

# Synthesis and characterization of non-symmetric tetradentate complexes of Zn(II), Co(II), and Cu(II)

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The non-symmetrical tetradentate Schiff-base  $H_2L$  was obtained using the half-unit N-(1-hydroxy-2-acetophenone)-1-amino-2-phenyleneimine (HL) with 2-hydroxyl-1-naphthaldehyde. ZnL, CoL, and CuL complexes were prepared and characterized by  $^1H$ -NMR, IR, electronic, and atomic absorption spectra. The single crystal X-ray structure of CuL was determined. Crystal data for CuL are triclinic space group P-1,  $a = 8.3933$  (17) Å,  $b = 11.197$  (2) Å,  $c = 13.381$  (3) Å,  $\alpha = 95.29$  (3)°,  $\beta = 94.37$  (3)°,  $\gamma = 95.82$  (3)°, and  $z = 2$ .

## Introduction

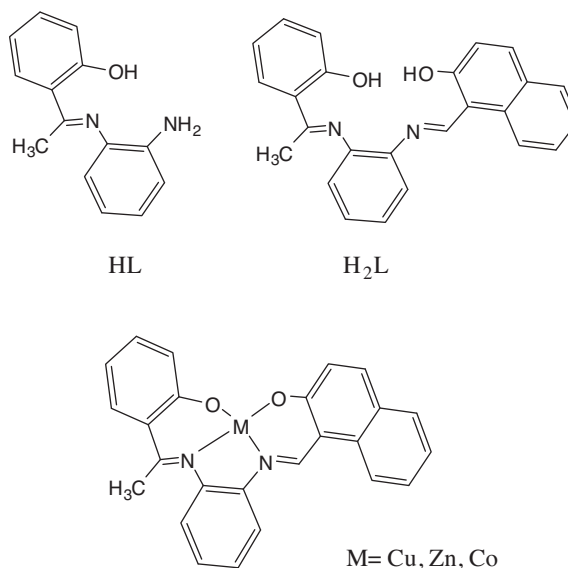
Unsymmetrical Schiff bases derived from the condensation of diamine with ketones represent an important class of chelating agents, the metal complexes of which have been studied widely in terms of catalysis,<sup>1</sup> magnetic properties,<sup>2</sup> isomers,<sup>3</sup> and reaction mechanisms.<sup>4</sup> In this work the half-unit Schiff-base N-(2-hydroxyacetophenone)-1-amino-2-phenyleneimine (HL) (Figure 1) was used as a precursor<sup>5</sup> for the preparation of non-symmetrical tetradentate Schiff-base ligand by simple condensation of its primary amino group with the carbonyl group of 2-hydroxy-1-naphthaldehyde ( $H_2L$ ) (Figure 1). In this study, the structure of the half unit and ligand were determined by  $^1H$ - and  $^{13}C$ -NMR spectra and elemental analysis.<sup>6</sup> Their corresponding Zn(II), Co(II), and Cu(II) complexes were synthesized and characterized. Single crystal X-ray analysis of CuL was carried out to determine the coordination stereochemistry. A square planar structure was tentatively assigned to all of the complexes.

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## Experimental

IR spectra were recorded using a Bruker Tensor 27 spectrometer. Visible spectra and atomic absorption were obtained using a Unicam 8700 series UV/Vis and Philips Pu 9100 spectrometer, respectively.  $^1\text{H}$  and  $^{13}\text{C}$  spectra were obtained on a Bruker FTAC-80 (80 MHz) spectrometer using TMS as internal standard.



**Figure 1.** Structure of HL, H<sub>2</sub>L, and ML.

**Preparation of the Half-Unit HL.** It was prepared by a previously described method.<sup>6</sup>

**Preparation of the Ligand H<sub>2</sub>L.** To a solution of HL (0.23 g, 1 mmol) and 2-hydroxy-1-naphthaldehyde (0.17 g, 1 mmol) in methanol (20 mL) at room temperature were added a few drops of piperidine. The mixture was then stirred for 30 min at room temperature and the solid product formed was collected by filtration, washed with methanol and further purified by crystallization from methanol-chloroform (1:3) and dried at 50 °C, yield, 0.28 g (75%), mp 160-163 °C.

**Preparation of the Complexes CuL and ZnL.** A mixture of the ligand H<sub>2</sub>L (0.38 g, 1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and a MeOH solution (10 mL) of the desired metal acetate salt (1 mmol) was stirred for 30 min at room temperature. The resulting precipitate was separated by filtration and washed with methanol and air dried. CuL yield g (80%), mp 280 °C (decomp.). ZnL yield 0.32 g (73%), mp 245 °C (decomp.).

**Preparation of the Complex CoL.** A mixture of the ligand H<sub>2</sub>L (0.38 g, 1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and a MeOH solution (10 mL) of cobalt acetate (0.25 g, 1 mmol) was stirred for 1 h at room temperature. The resulting red precipitate was separated by filtration and washed with methanol and air dried. The yield was 0.25 g (57%), mp 245 °C (decomp.).

## X-ray crystallography

Single crystals were mounted with oil on a quartz fiber and transferred into a cold nitrogen stream on a Siemens SMART (Siemens, 1994) 3-circle system with a CCD area detector. The crystal was held at 220 (2) K with the

Oxford Cryosystem Cryostream cooler (Cosier & Glazer, 1986). The structures were solved by direct methods using SHELXS (Sheldrick, 1990) (TREF) with light atoms found by Fourier methods.

## Results and discussion

A Schiff-base ligand ( $H_2L$ ) was prepared by a stepwise reaction procedure.<sup>7</sup> The 1:1 condensation products of *o*-hydroxyacetophene and phenylenediamine were prepared under refluxing conditions (Figure 1). Then one equivalent of 2-hydroxy-1-naphthaldehyde in the presence of piperidine at room temperature was reacted with the 1:1 condensation product to produce the unsymmetrical tetradentate ligand composed of *o*-hydroxyacetophene, phenylenediamine, and 2-hydroxy-1-naphthaldehyde (1:1:1) (Figure 1). Reaction of ligand with zinc(II), cobalt(II), and copper(II) acetate gave the complexes ZnL, CoL, and CuL, respectively. Atomic absorption spectroscopy of the complexes is consistent with the 1:1 ratio of ligand to metal ion. Details of the single compound are as follows.

Brown plate-like crystals of CuL suitable for X-ray analysis (0.24, 0.12, 0.06 mm) were obtained by recrystallization from chloroform/ethanol (3:1). The resolution of the structure is correct as confirmed by the acceptable R (F) (0.0633) and goodness-of-fit (0.912) value.

## IR Spectra

The IR spectrum for the ligand shows a broad and intense band at  $1615\text{ cm}^{-1}$ , which is assignable to the stretching vibration of the C=N bond.<sup>8,9</sup> The absorption values of the C=N vibration at 1603, 1606, and  $1600\text{ cm}^{-1}$  for ZnL, CoL, and CuL, respectively, are lower by about  $9\text{-}15\text{ cm}^{-1}$  than those for the free ligand, which indicates the coordination of azomethine nitrogen atom to metal ions in the complexes.<sup>7</sup>

## Electronic spectra

The d-d spectra of the CuL consist of a broad band (Table 1). This position is consistent with the square-planar structure of similar tetradentate Schiff-base ligands with *o*-phenylenediamine as diamine bridge.<sup>10</sup> For the CoL, d-d transition appears below 600 nm, which is characteristic of a square-planar or distorted square-planar structure.<sup>11</sup> The electronic spectra for ZnL are similar to those of the ligand and show very little shift in the position of the absorption maxima.<sup>12</sup> The high-energy band in the ligand at 331 nm and in the complexes at 260-400 nm may be assigned to intra-ligand or charge-transfer transition.

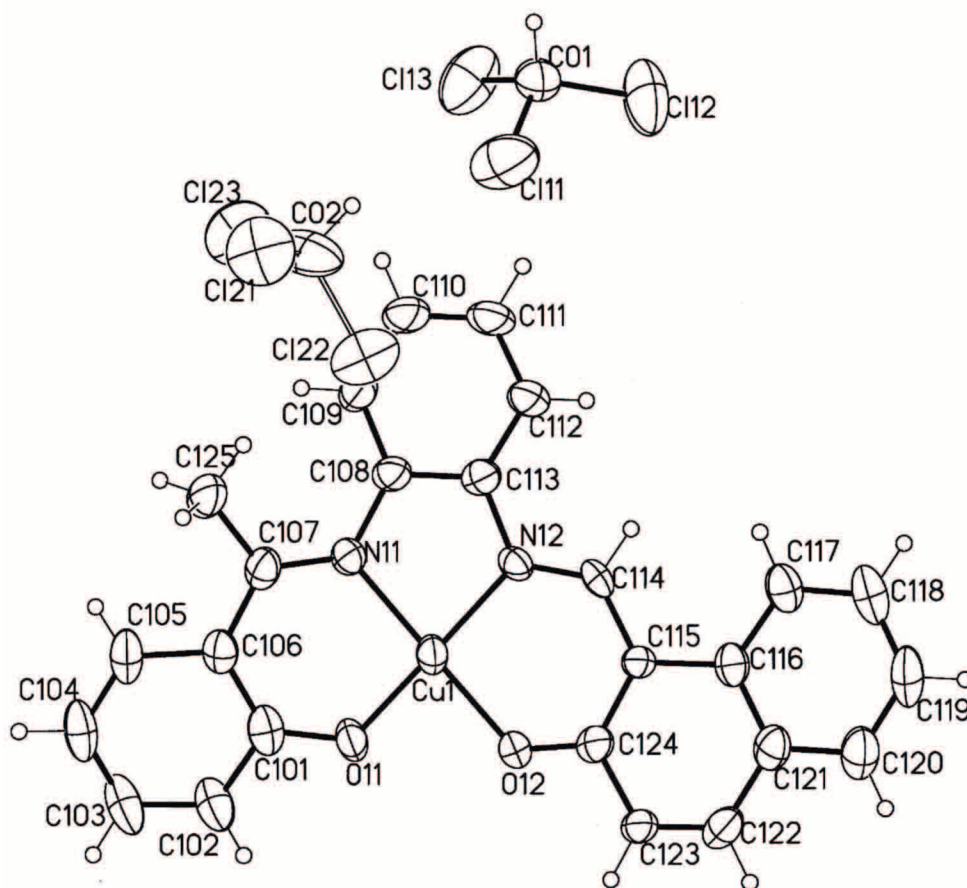
**Table 1.** Electronic spectra bands.

Complex	Bands nm, ( $\log \epsilon$ )
$H_2L$	473(sh), 329(), 234(4.5)
CoL	560(sh), 477(sh), 348(sh)
ZnL	484(sh), 399 (sh) 329(sh), 237(4.2)
CuL	616(2.9), 424(4.1), 350(4)

$\epsilon = \text{Mol}^{-1}\text{L cm}^{-1}$  In  $\text{CH}_2\text{Cl}_2$

## <sup>1</sup>H-NMR spectrum

The <sup>1</sup>H-NMR spectrum of H<sub>2</sub>L gives direct evidence of the formation of an unsymmetrical tetradentate ligand. As anticipated, the spectrum consists of 1 methyl at  $\delta$  2.3, 1 azomethine hydrogen at  $\delta$  9.3, 2 hydroxy hydrogens at  $\delta$  14.2 and 14.9, and aromatic protons at  $\delta$  6.8-8.1 signals. On the formation of ZnL complex the signals of the methyl group are shifted to  $\delta$  2.56 and of the azomethine hydrogen to  $\delta$  9.62, and the signals of the OH groups disappear.



**Figure 2.** ORTEP drawing of CuL with the atom numbering scheme.

## Structure of the complex CuL

Figure 2 show ORTEP drawing of the complex CuL. The present X-ray analyses verified the structure of copper(II) complexes with unsymmetrical tetradentate ligand composed of the condensation products of *o*-hydroxyacetophenone, phenylenediamine, and 2-hydroxy-1-naphthaldehyde in the mole ratio 1:1:1. The crystal structure analysis of this compound reveals the tetradentate ligand in which 2 nitrogen and 2 oxygen atoms are coordinated to the copper atom. The copper(II) ion shows a slightly distorted square-planar structure. The Cu-O and Cu-N distances (Table 2) are close to the limits of ranges 1.87-1.91 and 1.92-1.95 Å for Cu-O and Cu-N distances, respectively, normally observed in N<sub>2</sub>O<sub>2</sub> square-planar copper(II) complexes.<sup>13</sup> The asymmetric

unit included 2 molecules of chloroform, 1 with half occupancy. The crystal and experimental data are presented in Table 3.

**Table 2.** Selected bond lengths (Å) and bond angles (°) for CuL.

Cu1-O11	1.873(3)	Cu1-O12	1.915(3)
Cu1-N12	1.926(4)	Cu1-N11	1.950(4)
C101-O11	1.311(6)	N11-C107	1.326(6)
O11-Cu1-O12	88.33 (15)	O11-Cu1-N12	176.20(16)
O12-Cu1-N12	93.25 (16)	O11-Cu1-N11	94.00 (17)
O12-Cu1-N11	174.36 (16)	N12-Cu1-N11	84.74 (17)
C101-O11-Cu1	124.8(3)	C107-N11-Cu1	122.6(3)
C108-N11-Cu1	110.7(3)	C124-O12-Cu1	128.0(3)
C114-N12-Cu1	125.0 (3)	C113-N12-Cu1	112.8 (3)

**Table 3.** Experimental data for the X-ray diffraction of CuL.

Formula weight	C <sub>26.50</sub> H <sub>19.50</sub> Cl <sub>4.50</sub> N <sub>2</sub> CuO <sub>2</sub>	V (Å <sup>3</sup> )	1241.0 (4)
Molecular weight	621.01	Z	2
Crystal system	Triclinic	(mm <sup>-1</sup> )	1.394
Space group	P-1	Dc(g/cm <sup>3</sup> )	1.662
a (Å)	8.3933 (17)	F (000)	628
b (Å)	11.197 (2)	min, min/θ°	1.53 to 28.50
c (Å)	13.381 (3)	Total reflection	2655
α	95.29(3)	Independent reflections	5480 (R <sub>int</sub> = 0.0401)
β	94.37 (3)	Goodness of fit on F <sup>2</sup>	0.912
γ	95.82 (3)		

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