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Two isomers containing a [Cu(Me₂bpzb)] unit: Molecule (0-D) and 1-D

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ABSTRACT

Two isomers (molecule **1** and 1-D **2**) containing [Cu(Me₂bpzb)] 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^{2+} ions through the ligand. The photoluminescence of the free H₂Me₂bpzb 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_2 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_2Me_2bpb (1,2-bis(pyridine-2-carboxamido)-4,5-dimethylbenzene), $H_26-Me_2-Mebpb$ (1,2-bis (6-methylpyridine-2-carboxamido)-4-methylbenzene), and $H_26-Me_2-Me_2bpb$ (1,2-bis(6-methylpyridine-2-carboxamido)-4,5-dimethylbenzene)) [9]. 6-Methyl-substituted pyridyl bpb ligands ($H_26-Me_2-Mebpb$ and $H_26-Me_2-Me_2bpb$) 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_2Me_2bpb) 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 $Cu(NO_3)_2 2.5H_2O$ with a new type of carboxamide ligand 1,2-bis(2-pyrazinecarboxamido)-4,5-dimethylbenzene (H₂Me₂bpzb) (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 $[{\rm Cu}({\rm Me_2bpzb})]$ unit. Moreover, magnetic susceptibility, thermal stability, and photoluminescence are also discussed.

Ligand (H₂Me₂bpzb) 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 H₂Me₂bpzb has been reported previously [10].

 H_2M_2bpzb reacted with Cu(NO₃)₂ 2.5H₂O to give mononuclear and polymeric complexes under the different reaction conditions [11]. The 1:1 reaction of Cu(NO₃)₂ 2.5H₂O with the ligand H₂Me₂bpzb 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(NO₃)₂ 2.5H₂O was dissolved in DMSO and layered with H₂Me₂bpzb 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 cm⁻¹) of the ligand suggested the formation of these complexes **1** and **2**, which were confirmed by X-ray crystallography.

Me₂bpzb²⁻ 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 Me₂bpzb²⁻ 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_{water} 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 $(O3-H2O\cdots O2(1-x, -y, -z))$ 1.91(3) Å $(165(4)^{\circ}))$ and (b) one between the water hydrogen atom and the pyrazine nitrogen atom of the another neighboring molecule (03- $H10 \cdots N5(-x, 1-y, -z) 2.24(2) \text{ Å} (146(4)^{\circ}))$. 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_{apical} 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: $O3-H2O\cdots O2(1-x, -y, -z) 1.91(3)$ Å ($165(4)^{\circ}$) and $O3-H1O\cdots N5(-x, 1-y, -z) 2.24(2)$ Å ($146(4)^{\circ}$).



Fig. 2. (A) One-dimensional staircase chain structure of **2**. (B) Hydrogen bond interactions are shown in green dotted lines: O2S–H2A···O1 1.876(5) Å (178(5)°), O2S–H2B···O1S(x, -1+y, -z) 1.95(2) Å (151(2)°), and C17–H17C···S1S(x, 1.5 – y, -0.5 + z) 2.663(2) Å (163.7(3)°).

bonding interactions between the water hydrogen atoms and the DMSO oxygen atom and the carbonyl oxygen atom (O2S–H2A···O1 1.876(5) Å (178(5)°) and O2S–H2B···O1S(x, -1 + y, z) 1.95(2) Å (151(2)°)), and between the methyl hydrogen atom and the DMSO sulfur atom (C17–H17C···S1S(x, 1.5 - y, -0.5 + z) 2.663(2) Å (163.7(3)°)) (Fig. 2B). The Cu···Cu distance is 4.158(2) Å.

The temperature-dependent magnetic data for **2** were examined as shown in Fig. 3. The magnetic susceptibility data can be described using the Curie–Weiss law, $\chi = \chi_o + C/(T - \theta)$, which has a similar pattern to those for **1** (see Fig. S1). The effective magnetic moment at room temperature was 1.54 μ_B , which was less than the spin-only effective moment of 1.73 μ_B , and it can be explained by LMCT in the amido-Cu(II) complex **2**. There was no evidence of magnetic exchange coupling between the Cu(II) units through the ligand. In addition, to study the thermal stability of the complex **2**, thermal gravimetric analysis (TGA) of compound **2** was performed. The TGA result of **2** showed that it is stable below 370 °C, which indicates its good thermal stability (Fig. S2). The photoluminescence properties of free ligand H₂Me₂bpzb and complexes **1** and **2** were also studied in the solid-state at room temperature. The emission spectra of **1** and **2** and free ligand are depicted in Fig. 4. As shown in Fig. 4, the free H₂Me₂bpzb molecule displays an intense emission band centered at about 482 nm when excited at 261 nm, while complexes **1** and **2** exhibit no obvious emission bands ($\lambda_{ex} = 261$ nm). It can be presumed that the disappearance of the emission bands for **1** and **2** is attributed to the paramagnetic nature of Cu²⁺ ion and coordination of Cu²⁺ with the H₂Me₂bpzb ligand [13].

In summary, we have shown interestingly the synthesis and characterization of two isomers (mononuclear *vs* polymeric complexes) containing a [Cu(Me₂bpzb)] unit under the different reaction conditions. From the temperature-dependent magnetic data for **2**, there was no interaction between Cu²⁺ ions through the ligand. The photoluminescence of the free H₂Me₂bpzb molecule displayed an intense emission band centered at about 482 nm, while complexes **1** and **2** exhibit no obvious emission bands, suggesting that the paramagnetic nature of Cu²⁺ ion makes the emission bands for **1**



Fig. 3. Magnetic susceptibility data (open circle) and reciprocal susceptibility data (filled circle) of 2 as a function of temperature.



Fig. 4. Emission spectra of ligand, complexes 1 and 2.

and **2** disappear. Moreover, the TGA result of **2** showed a good thermal stability up to 370 °C.

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Appendix A. Supplementary data

CCDC 75260 and 75261 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j. inoche.2010.03.039.

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- [11] Preparation of 1: 0.16 g (0.5 mmol) of H₂Me₂bpzb was dissolved in 20 mL methanol and 0.12 g (0.5 mmol) of Cu(NO₃)₂ 2.5H₂O was added while being stirred vigorously under N2 mood. And then 140 µL (1.0 mmol) of triethylamine was carefully dropped to the mixture and stirred for 30 min. The red solid was precipitated and filtered and washed by 5 mL methanol three times. The red crystal was obtained under diethyl ether/pyridine in two weeks. Yield: 0.11 g (53%). IR(KBr): $\nu(cm^{-1}) = 3434(brm)$, 1618(s), 1578(s), 1541(w), 1485(m), 1455(w), 1391(m), 1170(m), 1045(m). 453(w), 418(w). Anal. Calc. for C₁₈H₁₆CuN₆O₃ (427.91): C, 50.52; H, 3.78; N, 19.64. Found: C, 50.43; H, 3.66; N, 19.88%. Preparation of 2: 18.6 mg (0.08 mmol) of Cu(NO₃)₂ 2.5H₂O was dissolved in 4 mL DMSO and carefully layered by 4 mL acetone solution of H2Me2bpzb ligand (55.7 mg, 0.16 mmol). Suitable dark brown crystals for X-ray analysis were obtained in a week. IR(KBr): $v(cm^{-1}) = 3456(brm)$, 2918(w), 1631(s), 1587(s), 1483(m), 1454(w), 1415(w), 1387(m), 1277(w), 1162(m), 1013(m), 959(w), 888(w), 850(w), 774(w), 708(w), 558(w), 499(w), 454(m). Anal. Calc. for C20H22CuN6O4S (506.04): C, 47.47; H, 4.39; N, 16.61. Found: C, 47.30; H, 4.41; N, 16.85%
- [12] Crystal Data for 1: $C_{18}H_{16}CuN_6O_3$, M = 427.91, P2₁/n, a = 8.1200(3) Å, b = 11.2660 (5) Å, c = 18.4920(8) Å, $\beta = 92.0480(18)^\circ$, V = 1690.57(12) Å³, Z = 4, μ (Mo K α) = 1.328 mm⁻¹, 11909 reflections measured, 3850 unique ($R_{int} = 0.1135$) which were used in all calculations, final R=0.0544 (wR=0.1307) with reflections having intensities greater than 2o, GOF(F²) = 1.022. Crystal Data for 2: C₂₀H₂₂CuN₆O₄S, M = 506.04, $P2_1/c$, a = 13.9851(11) Å, b = 9.7932(8) Å, c = 16.0191(13) Å, $\beta = 100.780(2)^\circ$, V = 2155.2(3) Å³, Z = 4, μ (Mo K α) = 1.151 mm⁻¹, 11669 reflections measured, 4214 unique (Rint=0.0516) which were used in all calculations, final R = 0.0484 (wR = 0.1232) with reflections having intensities greater than 2σ , $GOF(F^2) = 0.934$. The X-ray diffraction data for 1 and 2 were collected on a Bruker SMART APX diffractometer equipped with a monochromator in the Mo Ka (k=0.71073 A) incident beam. Each crystal was mounted on a glass fiber. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHEXTL V6.12. All hydrogen atoms were placed in the calculated positions. The crystallographic data for 1 and 2 are listed in Table S1. The selected bond distances and angles are listed in Table S2. Structural information was deposited at the Cambridge Crystallographic Data Center (CCDC reference numbers 75260 for 1 and 75261 for 2).
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