



# A new chromogenic and ratiometric agent for copper(II): Synthesis, structure and spectroscopy

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## ABSTRACT

A heterocyclic hydrazone ligand, pyridine-2-carboxaldehyde-2-hydrazino-2-imidazoline hydrobromide, HL (**1**), was investigated as a new chromogenic and ratiometric agent for selective detection of Cu<sup>2+</sup>. The ligand **1** gives a characteristic absorption peak in the UV region ( $\lambda_{\text{max}} = 328 \text{ nm}$ ). It interacts selectively with Cu<sup>2+</sup> and addition of Cu<sup>2+</sup> shifted the UV absorption wavelength from 328 to 410 nm due to formation of the complex [CuBr<sub>2</sub>(HL)] (**1a**). The red-shift of the absorption spectrum allowed a ratiometric analysis of the signalling behavior. The formation of **1a** was accompanied by a color change from light yellow to bright green, which can easily be distinguished from other metal complexes by the naked eye. The association constant ( $K_{\text{ass}}$ , UV-Vis) of **1a** was found to be  $(5.58 \pm 0.006) \times 10^4$  at 298 K. The molecular structures of **1** and **1a** have been successfully determined by single crystal X-ray diffraction studies.

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## 1. Introduction

The development of specific receptors to monitor targeted ions is currently a task of prime importance for clinical, environmental and biological applications [1–8]. By suitable design and synthetic strategies, it is possible to introduce specific properties whose integration can lead to useful functions. However, the selectivity and specificity of receptors for molecular sensors remain a significant challenge. In recent years, considerable interest has been placed on the creation of new chemosensors for heavy and transition metal (HTM) ions which allows naked eye real time and space detection of the change of color upon metal ion binding without the use of any spectroscopic instrument [9–14]. Copper(II) is not only an environmental pollutant at high concentrations [15,16], but also an essential trace element for many biological processes and systems [17–19]. Numerous methods for the detection of Cu<sup>2+</sup> have been reported [20–24], however, spectrophotometric methods are often preferred because it is a less labor-intensive technique, involve inexpensive instruments and provide high sensitivity [25–34]. Presently, one of the most attractive approaches focuses on the search for new water soluble chromogenic agents for copper(II) because in most cases the spectral changes can only be observed in non-aqueous solvents, which greatly limits their analytical application for real samples.

Among the large number of organic systems, hydrazones (>C=N–N<) received special interest due to their diverse environmental and biological applications [35–40]. Herein, we have investigated pyridine-2-carboxaldehyde-2-hydrazino-2-imidazoline hydrobromide, HL (**1**) as a new water soluble chromogenic and ratiometric agent for Cu<sup>2+</sup>, which is useful to develop a simple-to-use, naked eye diagnostic tool for the determination of Cu<sup>2+</sup> in water samples from different sources. The X-ray structure determination of [CuBr<sub>2</sub>(HL)] (**1a**) authenticates the tridentate binding of **1**.

## 2. Experimental

### 2.1. Materials

All starting materials and solvents were purchased from Sigma Aldrich Chemical Company and were used without further purification, unless otherwise stated.

### 2.2. Physical measurements

A Perkin Elmer 2400 C Elemental Analyzer was used to collect microanalytical data (C, H, N). A Sartorius CP64 balance was used for weighing purposes. FTIR data were collected with the help of a Shimadzu FTIR 8400 spectrophotometer. UV-Vis spectra of the ligand and its complex were measured on a Shimadzu UV-1700 spectrophotometer and were corrected for background due to solvent absorption. All the spectroscopic measurements were carried

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out in aqueous solution (methanol 1% v/v) at room temperature. For binding constant measurements, the solutions were prepared at fixed concentrations of HL (**1**) ( $2.0 \times 10^{-5}$  M) and at  $\text{Cu}^{2+}$  concentrations ranging from  $(0.2\text{--}2.0) \times 10^{-5}$  M at room temperature. The room temperature magnetic susceptibility was measured with a model 155 PAR vibrating sample magnetometer fitted with a Walker scientific L75FBAL magnet. An Orion 4 star pH.ISE Benchtop was used to measure pH values. A Perkin Elmer Analyst 400 atomic absorption spectrophotometer (AAS) was also used for copper(II) analysis.

### 2.3. Synthesis and characterization of the ligand HL (**1**) and the complex $[\text{CuBr}_2(\text{HL})]$ (**1a**)

The ligand HL (**1**) was synthesized and characterized following the reported method [41].

The complex  $[\text{CuBr}_2(\text{HL})]$  (**1a**) was synthesized by adding a methanolic solution (5 ml) of copper(II) bromide (0.2 mmol, 0.044 g) dropwise to a solution of **1**, (0.2 mmol, 0.053 g) in the same solvent (5 ml), taken in a 1:1 M ratio, with constant stirring for 1 h. The solvent was evaporated and the solid obtained was recrystallized from methanol giving pure complex **1a**. Yield 0.081 g (84%). Elemental Anal. Calc. for  $\text{C}_9\text{H}_{11}\text{Br}_2\text{CuN}_5$  (**1a**): C, 58.20; H, 3.73; N, 15.67. Found: C, 58.22; H, 3.72; N, 15.68%. FTIR (KBr pellets,  $\text{cm}^{-1}$ ): 3334, 1778, 1633, 1589, 1478, 1449, 1422, 1398, 1377, 1291, 1147, 1111, 1090, 1050, 1026, 858, 763, 709, 694, 680, 626. UV–Vis (aqueous methanol),  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 410 (4346), 298 (6433).

### 2.4. X-ray crystallography

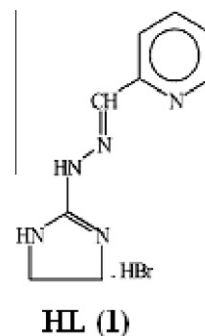
Suitable crystals of HL (**1**) and  $[\text{CuBr}_2(\text{HL})]$  (**1a**) were obtained by slow evaporation of methanolic solutions of the ligand and the complex, respectively. The intensity data of **1** (brown,  $0.20 \times 0.20 \times 0.25 \text{ mm}^3$ ) and **1a** (green blocks,  $0.25 \times 0.40 \times 0.40 \text{ mm}^3$ ) were collected at 173 K ( $-100^\circ\text{C}$ ) on a Stoe Mark II-Image plate diffraction system [42] equipped with a two-circle goniometer and using Mo  $K\alpha$  graphite monochromated radiation. The structures were solved by direct methods using the program SHELXS [43]. The refinement and further calculations were carried out using

SHELXL-97 [43]. The N–H H-atoms were located in difference fourier maps and freely refined. The C-bound H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on  $F^2$ . Molecular structures and the crystallographic numbering schemes are illustrated in the PLATON [44] drawings (Figs. 1 and 2). Further crystallographic data and details of the refinement are given in Table 1.

## 3. Results and discussion

### 3.1. Synthesis and characterization

The ligand HL (**1**) binds in a tridentate manner utilizing the imidazole, imine and

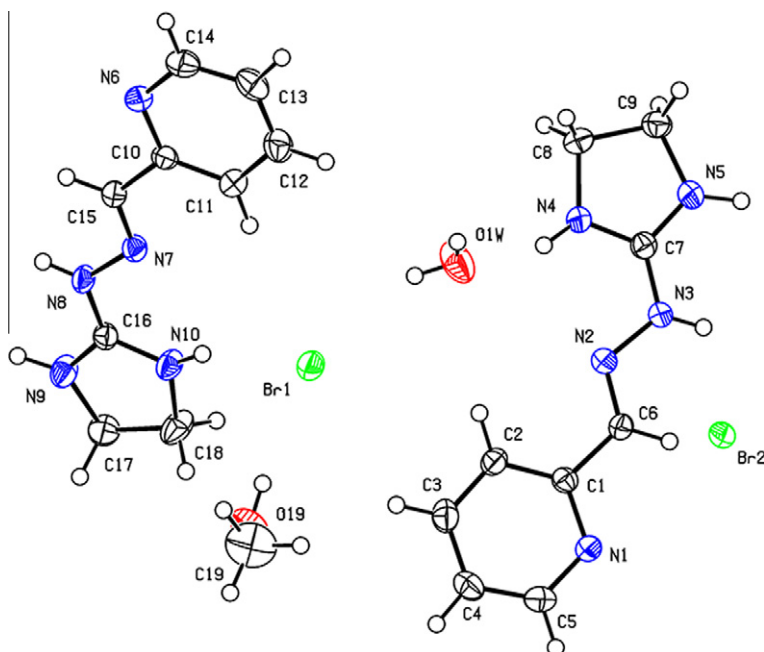


pyridyl functions as potential donor sites. The 1:1 reaction of HL (**1**) with copper(II) bromide in methanol at room temperature afforded the green colored complex  $[\text{CuBr}_2(\text{HL})]$  (**1a**) in excellent yields. The complex is soluble in water and methanol. The room temperature (298 K) magnetic moment of complex **1a** is  $1.82 \mu_B$  ( $S = 1/2$ ), as expected for  $d^9$  system.

### 3.2. X ray crystal structures of the ligand and the complex

#### 3.2.1. HL (**1**)

The ligand HL (**1**) crystallized as its hydrobromide salt with two independent molecules in the asymmetric unit, together with a



**Fig. 1.** The molecular structure and atom labelling of the two independent molecules of HL (**1**). Displacement ellipsoids are drawn at the 50% probability level.

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