

CHAPTER IV
SUPRAMOLECULAR STRUCTURE OF
***N,N*-BIS(2-HYDROXYBENZYL)ALKYLAMINE DERIVATIVES:**
A UNIQUE ASSEMBLY SYSTEM RESPONSIVE FOR
BOTH HYDROGEN BONDED HOST WITHOUT GUEST AND
CHARGE TRANSFER COORDINATED HOST WITH COPPER ION

Synopsis

A specific assembly structure responsive for both host without guest under hydrogen bond network and host with metal ion guest via charge transfer coordination is proposed.

Abstract

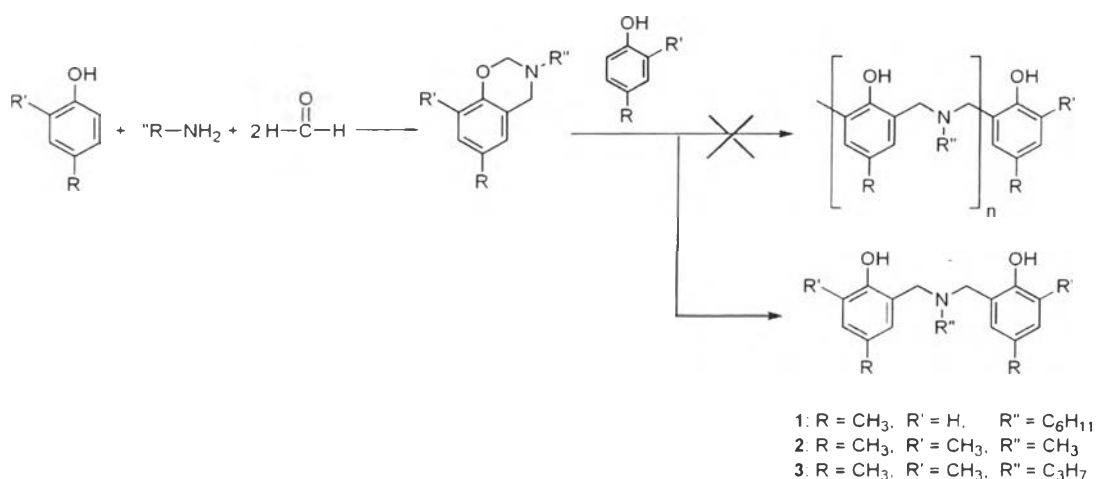
N,N-Bis(2-hydroxybenzyl)alkylamine is a highly stabilized compound by the inter- and intramolecular hydrogen bond networks. The successful crystallization with copper acetate and the structural studies by Fourier transform infrared spectroscopy (FTIR) and thermal analysis (TG-DTA) techniques clarify that *N,N*-bis(2-hydroxybenzyl)alkylamine changes its self-assembly hydrogen bond network to a coordinated complex with metal ion. Crystallography analysis proves a supramolecular structure of dimeric *N,N*-bis(2-hydroxybenzyl)alkylamine host with copper ion guest via a double-oxygen bridge under the host:guest ratio of 1:1. Cerius2 and MS modeling programs clarify that the host-guest interaction is based on a charge transfer system and the host network with guest is well superimposed with the one without guest. The present work demonstrates a unique assembly system of which the structure is responsive for both host without guest under hydrogen bond network and host with metal ion guest via charge transfer coordination.

Keywords: *N,N*-Bis(2-hydroxybenzyl)alkylamine derivatives; Inter- and intramolecular hydrogen bond; Supramolecular structure; Charge transfer; Double-oxygen bridge

Introduction

Benzoxazine is a unique heterocyclic compound obtained from the cyclization between phenol, formaldehyde, and amine (Holly and Cope, 1944; Burke *et al.*, 1961; Sainsbury, 1984). The ring opening reaction of benzoxazine by acid or base catalyst is reported to give the phenol with aza-methylene linkage compound (Burke *et al.*, 1964; Ishida and Krus, 1998). It is natural to expect that the chain reaction of *p*-substituted phenol based benzoxazine gives linear polymer. However, up to now there has been no report about linear polymer from benzoxazine. Concerning this point, we found that although, theoretically, monofunctional phenol based benzoxazines give linear polymer, the reaction tends to terminate at a single ring opening reaction to give *N,N*-bis(2-hydroxybenzyl)alkylamine derivatives (Scheme 1). In the practical reaction, the white precipitate of *N,N*-bis(2-hydroxybenzyl)alkylamine derivatives appears soon after the reaction was carried out at a certain time. Our studies on the single crystal analysis of *N,N*-bis(5-methyl-2-hydroxybenzyl)cyclohexylamine (**1**) revealed that the molecules are stabilized under the inter- and intramolecular hydrogen bonds (Figure 1) which might be the reason why the polymerization cannot be achieved as the theoretical pathway (Laobuthee, 2002).

Scheme 1



It should be noted that the structure of *N,N*-bis(2-hydroxybenzyl)alkylamine is similar to that of the repeating unit in calixarene with aza-methylene linkage, thus,

we expect for a novel supramolecule which might lead to various properties and applications, e.g., organometallic catalysts (Stibrany *et al.*, 2003; Evans *et al.*, 2003; Takacs *et al.*, 2004), biomimetic metalloproteins (Itoh *et al.*, 2000), and enzymatic complex systems (Lubben *et al.*, 1995).

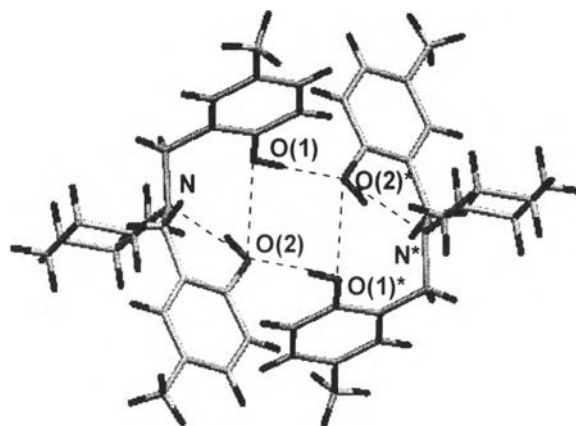


Figure 1. Crystal structure of **1** with the atomic numbering scheme.

In the past, Tshuva *et al.* (2001) reported that zirconium complex of amine-bis(phenolate) ligands whose structure is similar to *N,N*-bis(2-hydroxybenzyl)alkylamine can function as a catalyst for 1-hexene polymerization. Meanwhile, Malathy Sony *et al.* (2002) showed a biomimetic model complex of *N*-[(2-hydroxylato-5-methyl)benzyl-(2'-hydroxylato-3',5'-dimethylbenzyl)]ethyl amine dicopper(II). It is important to note that those studies showed mainly some specific structures between molecules and ions and the properties induced whereas the formation of specific structures is not clearly explained. In order to establish the supramolecular chemistry of *N,N*-bis(2-hydroxybenzyl)alkylamine with a well-understanding at molecular level, we focus our work on both molecular design and synthesis to obtain a series of the derivatives and clarify how the assembly system is possibly induced by the molecular interaction and/or complexation with neutral molecule and/or metal ion.

In the area of molecular design and synthesis, we succeeded in showing a simple condition to prepare a series of *N,N*-bis(2-hydroxybenzyl)alkylamine derivatives (Laobuthee *et al.*, 2003; Phongtamrug *et al.*, 2004) as well as macrocyclic compounds via esterification and etherification (Laobuthee & Chirachanchai, 2002; Chirachanchai *et al.*, 2003).

In the area of host-guest interaction, we reported the molecular assembly of a series of *N,N*-bis(2-hydroxybenzyl)alkylamine derivatives and the inclusion phenomena in solution state with various ions such as alkali, alkaline earth (Laobuthee *et al.*, 2003), and transition metals (Phongtamrug *et al.*, 2004) as evidenced from proton nuclear magnetic resonance (^1H NMR), wide angle X-ray diffraction (WAXD), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimeter analysis (DSC), and electrospray ionization mass spectroscopy (ESI MS).

Although a series of *N,N*-bis(2-hydroxybenzyl)alkylamine derivatives show the inclusion phenomena in the solution state, we put our effort to declare the solid state of host-guest structure which will not only give us the direct information about complexation between the derivatives and guest species but also confirm the formation of host molecular assembly system.

Among various metal ions, single crystals of copper complexes of *N,N*-bis(2-hydroxy-5-methylbenzyl)cyclohexylamine, **1**, *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)methylamine, **2**, and *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)propylamine, **3**, gave us important information to establish them as a unique example of a specific host network structure. This network structure was found to be responsive for both host without guest via hydrogen bonding and host-copper via the charge transfer ionic coordination. The present work, thus, demonstrates (i) how *N,N*-bis(2-hydroxybenzyl)alkylamine derivatives functions as a host molecule in accepting copper ion guest, (ii) how the structure of *N,N*-bis(2-hydroxybenzyl)alkylamine derivatives affects on the molecular assembly formation, and (iii) how a specific host framework is responsive for both host without guest and host with guest.

Experimental

Preparation of N,N-Bis(2-hydroxybenzyl)alkylamine Derivatives

p-Cresol, 2,4-dimethylphenol, formaldehyde, methylamine, propylamine, and cyclohexylamine were obtained from Merck, Germany. Copper (II) acetate monohydrate and sodium hydroxide were purchased from Fluka, Switzerland. 1,4-Dioxane, diethyl ether, isopropanol, methanol were from Labscan, Ireland. All chemicals and solvents used for synthesis were of reagent grade and used without purification. *N,N*-Bis(2-hydroxy-5-methylbenzyl)cyclohexylamine, **1**, *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)methylamine, **2**, and *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)propylamine, **3**, were prepared as previously reported (Phongtamrug *et al.*, 2004).

Instrumentation

FTIR spectra were recorded by KBr pellet in the range 4000-400 cm⁻¹ with 128 scans at a resolution of 2 cm⁻¹ on a HORIBA FT-720 spectrometer. Differential thermal analysis (DTA) was performed by a Rigaku Thermoplus TG8120 from 50°C to 300°C at a heating rate of 5°C/min.

Crystallography

Single crystal X-ray diffraction measurement was carried out on a Rigaku RAXIS RAPID/FS diffractometer with a graphite-monochromated Mo-K α radiation at 296 K. The structure was solved by direct method (SIR92) and refined by full-matrix least-squares procedure on F^2 with the program TEXSAN. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were (identified in the different Fourier map and) placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. All calculations were performed using the TEXSAN crystallographic software package.

Molecular Modeling

Superimposition of chemical structure before and after inclusion is done by MS modeling software. Atomic charges based on electrostatic potential theory are

computed by DMol³ (Material Studio Version 3.0, Accelrys) in Cerius² program. The atomic orbital basis set was DND (Double Numerical plus d-functions), and the type of exchange-correlation potential was a local LDA.

Results and Discussion

The preparation of single crystals of *N,N*-bis(2-hydroxybenzyl)alkylamine with various metal (alkaline, alkaline earth, transition metal) ions was carried out by dropping the methanolic copper acetate solution to **1-3** and leaving for several days. It is important to note that the single crystals of *N,N*-bis(2-hydroxybenzyl)alkylamine derivatives are colorless whereas those of the copper inclusion are dark green.

Structural Characterization of Copper Inclusion

The green crystals of **1-3** with copper, abbreviated as **1-Cu**, **2-Cu**, and **3-Cu**, were characterized by FTIR to observe the vibrational changes before and after copper inclusion. Nujol technique was applied in order to avoid the disturbance by water peaks.

Figure 2 shows FTIR spectra of a series of single crystals belonging to **1**, **2**, **3**, and their copper inclusion where the contribution of Nujol bands was subtracted. It is important to note that the OH peaks of **1**, **2**, and **3** are clearly observed, although the peak position and the broadness are different which might be due to the strength and the environment of hydrogen bond in each compound. When copper complexation is formed, only **2-Cu** and **3-Cu** show a trace of OH peak whereas **1-Cu** does not give any OH peak. This indicates that the loss of inter- and intramolecular hydrogen bonds after copper ion inclusion. The disappearance of hydrogen bonded OH vibrational peak is similar to that of bis(5,5-diethyl-babiturato)bis-pyridino copper(II) as reported by Peppas *et al.* (2001). This hinted that **1-3** might form the complex with copper ion and, as a result, the complexes obstruct the initial hydrogen bond network. Considering the C-N peak, **1-Cu** (Figure 2(b)) gives the new peaks at 1305 and 1289 cm⁻¹ whereas both **2-Cu** (Figure 2(d)) and **3-Cu** (Figure 2(f)) show the new peaks at 1267 and 1255 cm⁻¹ (Silverstein *et al.*, 1991). This reflects the change of aza group vibrational mode after copper ion inclusion. In this way, the OH and

C-N groups of *N,N*-bis(2-hydroxybenzyl)alkylamine are remarkably affected by introducing copper ions. The structural analysis relate to the crystal structure is further discussed in *Supramolecular Assembly revealed by Single Crystal Analysis*.

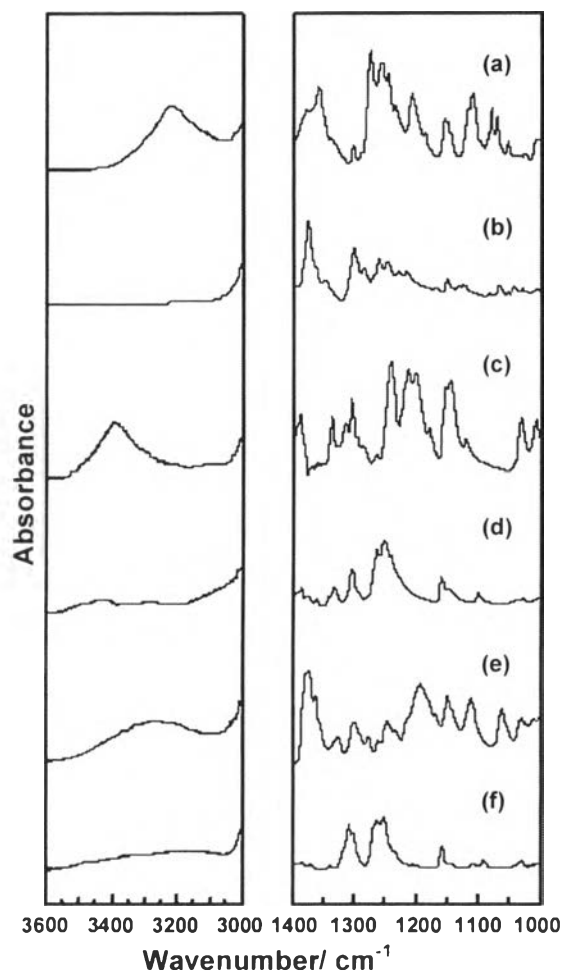


Figure 2. FTIR spectra of (a) **1**, (b) **1-Cu**, (c) **2**, (d) **2-Cu**, (e) **3**, and (f) **3-Cu**, after Nujol peaks were subtracted.

The thermal stability of the compound before and after inclusion with copper was also observed. Compound **1** (Figure 3(a)) gives a sharp melting peak at 177°C followed by an exothermic peak (185°C) and an endothermic peak (225-240°C) with a remarkable weight loss implying the consequent oxidation and degradation. However, in the case of **1-Cu** (Figure 3(b)), only an exothermic peak due to an oxidation was observed. The difference in thermal stability of **1** and **1-Cu**

confirmed us that the complexation with copper stabilized compound 1 so that the melting peak was hardly observed.

Comparing 2 (Figure 3(c)) to 1, the lower melting was found at 125°C implying the less stable packing structure. When complex with copper ion is formed (Figure 3(d)), only the thermal degradation peak without oxidation peak is declared at 250°C giving us an idea about the high stability of the complex.

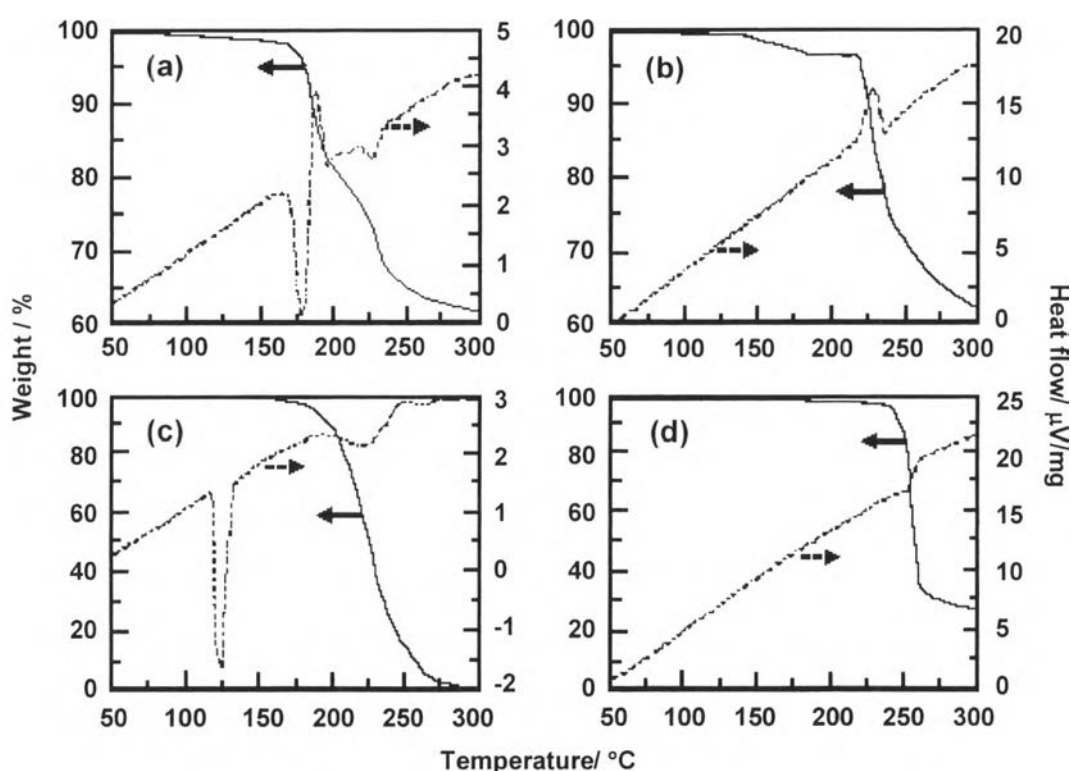


Figure 3. TG and DTA thermograms of (a) 1, (b) 1-Cu, (c) 2, and (d) 2-Cu.

Supramolecular Assembly Revealed by Single Crystal Analysis

In order to clarify the supramolecular structure of *N,N*-bis(2-hydroxybenzyl)alkylamine with copper ion, single crystal X-ray analysis was applied. As demonstrated in Figure 1, *N,N*-bis(2-hydroxybenzyl)alkylamine derivatives form inter- and intramolecular hydrogen bonds between N atoms and OH groups (O(1)-H...O(2)* (1.865 Å) and N...H-O(2) (1.826 Å)) to result a dimeric molecular assembly (Laobuthee *et al.*, 2001).

Figure 4 declares the inclusion structure of **1**-Cu under the double oxygen-bridged copper nuclei system via phenoxy oxygens. Each copper is bridged by three phenoxy oxygens and amine donors. It is important to note that the bond distances for Cu-O(1), Cu-O(2), Cu-O(2)*, and Cu-N are almost identical (1.85-2.05 Å). These distances are in the range suitable for coordination bond (Murphy, 1993). Considering the bond angles of O(1)-Cu-N, O(2)-Cu-N, O(1)-Cu-O(2)*, and O(2)-Cu-O(2)* which are nearly 90°, we concluded that the structure should be a distorted square planar geometry. The present case is similar to that of bis[3-(4-cyanophenyl)pentane-2,4-dionato- κ^2 O,O]copper(II) (Chen *et al.*, 2004). The bridge distances of Cu-O(2) and Cu-O(2)* are almost equal (1.928(3)Å and 1.976(3)Å). When **1** forms the supramolecular complex with copper ion, the original intermolecular hydrogen bond among O(1)-H...O(2)* and intramolecular hydrogen bond N...H-O(2) of **1** were disappeared whereas Cu-O(1), Cu-O(2), Cu-N, and Cu-O(2)* bonds are observed.

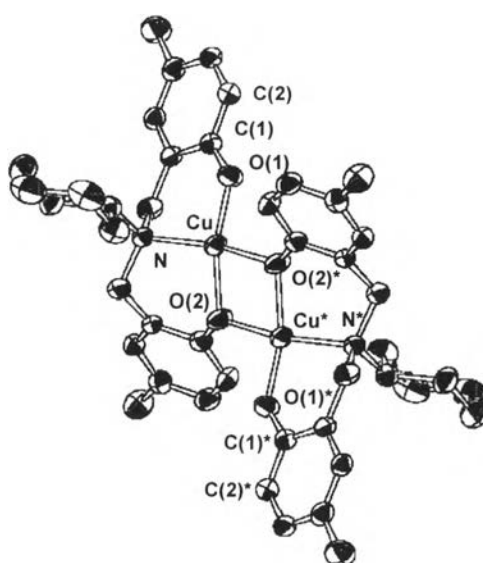


Figure 4. ORTEP plot of **1**-Cu, showing the atomic numbering scheme and the thermal ellipsoids at the 50% probability level. (Hydrogen atoms are omitted for clarity.)

It is important to note that although the bond length and bond angle of the dimeric network of **1** is changed, the dimeric network is maintained even the complexation with Cu ions is formed. In other words, the dimeric network of **1** might be a highly stable structure so that it is maintained even the Cu ions are in between. This clarifies a unique assembly structure which is stabilized either via hydrogen bond network or the double-oxygen bridges.

Stabilization of Dimeric Supramolecular Structure by Solvent Molecules

The unique molecular assembly of *N,N*-bis(2-hydroxybenzyl)alkylamine derivatives is further clarified. Surprisingly, in the cases of **2**-Cu and **3**-Cu (Figures 5 and 6), there are some water molecules existed in the complex network. For **2**-Cu, three water molecules are found whereas for **3**-Cu, one methanol and one water molecules are observed. Since recrystallization was carried out without adding water, the only speculation here is that those small molecules might come from the hydrated copper acetate salt and/or methanol (99% purity). Comparing with **1**-Cu of which the water or methanol molecules were not detected even the same recrystallization was carried out, it can be concluded that the water or methanol molecules in **2**-Cu and **3**-Cu function as a stabilization molecules in the assembly structure. Here, referring to Figure 2, the small broad OH peaks of **2**-Cu and **3**-Cu also support the existence of small molecules with hydrogen bonds.

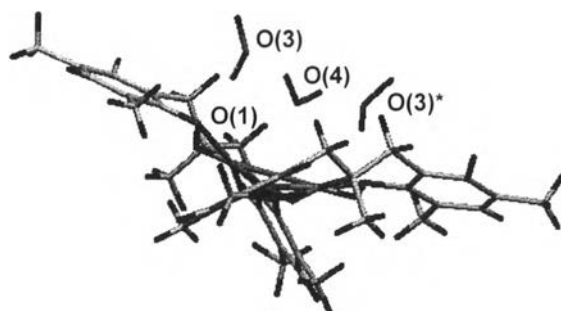


Figure 5. Crystal structure of **2**-Cu.

In details, as shown in Figure 5, three water molecules are coexistent with dimeric **2**-Cu molecules in the crystal lattice. The distances between phenoxy oxygen and oxygen in the water (O(3)-H...O(1) and O(4)-H...O(3)) are 2.703(5) and 2.819(5) Å, respectively. Here, the hydrogen atoms of waters were subtracted from the different Fourier map in order to clarify the position of hydrogen atom. As a result, the O(1)...H-O(3) distance is 1.781 Å which is almost equal to the interatomic distance of the hydrogen bond between phenol and water (1.796 Å) (Guedes *et al.*, 2003). This informed the unique dimeric molecules with a bowl shape network structure by two phenyl rings and copper atom. Here, three water molecules function as an additional bridge to stabilize the dimeric network.

In the case of **3**-Cu (Figure 6), water and methanol molecules are in the lattice and are stabilized to each other by hydrogen bonds at the distances of 2.7~3.0 Å. It should be noted that the molecular shape of **2**-Cu and **3**-Cu are a bowl shape structure and this might provide the space to accept other small molecules during the crystallization.

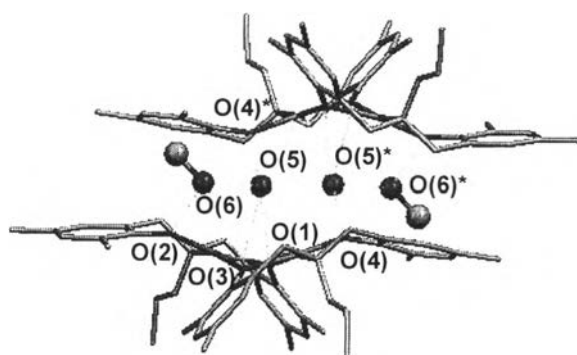


Figure 6. Crystal structure of **3**-Cu. (Hydrogens are omitted for clarity.)

The fact that **1**-Cu is formed without solvent and/or water molecules (Figure 4) might be explained as follows. The twisting of benzene rings and cyclohexyl groups affects the molecular distortion during the assembly formation either with or without copper ion. As a result, it is difficult to accept solvent molecules in the assembly network. In other words, *N,N*-bis(2-hydroxybenzyl)alkylamine derivatives

with bulky groups might not be a good host for small guests such as water and/or solvent. As seen in the case of **1**-Cu, it can be concluded that the bulky groups give a strong hindrance for other small molecules to enter the intermolecular layers.

In the past, Malathy Sony *et al.* reported bis[(3,5-dimethyl,2-hydroxy)-2'-hydroxy-5'-methyl]benzylethylamine formed copper complex with an existent of methanol and water molecules in the packing structure. At that time, the structural clarification did not include how those small molecules were stabilized.⁹ Here, in our cases, we found that the small molecules, i.e, water and methanol, are aligned at O(1)-O(3)-O(4) for **2**-Cu and O(2)-O(6)-O(5)-O(4)* for **3**-Cu which the bond distances are appropriate to consider as hydrogen bond distance.

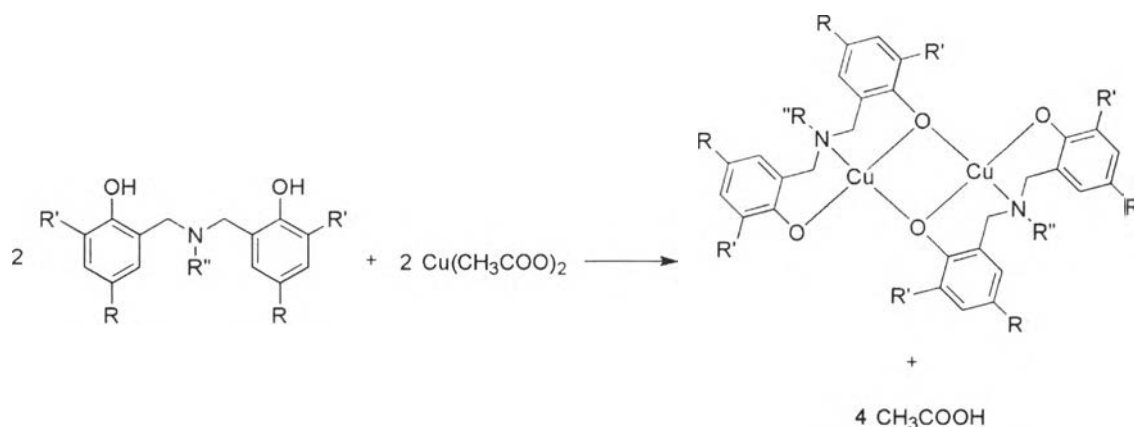
Atomic Charge Distribution and Charge-transfer Complex

Although it is difficult to determine the proton position by single crystal X-ray analysis, in the cases of **1**, **2**, and **3**, the protons and OH groups are simply clarified with a reasonable bond distance. In the case of **1**-Cu, the X-ray structural analysis declares the oxygen atoms of hydroxyl groups linking directly to Cu atom, whereas the hydrogen atoms and hydrogen bond networks belonging to hydroxyl groups could not be determined. In addition, most inclusion complexes show the counter-ion in the crystal structure. However, in our case, those acetate counter anions were not identified. Based on these results, one of the possibilities is that the hydrogen atoms of hydroxyl groups might combine with acetate ion to result acetic acid molecules in the system (Scheme 2). This speculation can be confirmed from the infrared spectral band of the **1**-Cu single crystal. The O-H stretching mode ($3200\sim 3400\text{ cm}^{-1}$) of **1**-Cu disappears significantly as shown in Figure 2.

In order to know the characteristic features of Cu-O bonds, the calculation of atomic charges for *N,N*-bis(2-hydroxybenzyl)alkylamine and the corresponding Cu complex on the basis of density function theory were carried out by using DMol³ (Material Studio Version 3.0, Accelrys). The atomic orbital basis set was DND (Double Numerical plus d-functions), and the type of exchange-correlation potential was a local LDA. Figure 7 shows the calculated electrostatic potential (ESP) charges (i.e., atomic centered charges that best reproduce the density functional theory under

Coulomb potential). In the case of **1** (Figure 7(a)), the typical charge distribution is identified among the O-H...O hydrogen bond. After complexation (Figure 7(b)), the charges of oxygen atoms connected directly to Cu atom of **1**-Cu change from -0.575 to -0.780 and from -0.472 to -0.526 eV. At the same time, that of nitrogen atom decreases from -0.335 to -0.554 eV. The phenol carbon atom connected to oxygen changes its charge from +0.167 to +0.333 eV. For Cu atom, the charge decreases from +2 (Cu^{2+} of $\text{Cu}(\text{CH}_3\text{COO})_2$) to +1.023 as shown in Figure 7(b). The significant decrease in atomic charge of oxygen atom (-0.078 eV) implied the charge transfer complexation with copper ion. It is important to note that the O-Cu-O-Cu is formed in planar square under double-oxygen bridge between two molecules of **1**. This confirms the supramolecular complexation.

Scheme 2



Considering the assembly network of **1**, it is natural to emphasize that the charge transfer coordination bond network of **1**-Cu is formed with little destruction of the original packing structure. In other words, the charge transfer complex is initiated by substituting the hydrogen atoms with Cu atoms. This type of dimeric charge transfer complexation is quite rare to find in the general complexation.

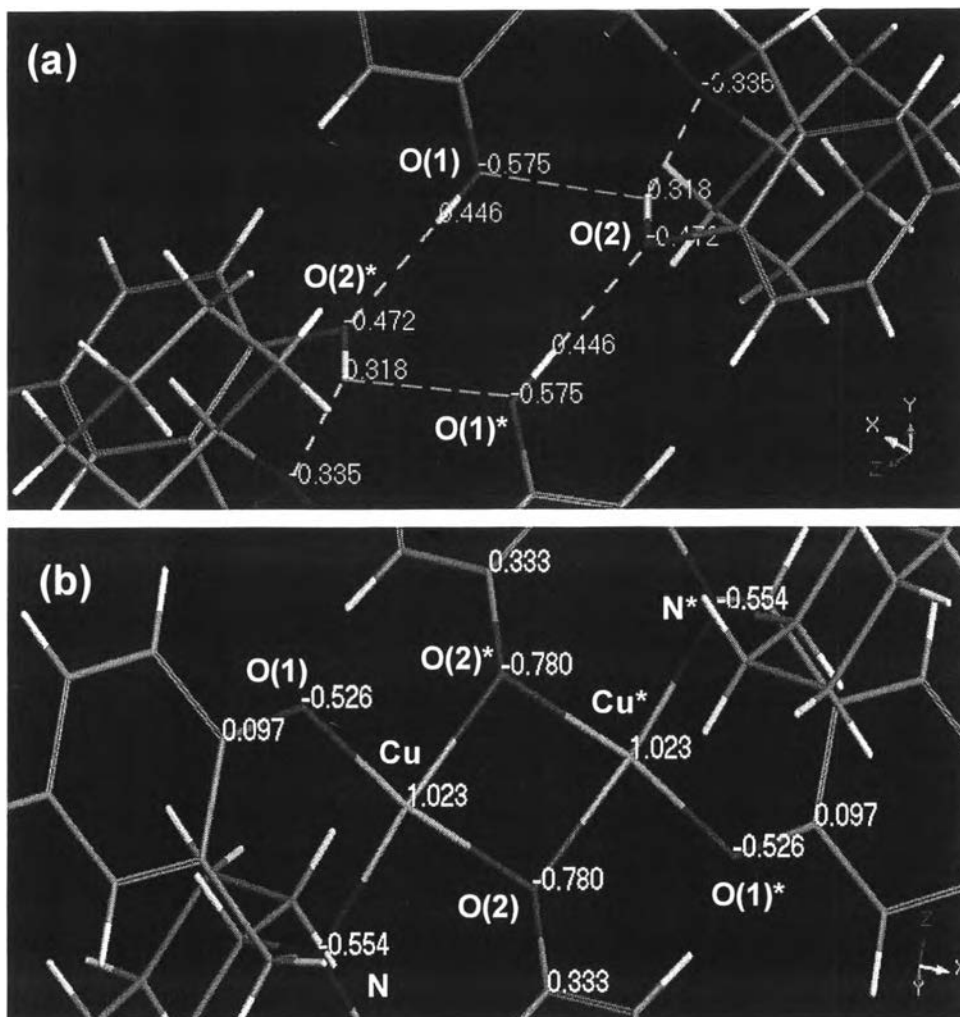


Figure 7. Atomic charges of (a) **1** and (b) **1-Cu**.

Superimposition of Dimeric Assembly Network.

In order to confirm the similar dimeric assembly network under hydrogen bond and charge transfer coordination bond (as discussed in Atomic Charge Distribution and Charge-transfer Complex), a superimposition using DS Viewer Pro program was carried out.

Figure 8 shows the crystallography data plotted in space with an extent rotation to obtain the most possible superimposed structure of **1** and **1-Cu**. The simulation results conclude that when **1** accepts Cu ion as a guest, the dimeric network structure still remains whereas the bond angle of O(1)-N-O(2) (80.61°) as well as the distance of O(1)-O(2) (3.729 \AA) in **1-Cu** are slightly larger than those of **1**

(64.21° and 2.998 Å). This suggests that the guest inclusion enlarges the pattern of dimeric formation without destruction, at that time the hydrogen bond network is changed to the coordination network. As expected, compound **2** also showed the well superimposition before and after Cu^{2+} inclusion.

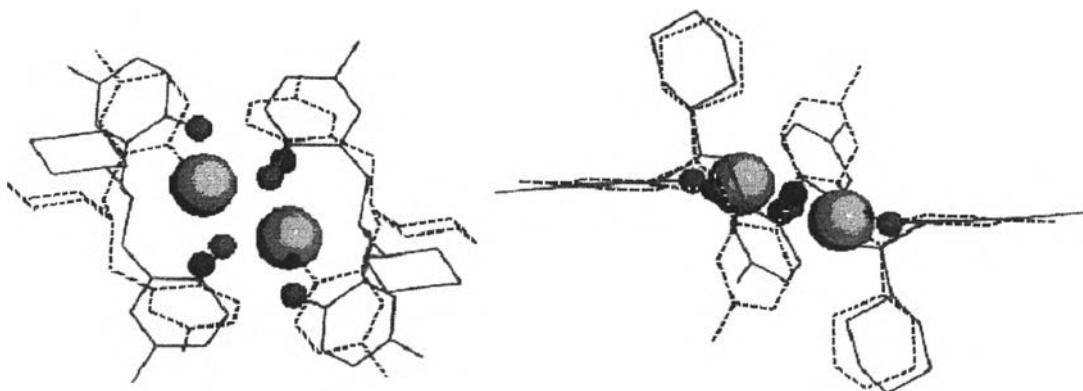


Figure 8. Superimposed structures of **1** (dotted line) and **1-Cu** (smooth line) with different views.

Conclusion

The complexation of *N,N*-bis(2-hydroxybenzyl)alkylamine with copper ion proved that the hydrogen bonded dimeric system of *N,N*-bis(2-hydroxybenzyl)alkylamine was changed to a supramolecular structured dimeric system of *N,N*-bis(2-hydroxybenzyl)alkylamine and copper ion with the host-guest ratio of 1:1. The single crystal analysis confirmed that the structure of *N,N*-bis(2-hydroxybenzyl)alkylamine played an important role to form a molecular assembly in accepting copper ion together with water and/or methanol molecules depending on the substituent at aza group. The energy calculation using Cerius² program clarified that the *N,N*-bis(2-hydroxybenzyl)alkylamine host accepted the copper ion guest by the atomic charge transfer among phenoxy oxygen atom, aromatic ring, and aza methylene group leading to a unique double oxygen bridges network. The MS modeling based on the single crystal analysis data showed a well superimposed structure of host without guest and host with copper ion to conclude that the charge transfer was initiated by substituting the hydrogen atoms with copper atoms. The

dimeric structure controlled either by hydrogen bond or charge transfer is quite rare and might even be the first example for the supramolecular complexation.

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