Dimeric Hydrogen-Bonded Transition Metal Complex Containing Bidentate Mono-deprotonated 2,2'-Biimidazolate Ligand

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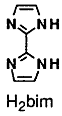
Synthesis and X-ray crystal structure of a capped type of dimeric H-bonded transition metal complex containing bidentate mono-deprotonated 2,2'-biimidazolate ligand were reported.

Introduction of hydrogen-bonding (H-bonding) interaction between ligands in transition metal complexes is an interesting molecular design for new molecular materials.[1] Since 2,2'-biimidazole (H_2bim) is a bidentate ligand with a multi-proton donor property, it can coordinate to a transition metal with three types of bidentate mode: neutral (H_2bim), mono-deprotonated (Hbim), and di-deprotonated (bim) types. All these types of complexes have already been actively investigated.[2] As for the complex having H-bonds, the polymeric structure was postulated for the complex $[M^{II}(Hbim)_2]$ (M= Co, Ni, Cu)[3] and the NH···N type dimeric H-bonded structure was proposed for several mono-deprotonated 2,2'-biimidazolate complexes based on the spectroscopic data.[4]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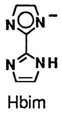
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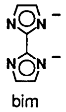
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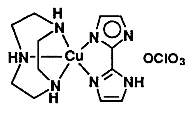
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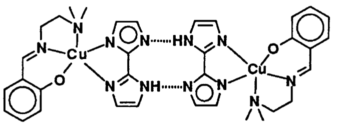
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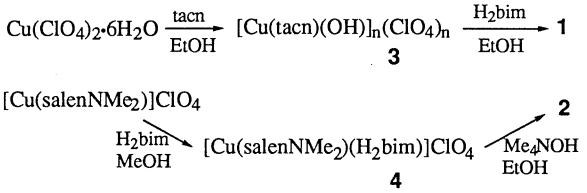
It is important to obtain such complexes as a crystalline form for material science. Here, we report the first example of a capped H-bonded dimer of the transition metal complex **2** containing the bidentate mono-deprotonated 2,2'-biimidazolate ligand, which is characterized by X-ray crystal structure analysis.

First, a monomeric complex containing the triazamacrocycle ligand, 1,4,7-triazacyclononane (tacn)[5], [Cu(tacn)(Hbim)]ClO_4 **1** was designed and synthesised as shown in Scheme 1. The tacn copper (II) complex, $[Cu(tacn)(OH)]_n(ClO_4)_n$ (**3**)[6] was prepared by treatment of tacn·HCl and excess NEt_3 with $Cu(ClO_4)_2 \cdot 6H_2O$ in ethanol[7] in 38% yield. Reaction of the tacn complex with equimolar amounts of H_2bim[8] in ethanol gave complex [Cu(tacn)(Hbim)]$ClO_4 \cdot 2H_2O$ (**1a**) as blue micro crystals in 75% yield.[9] The infrared spectrum shows broad absorption bands with fine structures in the region 2300 – 3200 cm^{-1}, which suggest the presence of the stretching vibration of N–H groups associated with H-bonding interaction.[10] The X-ray crystal structure analysis[9] of a single crystal, [Cu(tacn)(Hbim)]-ClO_4·MeOH (**1b**), shows that the NH groups of two ligands form H-bonds to the oxygen atoms of the couter anion, ClO_4^-. Therefore, no dimeric H-bonding of the NH···N type between the ligands is found in the crystal structure, although there exist the absorption bands assignable to H-bonds of the NH groups.[10]



$$Cu(ClO_4)_2 \cdot 6H_2O \xrightarrow[EtOH]{tacn} [Cu(tacn)(OH)]_n(ClO_4)_n \ \mathbf{3} \xrightarrow[EtOH]{H_2bim} \mathbf{1}$$

$$[Cu(salenNMe_2)]ClO_4 \xrightarrow[MeOH]{H_2bim} [Cu(salenNMe_2)(H_2bim)]ClO_4 \ \mathbf{4} \xrightarrow[EtOH]{Me_4NOH} \mathbf{2}$$

Scheme 1.

In order to preclude the association with the counter anion, we chose the mononegative, tridentate ligand N-salicylidene-N',N'-dimethylethylenediamine (salenNMe$_2$) in place of the neutral, triazamacrocycle ligand. Thus, a neutral complex of copper(II) with Hbim and salenNMe$_2$, $[Cu(salenNMe_2)(Hbim)]_2$ (**2**), was designed and synthesised (Scheme 1). Reaction of $[Cu(salenNMe_2)]ClO_4$[11] with H_2bim in ethanol gave the cationic complex, $[Cu(salenNMe_2)(H_2bim)]ClO_4$ (**4**) in 93% yield.[6] The desired neutral complex **2** was obtained by treatment of **4** with equimolar amount of Me_4NOH in ethanol in 26% yield. The infrared spectrum again shows broad absorption bands in a similar H-bonding region of the NH groups as in the complex **1**. The X-ray crystal structure analysis[9] shows the existence of the expected dimeric H-bonds of NH···N type between the mono-deprotonated biimidazole ligand (Fig. 1). This is the first example of the capped type of dimeric H-bonded transition metal complex having the mono-deprotonated biimidazolate, which is characterised by X-ray crystal structure analysis.

The most important intermolecular interaction found in the crystal packing is the formation of the dimeric H-bonding of the NH···N type between the Hbim ligands (Fig. 1). The H-bonded distance (R(N···N)) is 2.83 (10) Å. The two Hbim skeletons connected by the double NH···N type H-bonds are coplanar to each other. There are no short contacts between Cu···Cu,

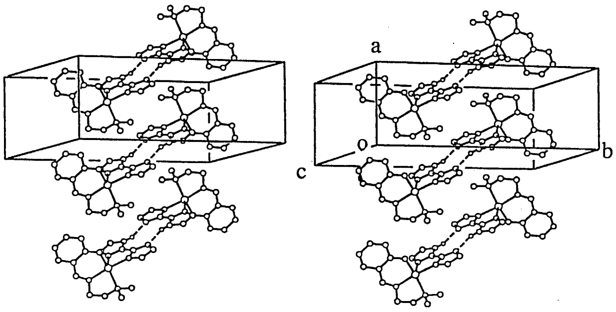


Figure. 1. Stereoview of crystal-packing for the complex **2**. The dotted lines represent intermolecular hydrogen bondings.

Cu···hetero atom, or π electron on the Hbim skeletons. The shortest Cu···Cu distance is 6.72 Å between the dimeric units along the *a* axis. The Cu···Cu distance through the H-bonded ligands in a dimeric unit is 10.60 Å. We measured magnetic susceptibility on powdered samples in the range 2.5 – 270 K. A weak antiferromagnetic interaction between Cu(II) ions (m_{eff} = 1.86 m_B (270 K), 1.70 m_B (2.5 K)) was observed, which is assigned to dipole-dipole interaction between the dimeric units. The exchange interaction in a H-bonded dimeric unit is presumed to be very weak, since the Cu···Cu distance is too long.

The crystal structure data allow us to discuss the infrared spectrum for **2** in more detail. The correlation between the NH stretching frequency (υNH) and the intermolecular H-bonding distance (R(N···N)) has been proposed.[10] One of the compounds used for the correlation is the triazole crystal which possesses the values, R(N···N) = 2.82 Å and υNH = 2720 cm^{-1}. The values, R(N···N) = 2.83 Å and υNH = 2660 cm^{-1} (the center position of the broad band), for **2** indicate good consistence with the proposed correlation. Furthermore, we found an additional broad absorption band at 1830 cm^{-1}, which can be assigned to be overtone out-of-plane bending vibration of NH···N.[10,12] The absorption bands in these two regions are characteristic for NH···N type H-bonding systems.[13]

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6 The selected data for new compounds are as follows: **1a**: Found: C, 31.66%; H, 5.25%; N, 21.16%. Calcd for $C_{12}H_{20}ClCuN_7O_4$: C, 31.24%; H, 5.24%; N, 21.25%. UV-vis (MeOH) λ_{max}; 914 nm (ε = 24), 600 nm (ε = 75), 381 nm (sh, ε = 51). **2**: Found: C, 52.69%; H, 5.20%; N, 21.78%. Calcd for $C_{34}H_{40}Cu_2N_{12}O_2$: C, 52.63%; H, 5.20%; N, 21.66%. UV-vis (MeOH) λ_{max}; 677 nm (ε = 146). **3**: Found: C, 23.50%; H. 5.28%; N, 13.50%. Calcd for $C_6H_{16}ClCuN_3O_5$: C, 23.30%; H, 5.21%; N, 13.59%. **4**: Found: C, 41.77%; H, 4.30%; N, 17.60%. Calcd for $C_{17}H_{21}ClCuN_6O_5$: C, 41.81%; H, 4.33%; N, 17.21%. UV-vis (MeOH) λ_{max}; 644 nm (ε = 183).

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9 The single crystals of **1b** and **2** for X-ray crystal structure analysis were obtained from slow evaporation of methanol and ethanol, respectively. Crystal data for **1b**: $C_{13}H_{24}CuClN_7O_5$, FW= 457.38, blue crystal with 0.30 x 0.30 x 0.25 mm^3, monoclinic, space group $P2_1/n$, a = 10.030(4), b = 12.393(5), c = 15.986(5) Å, b = 95.59(3)°, V = 1977(1) $Å^3$, Z = 4, r_{calc}= 1.536 gcm^{-3}, R = 0.067 and Rw = 0.073, 1331 reflections ($Io>3\sigma(Io)$). Hydrogen atoms were located at the calculated positions. Crystal data for **2**: $C_{17}H_{20}CuN_6O$, FW= 387.93, green crystal with 0.10 x 0.16 x 0.42 mm^3, Monoclinic, space group $P2_1/n$, a = 7.338(4), b = 22.016(6), c = 11.169(4) Å, b = 97.14(4)°, V = 1790(1) $Å^3$, Z = 4, r_{calc}= 1.439 gcm^{-3}, R = 0.047 and Rw = 0.053, 1576 reflections ($Io>3\sigma(Io)$). Hydrogen atoms were located on a ΔF map and refined isotropically.

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13 The asignment of NH···N type H-bonding in reference 4 has now been further confirmed, though no data for overtone out-of plane bending vibration are described.