New Copper(II) Complexes Connected by NH···O=C and NH···S=C Intermolecular Hydrogen Bonds

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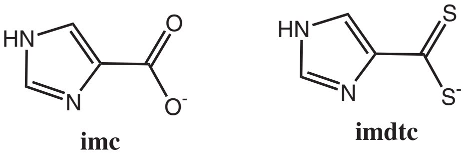
Two new copper(II) complexes with imidazole-4-carboxylate and imidazole-4-dithiocarboxylate have been synthesized. The monomeric units are connected by NH···O=C and NH···S=C intermolecular hydrogen bonds, respectively, yielding one-dimensional chains that stack with unusually short π–π distances.

Designed connections of metal complex units by weak chemical interactions such as hydrogen bonds and π–π interactions are fundamental for the synthesis of new self-assembled materials.[1–3] How to rationally create these interactions between the building units is an important subject not only for the development of self-assembled chemistry but also in understanding these chemical interactions.[4–6] To generate rational connections between monomeric metal complexes by these weak bonds, we have selected two chelate ligands, imidazole-4-carboxylate (imc) and imidazole-4-dithiocarboxylate (imdtc), whose uncoordinating NH and E=C (E = O and S) sites could be exploited for formation of NH···E=C type intermolecular hydrogen bonds. Here we report the synthesis and unique assembled structures of two new copper(II) complexes.



Scheme 1.

The Cu(II) complex $[Cu(imc)_2]$ (**1**) was obtained as deep blue single crystals by diffusion of a methanol solution of the sodium salt of imc into an aqueous solution of $CuSO_4{\cdot}5H_2O$. This complex is insoluble in water, and slightly soluble in methanol and DMF.

Figure 1 shows the monomeric unit and the assembled structures of **1**.[7] Two imc ligands bind to the copper(II) center with five-membered chelations with a *trans* arrangement. The crystallographic inversion center is located at the metal center. No additional atoms coordinate to the copper(II) center, forming a square planar copper(II) geometry. As shown in Figure 1b, NH and O=C sites of the imc ligands form NH···O=C intermolecular hydrogen bonds with the adjacent units (N···O = 2.782(4) Å) to produce a hydrogen-bonded one-dimensional chain.

This result indicates that imidazole-carboxylate type chelations are useful for the construction of new assembled structures, prompting us to create NH···S=C intermolecular hydrogen bonds between metal complex units by using imdtc, which is the dithio derivative of imc. This challenge is interesting because hydrogen-bonded networks via sulfur donors are still unexplored until now.[1,3] We have successfully obtained the complex $[Cu(imdtc)_2]$ (**2**) as deep brown single crystals by a similar synthetic procedure for **1** by combining the Himdtc and $CuCl_2{\cdot}2H_2O$ in DMF/ethanol media.

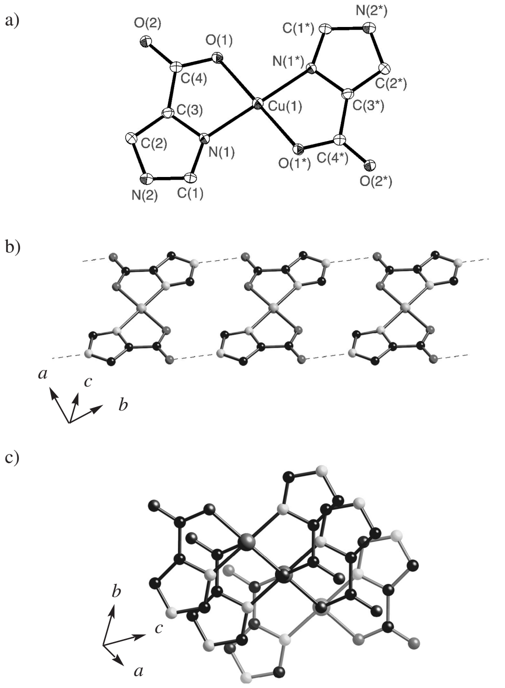


Figure 1. A view of the crystal structures of **1**. (a) The ORTEP drawing of the monomeric unit, (b) view of the one-dimensional structure formed by NH···O=C intermolecular hydrogen bonds, and (c) the perspective view of the monomeric units that form π–π stacked interactions. Selected bond distances (Å) and angles (°): Cu(1)–O(1) 1.969(3), Cu(1)–N(1) 1.955(3), O(1)–Cu(1)–N(1) 83.5(1), O(1)–Cu(1)–N(1*) 96.5(1). Symmetry equivalent positions $* = -x, -y, -z$.

Figure 2 shows the crystal structures of **2**.[7] As described below, the molecular arrangement of this complex is similar to that of **1**. **2** crystallizes in the same space group as **1** ($P\bar{1}$). The three cell axes of **2** are longer than those of **1**. As shown in Figure 2, the coordination conditions around the copper(II) center and the hydrogen bonded assembled form of **2** are similar

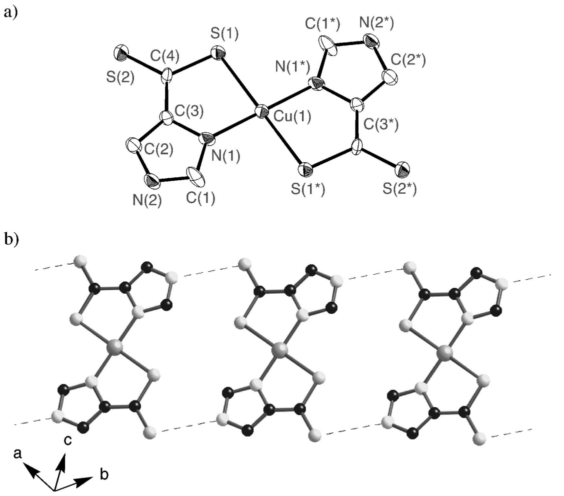


Figure 2. A view of the crystal structures of **2**. (a) The ORTEP drawing of the monomeric unit and (b) the one-dimensional structure formed by NH$\cdots$S=C intermolecular hydrogen bonds. Selected bond distances (Å) and angles (°): Cu(1)–S(1) 2.331(3), Cu(1)–N(1) 1.929(9), S(1)–Cu(1)–N(1) 85.0(3), S(1)–Cu(1)–N(1*) 95.0(3). Symmetry equivalent positions $* = -x, -y, -z$.

to those of **1**; the two imdtc bind to the copper(II) center with five-membered chelations, and each monomeric unit is connected by two NH$\cdots$S=C intermolecular hydrogen bonds (N$\cdots$S = 3.38(1) Å), forming one-dimensional chains. Effects of the larger size of the sulfur donors (imdtc) compared with the oxygen donors (imc) on the crystal structures are observed. For the coordination spheres, while the Cu–N distances of both compounds are similar (1.955(3) Å and 1.929(9) Å for **1** and **2**, respectively), the Cu(1)–S(1) distance (2.331(3) Å) of **2** is significantly longer than the Cu(1)–O(1) distance of **1** (1.969(3) Å). For the intermolecular hydrogen bonds, the N$\cdots$S distance in **2** (3.38(1) Å) is much longer than the N$\cdots$O distance in **1** (2.782(4) Å). To the best of our knowledge, this is the first example of a well-characterized coordination network assembled by designed NH$\cdots$S intermolecular hydrogen bonds.

One of the structural features of the imc and imdtc ligands is the large conjugated system. This property contributes to the almost planar structures of each monomeric unit and the formation of the short π–π distances observed between the ligands in adjacent chains; their plane–plane distances are about 3.0 Å and 3.2 Å for **1** and **2**, respectively; both complexes having similar stacking structures. Figure 1c shows the stacking aspect of **1**, this view illustrating three monomeric units for clarity. The shortest nonbonded distances between the adjacent chains are observed between the copper(II) atom and the oxygen or sulfur donor (3.014(4) Å and 3.212(5) Å for **1** and **2**, respectively). These monomeric complex units do not stack in a columnar fashion but in a stepwise fashion. The π system of each ligand partially overlaps on one side of the ligand plane, with an edge-on relationship between the adjacent chains.

Compared with other examples (3.4–3.6 Å), the π–π distances found in **1** and **2** are unusually short. The π–π interactions between aromatic systems are affected by various electronic factors. For example, it has been demonstrated that electron-deficient aromatic rings prefer a stacking interaction over an electron-rich interaction.[5] The remarkably short π–π interactions found in **1** and **2** could be a result of the withdrawing effects of the coordinating metal ions.

In summary, we have succeeded in the systematic synthesis and structural characterization of two new copper(II) complexes with imc and imdtc. Their monomeric units are connected by NH$\cdots$O=C and NH$\cdots$S=C intermolecular hydrogen bonds to yield one-dimensional chains. These complexes show unusually short π–π stacks between their conjugating ligands in the adjacent chains. These compounds offer good examples for investigation of these weak chemical interactions.

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7 Crystal data for **1**: fw = 285.7, triclinic, space group $P\bar{1}$, $a = 3.639(4)$, $b = 6.522(8)$, $c = 9.74(1)$ Å, $\alpha = 78.73(2)$, $\beta = 87.36(2)$, $\gamma = 82.04(3)°$, $V = 224.4(4)$ Å^3, $Z = 1$, $D_{\mathrm{calcd}} = 2.114\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo}\ K\alpha) = 2.444\ \mathrm{mm^{-1}}$, $F(000) = 143$, $T = 293$ K, $\lambda = 0.07107$ Å, ω scans, $R = 0.049$, $wR = 0.068$ for 932 unique reflections ($R_{\mathrm{int}} = 0.031$) with $I > 2\sigma(I)$ and 79 parameters. Crystal data for **2**: fw = 345.0, triclinic, space group $P\bar{1}$, $a = 3.936(8)$, $b = 6.82(1)$, $c = 10.81(2)$ Å, $\alpha = 80.43(4)$, $\beta = 85.54(4)$, $\gamma = 86.89(4)°$, $V = 285.0(8)$ Å^3, $Z = 1$, $D_{\mathrm{calcd}} = 2.039\ \mathrm{g\,cm^{-3}}$, $T = 293$ K, $\mu(\mathrm{Mo}\ K\alpha) = 2.625\ \mathrm{mm^{-1}}$, $F(000) = 175$, $T = 293$ K, $\lambda = 0.07107$ Å, ω scans, $R = 0.095$, $wR = 0.115$ for 820 unique reflections ($R_{\mathrm{int}} = 0.055$) with $I > 2\sigma(I)$ and 79 parameters. The data collection were performed on a Rigaku-CCD Mercury system. The structures were solved by direct methods using SIR-92.[8] All nonhydrogen atoms were treated anisotoropically. The hydrogen atoms were included but not refined.

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