The Copper(II) Complex with Two Didentate Schiff Base Ligands. The Unique Rearrangment that Proceeds under Alcohol Vapor in the Solid State to Construct Noninclusion Structure

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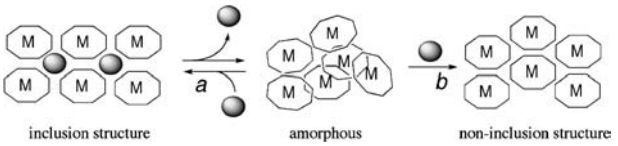
The complexation reaction of copper(II) ion and *N*-(*m*-hydroxyphenylene)salicylideneaminate (mhsa) in EtOH yields EtOH-inclusion and noninclusion crystalline samples, [Cu(mhsa)$_2$]·2EtOH (**1**) and [Cu(mhsa)$_2$] (**2**), respectively. The amorphous sample obtained by drying **1** rearranges to the noninclusion complex **2** under alcohol vapor in the solid state.

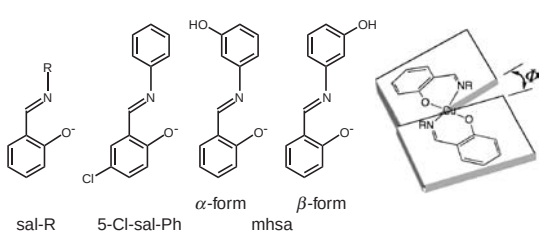
Metal complex-assembled compounds that contain solvent molecules in the structure have often shown unique structural changes caused by removal and reinclusion of solvent molecules.[1,2] Such structural changes generally reconstruct the initial assembled inclusion structures (route *a* in Scheme 1).[2] On the other hand, transformation from the amorphous state to a new noninclusion state by exposure of the removed vapor is unusual (route *b* in Scheme 1).

We have studied the preparation and functions of new monomeric metal complexes that assemble by intermolecular hydrogen bonds. For example, a new hydrogen-bonded network structure has been shown for a nickel complex with a tetradentate Schiff base ligand that has two hydroxy groups.[3] Recently, we selected *N*-(*m*-hydroxyphenylene)salicylideneaminate (mhsa) as a bidentate Schiff base ligand (Scheme 2) for construction of metal complexes with new hydrogen-bonded assembled structures. We found that the resulting Cu^{II}–mhsa complexes show a unique transformation, shown as route *b* in Scheme 1.

The two crystalline samples were obtained by refluxing an EtOH solution of [Cu(salicylaldehyde)$_2$][4] and *m*-aminophenol. Standing of the solution for a few hours afforded columnar crystals of [Cu(mhsa)$_2$]·2EtOH (**1**), which were collected by filtration (Elemental analysis (%) Calcd for $C_{30}H_{32}N_2CuO_6$: C, 62.11; H, 5.56; N, 4.83%; Found: C, 62.56; H, 5.27; N, 4.37%). The filtrate further afforded plate crystals of [Cu(mhsa)$_2$] (**2**) within a few days (Elemental analysis (%) Calcd for $C_{26}H_{20}N_2CuO_4$: C, 63.99; H, 4.13; N, 5.74%; Found: C, 63.69; H, 4.23; N, 5.74%).



Scheme 1.



Scheme 2. Structure of didentate Schiff base ligands and definition of the Φ angle of copper(II) complexes with the chelate ligands.

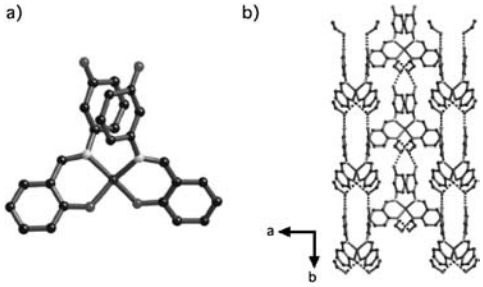


Figure 1. Structures of the monomeric unit (a) and the one-dimensional chain (b) of **1**.

Their crystal structures were clarified by X-ray diffraction studies. Figure 1 shows the monomeric units and the hydrogen-bonded chain structure of **1**.[5] The copper(II) center is not based on a trans-arrangement but on a cis-structure. The distortion around the copper(II) centers can be estimated by the plane–plane angle Φ defined by the two chelate rings, as illustrated in Scheme 2, in which Φ angles of 0, 90, and 180° correspond to the trans-square planar, tetrahedral, and cis-square planar geometries, respectively. It has been reported that in the series of [Cu(sal-R)$_2$] complexes, their Φ angles systematically increase with increases in the steric hindrances of the R groups: Φ angles are 0, 39, 58, and 59° for R groups of Me, Et, ^{i}Pr, and ^{t}Bu, respectively.[6] On the other hand, [Cu(sal-Ph)$_2$] shows trans-square planar geometry ($\Phi = 0°$).[7] The Φ angles of **1** are about 126°, demonstrating that the copper(II) centers are based on geometries between cis-square planar and tetrahedral.

As illustrated in Figure 1b, the hydroxy groups of mhsa ligands form hydrogen bonds with the two EtOH molecules (O···O = 2.69(2) and 2.72(0) Å), which further form hydrogen

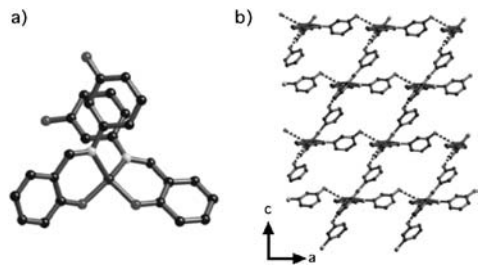


Figure 2. Structures of the monomeric unit (a) and the two-dimensional layer (b) of **2**.

bonds to an adjacent [Cu(mhsa)$_2$] unit (O···O = 2.76(5) and 2.77(7) Å). These hydrogen-bonding interactions create a one-dimensional chain along the *b* axis.

Figure 2 shows the monomeric units and crystal structure of **2**.[8] Similarly to **1**, the copper(II) center is based on the geometry between cis-square planar and tetrahedral, in which the Φ angle is also about 126°. In contrast to **1**, two hydroxy groups of the mhsa of **2** form direct hydrogen bonds with the coordinating oxygen atoms of mhsa in the different adjacent [Cu(mhsa)$_2$] units, creating a two-dimensional layer in the *ac* plane.

In contrast to [Cu(sal-R)$_2$], [Cu(5-Cl-sal-Ph)$_2$] crystallizes not only in the trans-square planar structure ($\Phi = 0°$) but also in the cis-arranged structure ($\Phi = 141°$).[9] The structures of the monomeric units of **1** and **2** are close to the cis-formed structure.[9,10] For the mhsa ligand, two structural isomers are defined by orientations of the hydroxy groups as illustrated in Scheme 1, and the two forms are designated α- and β-forms. For the mhsa ligands in this Cu–mhsa system, **1** contains only α-forms (Figure 1), while **2** involves both α- and β-forms (Figure 2).

As mentioned, one of the interesting aspects of hydrogen-bonded complexes containing solvent molecule is the structural rearrangements as they respond to the removal and reinclusion of the solvent molecules in the solid state. Complex **1** contains EtOH molecules. We have studied the structural changes of **1** by removal of the EtOH molecules, followed by exposure of it to EtOH vapor by monitoring the X-ray powder diffraction (XRPD) patterns (Figure 3).

Thermogravimetric (TG) measurements indicate that the EtOH molecules are removed on heating at about 120 °C (see Supporting Information).[11] Based on the TG data, the included EtOH molecules of **1** were removed on heating at 120 °C under reduced pressure. No intense XRPD peaks were observed for the dried sample (Figure 3c), indicating that the sample obtained is amorphous. Exposure of the amorphous sample to EtOH vapor overnight gave a new XRPD pattern (Figure 3d). Curiously, the pattern obtained is not consistent with that of the initial crystal structure of **1** but is consistent with the simulation pattern of **2** (Figure 3e), even though this complex contains no inclusion molecules. This means that the amorphous sample obtained from **1** transforms to **2** in the solid state under EtOH vapor. Interestingly, this transformation also proceeds by exposure to acetonitrile and other alcohol vapor such as MeOH and PrOH, while other solvents such as Et_2O, hexane, $CHCl_3$, CH_2Cl_2, THF, and water do not cause this transformation. It is noteworthy that the transformation does not proceed under the vapor of $CHCl_3$, CH_2Cl_2, and THF, despite **1** is easily soluble in these solvents, implying that hydrophilic property and enough solubility of solvents are required for the transformation. This transformation is new and unique in the field of hydrogen-bonded assembled metal complexes.

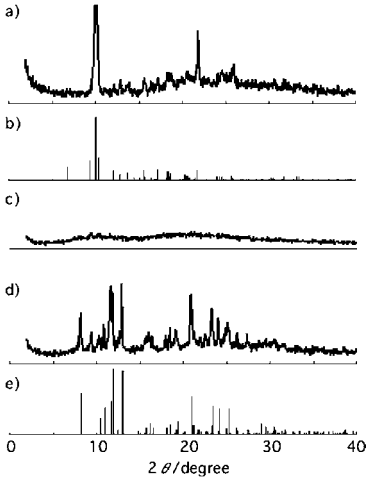


Figure 3. XRPD patterns of freshly prepared sample of **1** (a), the simulation pattern of **1** (b), dried sample (c), sample obtained by exposure of EtOH vapor (d), and the simulation pattern of **2** (e).

In summary, we have prepared new copper(II) complexes, **1** and **2**, with two mhsa ligands. An amorphous sample obtained from **1** shows a unique transformation to **2** in the solid state under alcohol vapor, even though the resulting sample is a non-inclusion sample. Further studies of this unique transformation are currently in progress.

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5 Crystallographic data for the complex: $C_{30}H_{32}N_2CuO_6$, $M_r = 580.14$, monoclinic, space group $P2/n$ (No. 13), $a = 14.50(4)$, $b = 11.36(2)$, $c = 18.43(4)$ Å, $\beta = 107.93(3)°$, $V = 2889(12)$ Å^3, $Z = 4$, D_{calcd} 1.334 g cm^{-3}, μ(Mo Kα) = 0.800 mm^{-1}, $T = 293$ K, $\lambda = 0.7107$ Å, ω scan, 21272 reflections measured, 5870 unique, $R = 0.0869$ (all data). The data collection was performed on a Rigaku CCDC Mercury system. The structure was solved by a direct method using SIR-92 and refined on F^2. Geometrical hydrogen atoms were located on the calculated positions. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included but not refined. Crystallographic data reported in this paper has been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-xxxx.

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8 Crystallographic data for the complex: $C_{26}H_{20}N_2CuO_4$, $M_r = 488.00$, monoclinic, space group $P2/n$ (No. 13), $a = 9.826(6)$, $b = 15.11(3)$, $c = 15.174(9)$ Å, $\beta = 93.01(2)°$, $V = 2249(5)$ Å^3, $Z = 4$, D_{calcd} 1.441 g cm^{-3}, μ(Mo Kα) = 1.007 mm^{-1}, $T = 293$ K, $\lambda = 0.7107$ Å, ω scan, 13826 reflection measured, 5854 unique, $R = 0.0850$ (all data). The data collection was performed on a Rigaku CCDC Mercury system. The structure was solved by a direct method using SIR-92 and refined on F^2. Geometrical hydrogen atoms were located on the calculated positions. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included but not refined. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-xxxx.

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11 Supporting Information is available electronically on the CSJ-Journal web site; http://www.csj.jp/journals/chem-lett/.

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