The First Metal Complexes of 4,4′-Biimidazole and 4,4′-Biimidazolate with Hydrogen-Bonding Networks on the Cu(II) Complexes: 1-D Structures by N–H···X···H–N Hydrogen-Bonding

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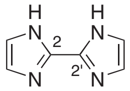
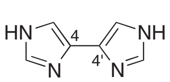
The Cu(II) complexes based on 4,4′-biimidazole and its deprotonated mono-anionic ligands were synthesized as the first metal complexes, which exhibit hydrogen-bonding networks. X-ray crystal structure analyses reveal the π-stacking structure of each complex and N–H···X or N···H–X type hydrogen-bondings.

The cooperative interaction between proton- and electron-transfer (PET) on hydrogen-bonded (H-bonded) molecular systems has opened a new opportunity for design of intriguing molecular materials.[1] A variety of H-bonded charge-transfer (CT) complexes including metal complexes[2a,2b] are candidates to realize PET systems.[2c-2g,3] 2,2′-Biimidazole (2,2′-H_2Bim) has been utilized as a part of building blocks of CT complexes with multiple PET processes[3] and also as ligands of assembled metal complexes with H-bonding nature.[4]

In order to explore novel H-bonded CT complexes based on imidazole ring system, we have recently synthesized novel 4,4′-biimidazole (4,4′-H_2Bim) and oligo(imidazole)s.[2e] Then we have demonstrated the H-bonded zigzag-ribbon structure of 4,4′-H_2Bim derivative, whose structure originates from the different H-bonding directions from those of 2,2′-H_2Bim.[5] These studies have encouraged us to design and synthesize the transition metal complexes based on 4,4′-H_2Bim system.[6] In this report, we describe the first synthesis and crystal structures of the two Cu(II) complexes, [Cu(4,4′-H_2Bim)$_2$](ClO$_4$)$_2$ (**1**) and [Cu(4,4′-HBim)$_2$]·3H_2O (**2**), composed of 4,4′-H_2Bim and 4,4′-HBim as neutral and mono-anionic ligands, respectively. Furthermore, we have investigated magnetic properties of the two complexes with exotic assembled H-bonding networks.



2,2'-H_2Bim



4,4'-H_2Bim

The 4,4′-H_2Bim complex **1** was prepared by mixing 4,4′-H_2Bim with 0.5 equimolar amount of Cu(ClO$_4$)$_2$·6H_2O in hot EtOH. Single crystals of **1** suitable for X-ray structure analysis were obtained by vapor diffusion of ethyl acetate into 10:1 mixture (v/v) of EtOH and DMSO.[7] This complex consists of two 4,4′-H_2Bim and a Cu(II) ion, and the molecular structure with the square-planar metal configuration possesses an inversion center at the Cu(II) ion. Each [Cu(4,4′-H_2Bim)$_2$] complex is connected by the three-centered double H-bondings of N(1)–H···O(1)···H–N(1) across the O(1) atom of ClO$_4^-$ with 2.90 Å of N(1)···O(1) distance, to form an 1-D chain along the b axis (Figure 1a). The 4,4′-H_2Bim ligand of **1** partially stacks with the same ligand belonging to another chain along the c axis with shortest stacking distance of 3.26 Å (Figures 1b and 1c). Figure 2 shows a relationship between the H-bonded networks and the π–π interactions on the crystal structure of **1**. The Cu–Cu distance in the H-bonded intra-chain is 10.79 Å, and the shortest Cu–Cu distance between the chains is 7.42 Å (Figure 1c).

The 4,4′-HBim complex **2** was obtained by mixing CuCl$_2$ with 4,4′-H_2Bim followed by Et$_3$N-induced deprotonation.[8] The single crystal of **2** contains three water molecules. Similarly to the molecular structure of **1**, the complex **2** possesses a square-planar configuration with an inversion center at Cu(II) ion. In the crystal, **2** forms uniform stacking columns along the b axis with

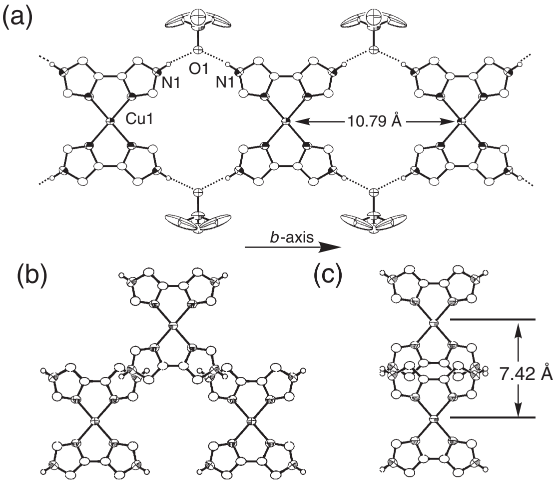


Figure 1. One-dimensional structure of **1** by N(1)–H···O(1)···H–N(1) double H-bonding elongated along the b-axis (a) and overlap mode of the π-stacking (b and c).

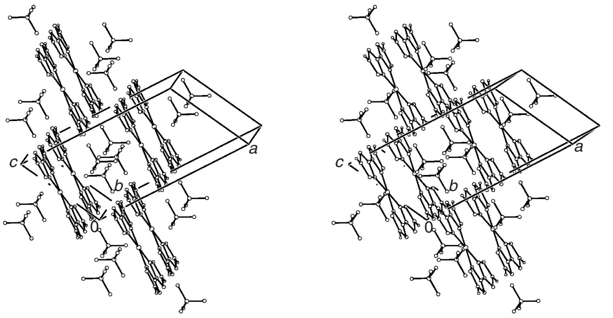


Figure 2. Stereoview of crystal packing for **1** viewed along the b-axis, showing the one-dimensional H-bonding network and π-stacking structure.

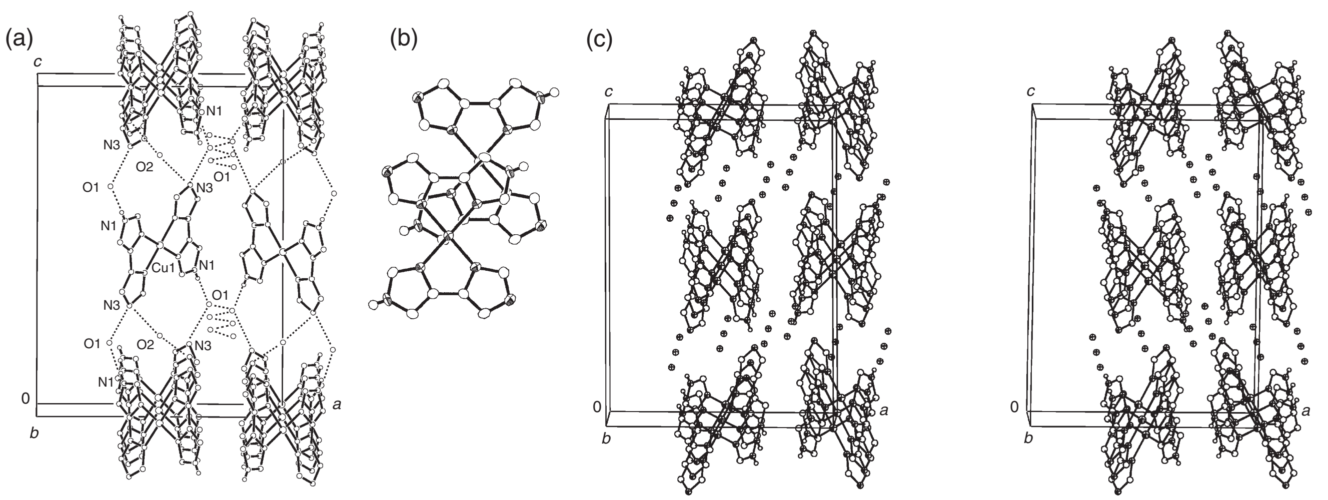


Figure 3. π-Stacking columns elongated along the *b*-axis, and N(1)–H···O(1)–H···N(3) and N(3)···H–O(2)–H···N(3) H-bonding interactions (a), overlap mode in a π-stacking column (b) and stereoview of crystal packing for **2** viewed along the *b*-axis, showing the arrangement of the π-stacking column structure of the complex and water molecules (c).

3.09 Å of interplanar distance (Figures 3a and 3b). These columns are connected along the *c* axis by the two types of H-bondings of N(1)–H···O(1)–H···N(3) and N(3)···H–O(2)–H···N(3) mediated by water molecules, forming herringbone arrays (Figure 3c). The O(1) atom forms H-bonded chains parallel to the stacking column of **2**, resulting in the formation of 3-D network of this crystal. The H-bonding lengths, N(1)···O(1) (2.78 Å), N(3)···O(1) (2.74 Å), N(3)···O(2) (2.98 Å), and O(1)···O(1) (2.85 Å), are shorter than the sums of van der Waals radius of N and O atoms (3.07 Å) and two O atoms (3.04 Å). The nearest Cu···Cu distance within the column of **2** is 4.99 Å.

The magnetic susceptibilities with the range of 1.9–298 K were measured on polycrystalline sample of **1** and **2**. The $\chi_{\rm p}T$ value for **2** steadily decreases as the temperature is lowered, and the antiferromagnetic interaction is very weak. On the other hand, the magnetic interaction for **1** is vanishingly small even at 1.9 K because of the long distance between Cu ions in the crystal of **1**.

In conclusion, we have prepared the metal complexes **1** and **2** with 4,4′-H_2Bim and 4,4′-HBim ligands, respectively, and studied their crystal structures for the first time. These complexes were constructed by both Cu(II) coordination bonds and the H-bonding networks based on 4,4′-H_2Bim framework. These observations serve as an important step for the exploration of novel molecular architectures and realization of PET system. Investigations are currently being conducted for the construction of assembled metal CT complexes based on 4,4′-H_2Bim with organic electron-acceptors.

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6 Although the preparation and structural analyses of Cu(II) complexes of *N*-trityl-protected 4,4′-biimidazole have been recently reported, metal complex composed of free 4,4′-biimidazole is still unknown, see: G. Aromí, P. Gamez, H. Kooijman, A. L. Spek, W. L. Driessen, and J. Reedijk, *Eur. J. Inorg. Chem.*, **2003**, 1394.

7 **1**: mp: >300 °C; IR (KBr) 3600–2700, 1660, 1566, 1121, 1086, 1046 cm^{-1}; UV (KBr) 218, 268 nm; Anal. Calcd for $C_{12}H_{12}CuN_8O_8Cl_2$: C, 27.16; H, 2.28; N, 21.10%. Found: C, 27.10; H, 2.24; N, 20.97%. Crystal data for **1**: $C_{12}H_{12}N_8O_8Cl_2Cu$, $M_{\rm r} = 530.74$; monoclinic, *C*2/*m*; $a = 13.038(1)$, $b = 10.7926(6)$, $c = 7.4191(5)$ Å, $\beta = 117.496(7)$, $V = 926.0(1)$ Å^3, $Z = 2$, $D_{\rm calcd} = 1.903$ gcm^{-3}, $T = 296$ K, $R_1 = 0.070$, $wR_2 = 0.191$, and GOF = 1.47. The data was deposited in Cambridge Crystallographic Data Centre (CCDC 225752).

8 **2**: mp: 280–282 °C (dec); IR (KBr) 3600–2600, 1639, 1539 cm^{-1}; UV (KBr) 254 nm; Anal. Calcd for $C_{12}H_{16}N_8O_3Cu$; C, 37.55; H, 4.20; N, 29.19%. Found: C, 37.90; H, 3.90; N, 29.14%. Crystal data for **2**: $C_{12}H_{16}N_8O_3Cu$, $M_{\rm r} = 383.86$; orthorhombic, *Pbcn*; $a = 14.921(7)$, $b = 4.993(2)$, $c = 20.56(1)$ Å, $V = 1531.5(1)$ Å^3, $Z = 4$, $D_{\rm calcd} = 1.665$ gcm^{-3}, $T = 200$ K, $R_1 = 0.039$, $wR_2 = 0.101$, and GOF = 0.77. The data was deposited in Cambridge Crystallographic Data Centre (CCDC 225753).