Enantioselective Assembly Structures of Copper(II) Complexes with the 1:1 Condensation Products of DL-Phenylalanine and Either 2- or 5-Methyl-4-formylimidazole

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Copper(II) complexes with the 1:1 condensation products of DL-phenylalanine and either 2- or 5-methyl-4-formylimidazole, [CuCl($HL^{2\text{-}Me}$)] (**1**) and [CuCl($HL^{5\text{-}Me}$)]•MeOH (**2**), were prepared, and their assembly structures were determined. Both complexes assumed two-dimensional (2D) assembly structures due to a helical chain structure constructed by the intermolecular imidazole–carboxylate hydrogen bond and interchain Cu*–Cl coordination bond. **2** crystallized in acentrosymmetric space group $C222_1$ showing a spontaneous resolution, while **1** crystallized in centrosymmetric space group $P2_1/a$.

The fields of crystal engineering and supramolecular chemistry have attracted much attention in which a self-assembly process plays an important role and a number of synthetic strategies have been proposed.[1] The self-assembly process involving a metal ion is especially attractive and useful for the purpose of the constructing a variety of molecular architectures and functional materials.[2] Chirality has been one of the most important subjects because asymmetric synthesis and optical resolution are not only important in chemistry but also practically important in pharmacology and industry. Numerous studies have been devoted to elucidating the detailed mechanism of enantioselectivity.

We have studied metal complexes with multidentate Schiff-base ligands involving the imidazole group that can function as a self-complementary building block for the assembly reaction.[3] Depending on the ligand framework and metal ion, a variety of assembly structures, such as the cyclic-oligomer, zigzag-chain polymer, and 2D network structures, have been generated. In this study, we studied the enatioselective self-assembly structures of the Cu^{II} complexes with the tridentate Schiff-base ligands of the 1:1 condensation products of DL-phenylalanine and either 2- or 5-methyl-4-formylimidazole, [CuCl($HL^{2\text{-}Me}$)] (**1**) and [CuCl($HL^{5\text{-}Me}$)]•MeOH (**2**). Here, we report enantioselective assembly 2D structures depending on the substituent and spontaneous resolution of **2**.

The tridentate ligands, $HL^{2\text{-}Me}$ and $HL^{5\text{-}Me}$, were prepared by mixing DL-phenylalanine and either 2- or 5-methyl-4-formylimidazole in 1:1 molar ratio in methanol. To the ligand solution was added a methanol solution of $CuCl_2 \cdot 2H_2O$, and the resulting solution was allowed to stand for several hours to produce the Cu^{II} complex.[4] The complexes **1** and **2** were obtained as plate-like and needle crystals, respectively.

The complex **1** crystallized in the monoclinic centrosymmetric space group $P2_1/a$ (No. 14).[5] The molecular structure with the atom numbering scheme is shown in Figure 1. As shown in Figure 2, the imidazole group of a Cu^{II} complex is hydrogen-bonded to the carboxylate oxygen atom O(1) of the adjacent Cu^{II} complex with the hydrogen-bond distance of N(2)···O(1) = 2.810(2) Å. It should be noted that the oxygen atom O(1) is coordinated to the Cu^{II} ion. As a result of the repeating hydrogen bonds, the complex produces a helical chain structure running along the *b* axis, where within a helical chain the adjacent two Cu^{II} complexes are related by a twofold screw axis and have the same chirality. The crystal consists of the helical chains, where the adjacent two helical chains with opposite chiralities are linked by the interchain Cu*–Cl weak coordination bond with Cu*–Cl = 2.8936(7) Å to produce a hetero-chiral 2D network structure, as being seen in Figure 2.

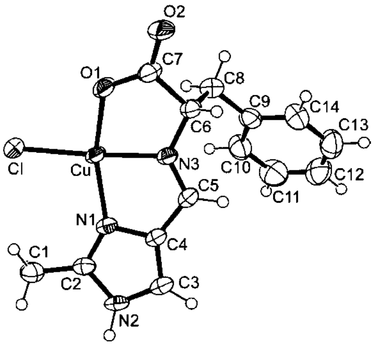

Figure 1. Molecular structure of [CuCl($HL^{2\text{-}Me}$)] (**1**) with the atom numbering scheme. Thermal ellipsoids are drawn with the 50% probability level.

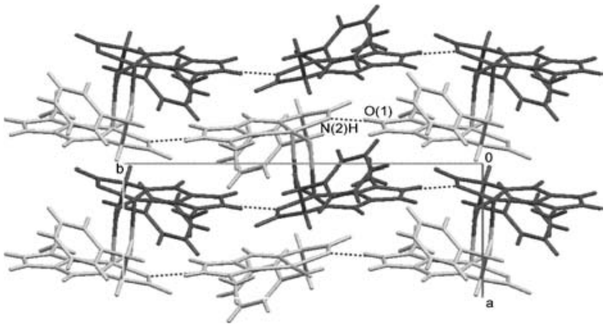

Figure 2. Hetero-chiral 2D network structure of [CuCl($HL^{2\text{-}Me}$)] constructed by intrachain imidazole–carboxylate hydrogen bond of N(2)···O(1) = 2.810(2) Å and the interchain Cu*–Cl coordination bond of Cu*–Cl = 2.8936(7) Å. Two complex species of the adjacent chains are related by an inversion center and are bridged by two Cl^- ions with Cu–Cl = 2.2326(6) Å and Cu*–Cl = 2.8936(7) Å to give a di-μ-chloro binuclear structure.

Although the complex **2** was prepared from the reaction of $CuCl_2 \cdot 2H_2O$ and the ligand involving DL-phenylalanine, a piece of the crystals crystallized in acentrosymmetric space group $C222_1$ (No. 20), demonstrating that a spontaneous resolution occurs.[5] The Flack parameter calculated indicates that the crystal consists of D-phenylalanine moiety. Figure 3 shows the molecu-

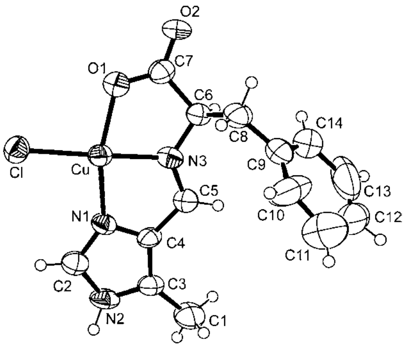

Figure 3. Molecular structure of [CuCl($HL^{5\text{-Me}}$)]•MeOH (**2**) with the atom numbering scheme. Thermal ellipsoids are drawn with the 50% probability level.

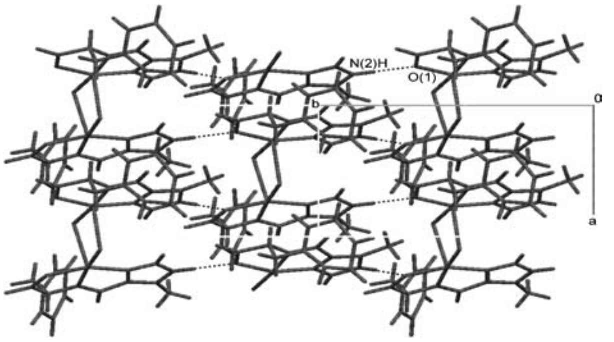

Figure 4. Homo-chiral 2D network structure of [CuCl($HL^{5\text{-Me}}$)] constructed by intrachain imidazole–carboxylate hydrogen bond of N(2)···O(1) = 2.903(5) Å and the interchain Cu*–Cl coordination bond. Two complex species of the adjacent chains are bridged by two Cl^- ions with Cu–Cl = 2.244(2) Å and Cu*–Cl = 2.737(2) Å.

lar structure with the atom numbering scheme. Figure 4 shows the 2D network structure, in which the imidazole group of a Cu^{II} complex is hydrogen-bonded to the carboxylate oxygen atom O(1) of the adjacent Cu^{II} complex with the hydrogen-bond distance of N(2)···O(1) = 2.903(5) Å. As a result of the repeating hydrogen bonds, the complex species with the same chirality produce a helical chain structure. In the crystal, the adjacent chains with the same chirality (D-form) are linked by the weak interchain Cu*–Cl coordination bond of Cu*–Cl = 2.737(2) Å to produce a homo-chiral 2D network structure. It should be noted that the interchain Cu*–Cl distance of **2** is shorter than that of **1** (Cu*–Cl = 2.8936(7) Å).

In summary, the two Cu^{II} complexes with the tridentate ligands involving imidazole and chiral amino acid moieties, **1** and **2**, were prepared. Each complex functions as a chiral self-complementary building block to produce an assembly helical chain structure due to the intrachain imidazole–carboxylate hydrogen bond. The same chirality is preserved at least within a helical chain. The adjacent chains are linked by the weak interchain Cu*–Cl coordination bond. Homo- or hetero-chiral interchain discrimination depends on the steric effect of the substituent at the imidazole moiety. Homochiral interchain interaction due to the shorter Cu*–Cl distance is preferable for **2** and the spontaneous resolution occurs.

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4 The tridentate ligands $HL^{2\text{-Me}}$ and $HL^{5\text{-Me}}$ were prepared by the 1:1 condensation reactions of DL-phenylalanine and either 2- or 5-methyl-4-formylimidazole, respectively, in a mixture of methanol and water on a hot plate for 30 min. The ligand solutions were used for the syntheses of the Cu^{II} complexes without the isolation of the ligands. To a solution of the ligand (0.5 mmol) was added a solution of $CuCl_2 \cdot 2H_2O$ (0.5 mmol). The mixture was warmed and stirred for 10 min and then filtered. The filtrate was kept to stand for overnight, during which time crystals precipitated. They were collected by suction filtration, washed with methanol and dried. Yield 34%. [CuCl($HL^{2\text{-Me}}$)]: blue plate crystals, Anal. Calcd for $C_{14}H_{14}N_3O_2ClCu$: C, 47.33; H, 3.97; N, 11.83%. Found: C, 47.10; H, 4.16; N, 11.60%. IR(KBr): $\nu_{C=O}$, 1670 cm^{-1}, $\nu_{C=N}$(imine), 1624 cm^{-1}. [CuCl($HL^{5\text{-Me}}$)]: blue needle crystals and efflorescence, Yield 22%. Anal. Calcd for $C_{14}H_{14}N_3O_2ClCu$: C, 47.33; H, 3.97; N, 11.83%. Found: C, 47.35; H, 4.17; N, 11.72%. IR(KBr): $\nu_{C=O}$, 1665 cm^{-1}, $\nu_{C=N}$(imine), 1638 cm^{-1}.

5 The X-ray diffraction data were collected using a Rigaku R-Axis Rapid diffractometer at 296 K and the structures were solved by CrystalStructure software package. Hydrogen atoms were fixed at the calculated positions and refined using a riding model. X-ray crystallographic data [CuCl($HL^{2\text{-Me}}$): formula = $C_{14}H_{14}N_3O_2ClCu$, fw 355.28, monoclinic, space group $P2_1/a$ (No. 14), $a = 6.843(3)$, $b = 16.727(7)$, $c = 12.671(5)$ Å, $\beta = 90.13(2)°$, $V = 1450(1)$ Å^3, $T = 296$ K, $Z = 4$, $D_{calcd} = 1.627$ g cm^{-1}, μ(Mo Kα) = 16.90 cm^{-1}, total of independent reflections 3275, $R = 0.028$, $R_w = 0.074$. X-ray crystallographic data [CuCl($HL^{5\text{-Me}}$)]•CH_3OH: formula = $C_{15}H_{18}N_3O_3ClCu$, fw 3587.32, orthorhombic, space group $C222_1$ (No. 20), $a = 7.254(3)$, $b = 17.409(5)$, $c = 26.921(9)$ Å, $V = 3399(2)$ Å^3, $T = 296$ K, $Z = 8$, $D_{calcd} = 1.513$ g cm^{-1}, μ(Mo Kα) = 14.58 cm^{-1}, total of independent reflections 3901, $R = 0.056$, $R_w = 0.141$. Flack parameter for D-form = 0.028. Crystallographic data in CIF format has been deposited at the deposition Nos. 299424 and 604561 of CCDC.

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