

## Two isomers containing a [Cu(Me<sub>2</sub>bpzb)] unit: Molecule (0-D) and 1-D

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### ABSTRACT

Two isomers (molecule **1** and 1-D **2**) containing [Cu(Me<sub>2</sub>bpzb)] units have been obtained under the different reaction conditions, and their structures have been determined by X-ray crystallography. From the temperature-dependent magnetic data for **2**, there was no interaction between Cu<sup>2+</sup> ions through the ligand. The photoluminescence of the free H<sub>2</sub>Me<sub>2</sub>bpzb molecule displayed an intense emission band centered at about 482 nm, while complexes **1** and **2** exhibited no obvious emission bands.

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Much attention has been paid to pyridine carboxamide ligands containing ubiquitous carboxamide [–C(O)NH–] group in the primary structure of proteins because they are important for construction of metal complexes [1]. The pyridine carboxamide can be readily obtained from the simple one-step condensation of pyridine carboxylic acids and amines, and deprotonation of the carboxamide nitrogen atom makes the ligand act as a tetradentate ligand to chelate a metal ion. Therefore, the pyridine carboxamide ligands have been widely used to make a variety of metal complexes. Importantly, metal complexes containing pyridine carboxamide ligands can show excellent characteristics in hydroxylation, epoxidation and asymmetric catalysts [2], NO deliver [3], molecular receptor [4], and spin ground state control [5] as well as magnetic interactions [6].

Vagg et al. reported the synthesis of a number of potentially tetradentate bis-carboxamide ligands derived from picolic acid and various diamines [7]. One such ligand, H<sub>2</sub>bpb (N,N'-bis(2'-pyridine carboxamide)-1,2-benzene), has been shown to coordinate to transition metal ions as a planar N4 tetradentate resulting in a marked increase in the lability of the amide protons [2,7].

Copper among biologically relevant d-block metals widely investigated is a particularly fruitful element towards the behavior study of pyridine carboxamides. Pyridine dicarboxamide ligands support a

range of coordination numbers, geometries and nuclearities for copper(II) [8].

We have also reported the structures of three Cu(II) complexes with pyridine carboxamide ligands (H<sub>2</sub>Me<sub>2</sub>bpb (1,2-bis(pyridine-2-carboxamido)-4,5-dimethylbenzene), H<sub>2</sub>6-Me<sub>2</sub>-Mebpb (1,2-bis(6-methylpyridine-2-carboxamido)-4-methylbenzene), and H<sub>2</sub>6-Me<sub>2</sub>-Me<sub>2</sub>bpb (1,2-bis(6-methylpyridine-2-carboxamido)-4,5-dimethylbenzene)) [9]. 6-Methyl-substituted pyridyl bpb ligands (H<sub>2</sub>6-Me<sub>2</sub>-Mebpb and H<sub>2</sub>6-Me<sub>2</sub>-Me<sub>2</sub>bpb) produced dimeric compounds with Cu(II) ions, and weak interactions between dimers can make even polymeric compounds, while bpb ligands without 6-methyl-substitution (H<sub>2</sub>Me<sub>2</sub>bpb) produced monomeric Cu(II) complexes. This result suggests that the steric effect of 6-methyl-substitution plays important role for distortion of the structure, and 6-methyl-substitution can also influence to make polymeric compounds with interactions between Cu(II) ions and neighbor carbonyl oxygen atoms.

In order to produce new copper complexes having interesting physical property and develop new catalysts, therefore, we have reacted Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O with a new type of carboxamide ligand 1,2-bis(2-pyrazinecarboxamido)-4,5-dimethylbenzene (H<sub>2</sub>Me<sub>2</sub>bpzb) (see Scheme 1). Interestingly, two kinds of complexes, a monomeric complex (**1**) and a polymeric complex (**2**) have been obtained under the different reaction conditions.

We report here on the synthesis and characterization of two isomers (**1** and **2**) containing a [Cu(Me<sub>2</sub>bpzb)] unit. Moreover, magnetic susceptibility, thermal stability, and photoluminescence are also discussed.

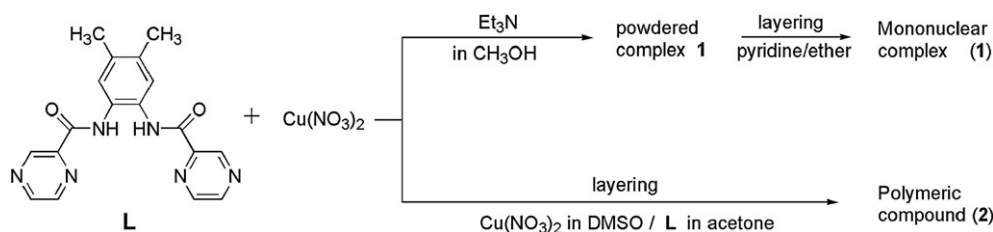
Ligand (H<sub>2</sub>Me<sub>2</sub>bpzb) was prepared in moderate yield (60%) by the reaction between 4,5-dimethyl-1,2-phenylenediamine with 2-

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Scheme 1. Synthesis of two isomers **1** and **2**.

pyrazinecarboxylic acid in pyridine in the presence of triphenyl phosphite according to the literature method. The crystal structure of  $H_2Me_2bpzb$  has been reported previously [10].

$H_2Me_2bpzb$  reacted with  $Cu(NO_3)_2 \cdot 2.5H_2O$  to give mononuclear and polymeric complexes under the different reaction conditions [11]. The 1:1 reaction of  $Cu(NO_3)_2 \cdot 2.5H_2O$  with the ligand  $H_2Me_2bpzb$  in methanol, in the presence of added base, gave a powdered complex (**Scheme 1**), that was dissolved in pyridine and layered with ether to produce a red crystalline solid (**1**). The complex **2** was obtained from the layering method that  $Cu(NO_3)_2 \cdot 2.5H_2O$  was dissolved in DMSO and layered with  $H_2Me_2bpzb$  in acetone to produce a dark-brown crystalline solid (**2**). **1** and **2** are air- and moisture-stable, and soluble in DMF and DMSO.

Two strong bands at  $1618/1391\text{ cm}^{-1}$  for **1** or  $1631/1387\text{ cm}^{-1}$  for **2** are assignable to the asymmetric and symmetric C=O stretching modes of the ligand, respectively. Further, the disappearance of N–H band ( $3315\text{ cm}^{-1}$ ) of the ligand suggested the formation of these complexes **1** and **2**, which were confirmed by X-ray crystallography.

$Me_2bpzb^{2-}$  ligands are coordinated to Cu(II) ions to form a monomeric complex (**1**) and a polymeric compound (**2**) [11,12]. In both compounds, four N atoms of the  $Me_2bpzb^{2-}$  ligand are coordinated to the Cu(II) ion. The Cu–N(amide) distances (1.926(3) and 1.931(3) Å for **1**, and 1.914(3) and 1.930(3) Å for **2**) are shorter than the Cu–N(pyridyl) distances (2.019(3) and 2.054(3) Å for **1**, and 2.019(3) and 2.039(3) Å for **2**). The geometry of a Cu(II) in **1** is square pyramid with O atom of a water molecule in the apical position (Fig. 1A). The Cu–O<sub>water</sub> distance is 2.313(3) Å. There are two kinds of hydrogen bonding to form a two-dimensional polymeric compound (Fig. 1B): (a) one between the water hydrogen atom and the carbonyl oxygen atom of the neighboring molecule ( $O3-H_2O \cdots O2(1-x, -y, -z)$  1.91(3) Å (165(4)°)) and (b) one between the water hydrogen atom and the pyrazine nitrogen atom of the another neighboring molecule ( $O3-H10 \cdots N5(-x, 1-y, -z)$  2.24(2) Å (146(4)°)). For **2**, a pyrazine nitrogen atom of the neighboring molecule occupies the apical position of the square pyramid geometry to form a stair-type one-dimensional compound (Fig. 2A). The Cu–N<sub>apical</sub> distance is 2.373(3) Å. There are hydrogen

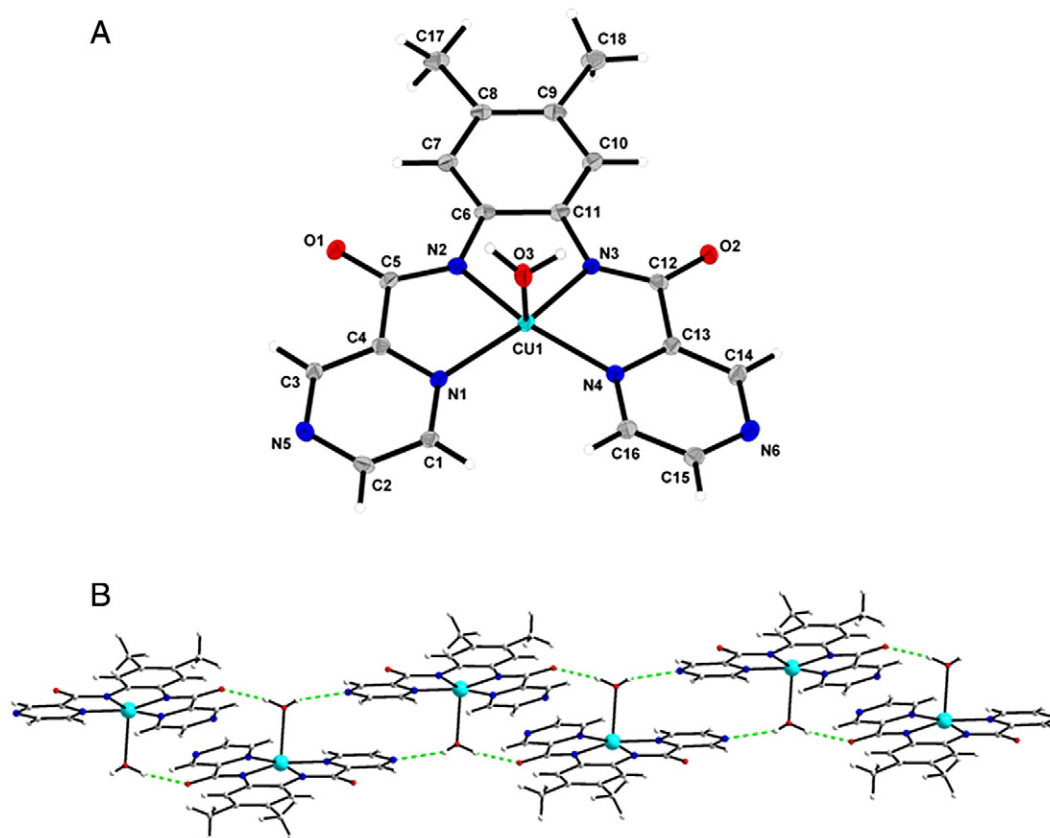


Fig. 1. (A) Crystal structure of **1**. Displacement ellipsoids are shown at the 50% probability level. (B) Hydrogen bond interactions (green dotted lines) in a two-dimensional structure:  $O3-H_2O \cdots O2(1-x, -y, -z)$  1.91(3) Å (165(4)°) and  $O3-H10 \cdots N5(-x, 1-y, -z)$  2.24(2) Å (146(4)°).

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