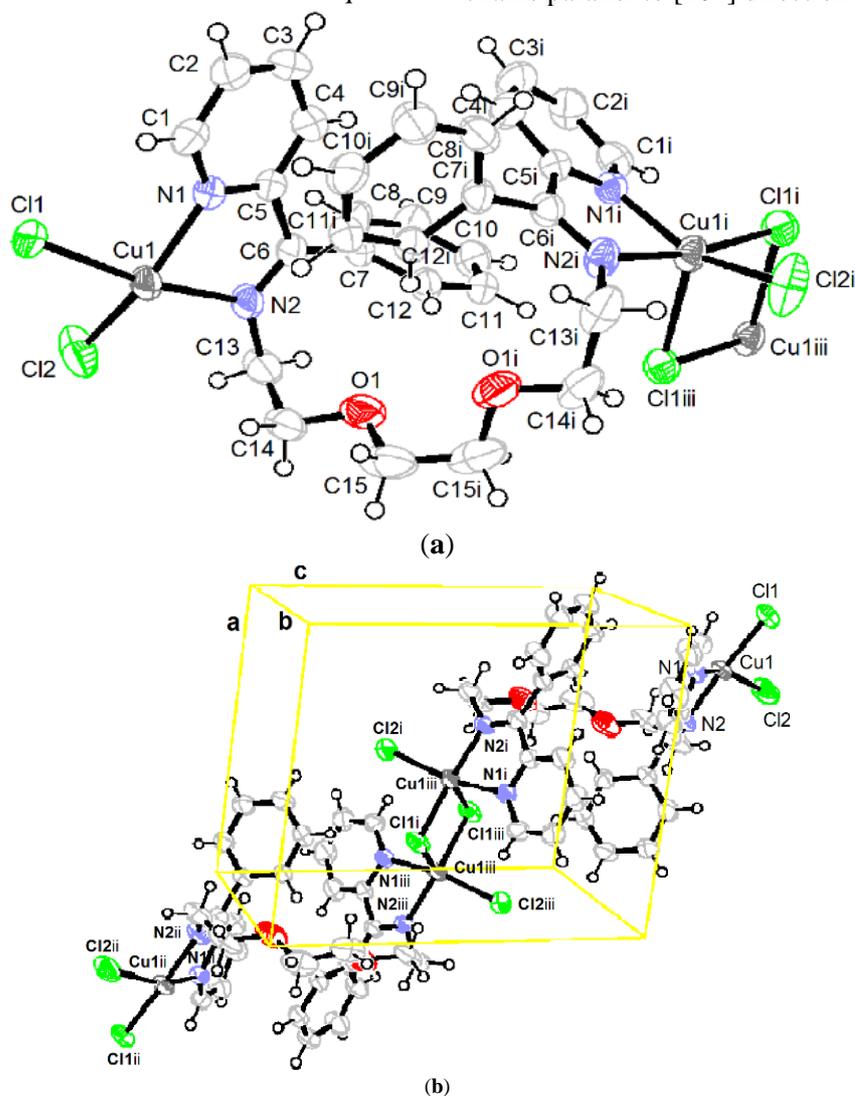
The compound **2** crystallizes in the space group  $C2/c$ . An *ORTEP* view of the polymeric chain of compound **2** with the atom-labeling scheme is shown in Figure 2a and the crystallographic data are summarized in Table I. Each arm of the tetradentate ligand coordinates one copper atom ion via the imine N atom and the pyridine N atom forming a five membered chelate ring. Three chloride atoms coordinate with each copper ion forming a distorted square-pyramidal structure. Two of the chloride atoms act as bridge between two copper ions and

form with the N donor atoms of the ligand the basal plane of the square-pyramidal environment while the third chloride atom lies in the apical position.

The coordination geometry around the Cu(II) ion is a distorted square pyramidal as indicated from the value of the Addison structural parameter,  $\tau = 0.267$  defined as  $\tau = [\alpha - \beta]/60$ , where  $\alpha$  and  $\beta$  are the two largest coordination angles. The expected values of  $\tau$  is 0 for perfect square-pyramidal and 1 for ideal trigonal-bipyramidal coordination sphere<sup>[36]</sup>. The sum of the angles around atom Cu ion is  $356.39^\circ$ , confirming that the geometry around the copper

atom is distorted square-planar. Deviations of the coordinating atoms N1, N2, Cl1 and Cl2 from the least-square basal plane are 0.241(1), -0.115(1), -0.078(1) and 0.205(1) Å respectively. The copper atom deviation from the same plane is 0.252(1) Å. The equatorial bond length of Cu1–N1, Cu1–N2, Cu1–Cl1 and Cu1–Cl2 are 2.043(3), 2.037(3), 2.301(1) and 2.240(1) Å (Table II), respectively. The apical position of the distorted square pyramidal geometry is occupied by the second bridging chlorido Cl1<sup>i</sup> with a distance of 2.582(1) Å which is longer than those in equatorial positions. The bridging chlorido moieties are coordinated to the two copper atoms in an asymmetric fashion with a different bond lengths of 0.2813 Å. This observation can be explained by the Jahn–Teller distortion of the copper(II) ion<sup>[37]</sup>. These values are comparable with those found in the distorted square

pyramidal bridged binuclear Cu(II) complex  $[(\text{pmtpm})\text{Cu}]_2(\mu\text{-Cl})_2(\text{ClO}_4)_2$  derived from a tridentate Schiff base ligand, 2-pyridyl-N-(20-methylthiophenyl)methyleneimine (pmtpm)<sup>[38]</sup>. The equatorial bond angles differ from the ideal value for a square pyramid and fall in the range  $[78.91(11)\text{-}169.45(9)^\circ]$  and are consistency with the values found for a similar polymeric complex where the Cu atoms are bridged by two chloride atoms<sup>[39]</sup>. These Cu atoms bridged by two chloride displays relatively short contact of 3.5120(8) Å. The Cu1–Cl1–Cu1<sup>i</sup> and the Cl1–Cu1–Cl1<sup>i</sup> angle are respectively 91.81(3) and 88.19(3)°. Each organic ligand molecule acts as a bridging ligand via the imino and the pyridyl nitrogen atoms between two copper atoms which are bridged by two chloride anions leading a polymeric structure consisting of chains parallel to [101] direction Figure 2b.



**Figure 2:** Molecular representation of the compound (a). Polymeric chains made up of organic ligands connected by Cu polyhedral (b).

#### 4. Conclusion

In this paper, we described a Schiff's base ligand obtained by condensation of 2-(2-(2-aminoethoxy)ethoxy)ethanamine with 2-benzoylpyridine affording a neutral potential hexadentate O<sub>2</sub>N<sub>4</sub> ligand L. The reactions of this Schiff's base ligand with Co(II) and Cu(II) yielded a colored complexes. The organic ligand and the synthesized complexes have been characterized on the basis of elemental analyses, FT-IR and UV-VIS spectroscopies and as well as molar conductivity and room magnetic susceptibility measurements suggesting N<sub>4</sub> tetradentate donors. The structure with octahedral and square pyramidal environment have been proposed respectively for Co(II) and Cu(II) complexes. X-ray diffraction analysis shows the versatility behavior of the flexible ligand. In treatment with Co(II) the flexible ligand prefers coordinate the cobalt ion with his two arms leading a monomeric complex. In treatment with Cu(II) ions, it acts as a bridge between copper atoms leading a polymeric chains parallel to [101] direction.

#### Supporting Information

CCDC 1435616 and 1435762 contain the supplementary crystallographic data for {[Co(L)(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)} and [CuCl<sub>2</sub>(L<sub>0.5</sub>)<sub>n</sub>] respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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