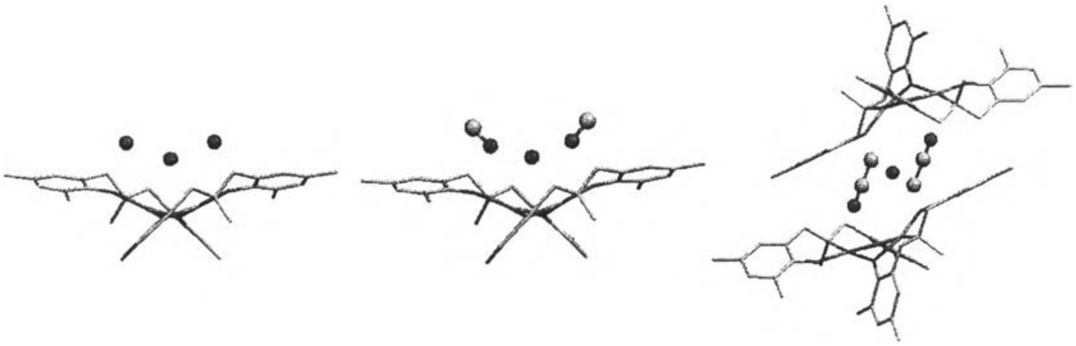
CHAPTER V

CONCERTED CONTRIBUTION OF COPPER-OXYGEN COORDINATION AND HYDROGEN BONDS IN *N,N*-BIS(2-HYDROXYBENZYL)ALKYLAMINE-COPPER-SOLVENT SYSTEM

Graphical Abstract

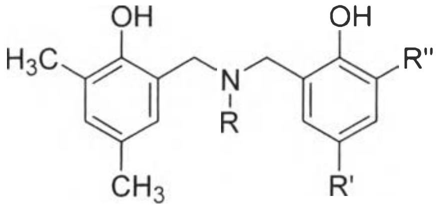


Abstract

N,N-Bis(2-hydroxy-3,5-dimethylbenzyl)methylamine shows a dimeric molecular assembly to accept copper ions and neutral molecule guests, i.e., water, methanol, and ethanol. The present work declares a representative supramolecular structure of which the host-guest interactions are based on the simultaneous coordination and hydrogen bonds.

Supramolecular chemistry has received much attention due to its specific properties for various practical materials such as sensors,[1] ultrapurification membranes,[2] toxic exclusion resins,[3] etc. It is known that host molecules can either be macrocyclic compounds or self assembly-structured molecules.[4] There, the host-guest interactions are satisfied by non-covalent bonds, for example, ionic interaction,[5] polar-polar interaction,[6] stacking conformation,[7] and hydrogen bonding.[8] In general, the specific structure of host and its consequent host-guest interaction induce a particular non-covalent bond as seen in the cases of ionic bond in crown ether-alkali metal[9] and hydrophobic interaction in cyclodextrin-benzenesulfonate.[10] It is important to note that there are some reports about the interaction of host with more than a single species of guest. For example, *N,N'*-bis(phosphonomethyl)-1,10-diaza-18-crown-6 formed the complex with cadmium and entrap water as a neutral guest,[11] however, the water is explained as a stabilizing species.[12] Here, we consider that *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)methylamine, **1**, (Scheme 1) is a good example to study the simultaneous inclusion of guest species in a host due to its unique structure which the interactions of coordination via the lone pair electrons and the hydrogen bond based on phenyl group are available in the system.

Scheme 1



1 : R = CH_3, R' = CH_3, R'' = CH_3
1a : R = C_2H_5, R' = CH_3, R'' = H

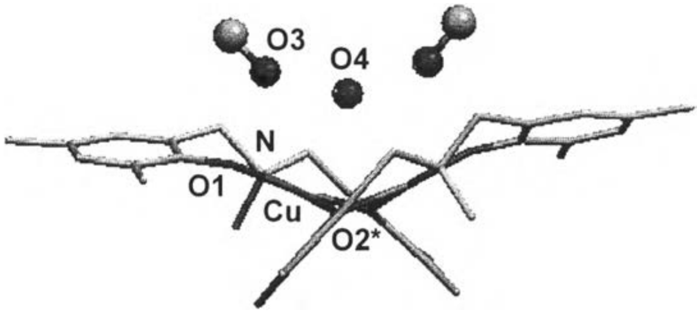
N,N-Bis(2-hydroxy-3,5-dimethylbenzyl)methylamine (**1**) was prepared as reported elsewhere.[13] The green crystal (Type I) was obtained by dropping the methanolic solution of copper acetate monohydrate (1 M) into that of *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)methylamine. The single crystal obtained was cooled below 0 °C for a day to obtain Type II. Similar procedures were done in ethanolic solution to achieve Type III. The X-ray diffraction system used was Rigaku RAXIS-RAPID imaging plate with a software TEXSAN.[14] The results are summarized in Table 1.

Table 1 Crystal data of Types I-III

	Type I	Type II	Type III
Empirical formula	$C_{20}H_{27}CuNO_{3\,5}$	$C_{19}H_{26}CuNO_{3\,5}$	$C_{40}H_{54}Cu_2N_2O_6$
Formula weight	400.98	387.96	785.97
Crystal system	monoclinic	monoclinic	triclinic
Space group	*C*2/c (no.15)	*C*2/c (no.15)	*P*1 (no.2)
a/Å	19.495(2)	18.972(1)	11.9528(2)
b/Å	14.145(2)	14.075(1)	12.9382(5)
c/Å	16.379(3)	15.806(1)	13.8307(8)
α/°	90	90	79.439(1)
β/°	115.483(5)	114.051(2)	75.505(2)
γ/°	90	90	67.517(3)
V/Å^3	4077.0(9)	3854.2(5)	1904.2(1)
Z, calculated density	8, 1.306	8, 1.337	2, 1.371
R_1, wR_2	0.0540, 0.1617	0.0508, 0.1289	0.0591, 0.1511
GOF	0.841	1.074	1.258
μ/mm^{-1}	1.09	1.15	1.371
No. of total, unique reflections measured (R_{int})	22905, 3715	14047, 3478	13638, 6803
CCDC	261408	258999	261409

The single crystal Type I shows a bowl-like structure consisting of the two molecules of **1** with two copper ions by double oxygen bridges (Figure 1). Moreover, there are two methanols and a water existed in between the dimeric **1**-Cu. Considering the bond angles and distances, we suspect that hydrogen bonds are formed between O1···O3 and O3···O4.

Type I



Type II

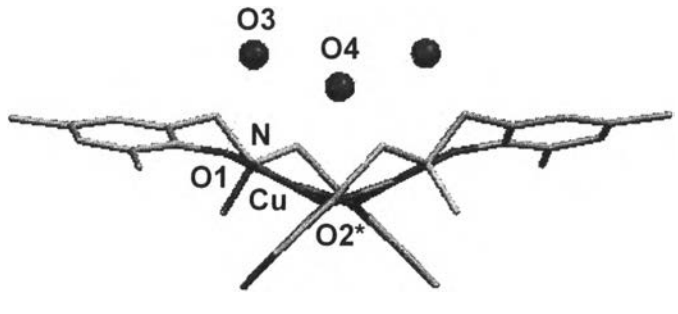


Figure 1. Crystal structures of Types I and II.

In the case of Type II, the structure of the dimeric **1**-Cu complex is found to be similar to that of Type I, however, two methanol molecules are substituted by water as shown in Figure 1. Although the space groups of Types I and II are the same, it is important to note that all dimensions of Type II (*a*, *b*, *c*) are lower than those of Type I. This reflects the shrinkage of crystal structure when the water molecules replaced methanol after cooling. It is a surprise to see the simple cooling initiated the different guest inclusion, however, the procedure was repeated to find the similar crystal information with the $R1$ as low as 0.0508 (Table 1) suggesting the high reliability data. In other words, **1** requires some neutral molecules, either water or methanol molecules, via the hydrogen bond network to stabilize the host-metal molecular assembly system.

An attempt to focus on the effect of solvent molecules was carried out. The solvent used in recrystallization was changed from methanol to ethanol to obtain Type III. The crystal system was clarified to be triclinic $P\bar{1}$ with a double oxygen-bridged structure. It is important to note that Type III includes an ethanol and a water in the system whereas the water is hydrogen bonded with two of the dimeric **1**-Cu as shown in Figure 2. Here, the water molecule functions as a linkage between two **1**-Cu complexes resulting in the host-guest system of four molecules of **1** coordinated by four coppers and bound with a water molecule and two ethanol molecules.

Taking all Types of I-III into our consideration, we would like to propose that **1** is a good example for the case that the host molecule offers the hydrogen-bond network. In other words, this host-guest system is controlled by the hydrogen bonding with small molecules to result various types of highly stabilized packing crystal structures.

In previous work, Malathy Sony et al. reported the similar derivative (bis[(3,5-dimethyl,2-hydroxy)-2'-hydroxy-5'-methyl]benzyl ethylamine, **1a**) formed a copper complex with water and methanol.[15] Although the existence of those small molecules was suspected to be based on CH···O and CH···π interactions, the result supported the unique simultaneous interactions in the supramolecular structure of **1**. It is important to note that the difference in the structure of **1** and **1a** is that **1** shows a symmetrical structure of two phenolic groups binding with methylene-aza-methylene unit to provide the space for the neutral molecules. This symmetrical structure and the availability of hydrogen bond including the lone pair electron system might be key factors to allow simultaneous coordinated and hydrogen bonded molecular assembly.

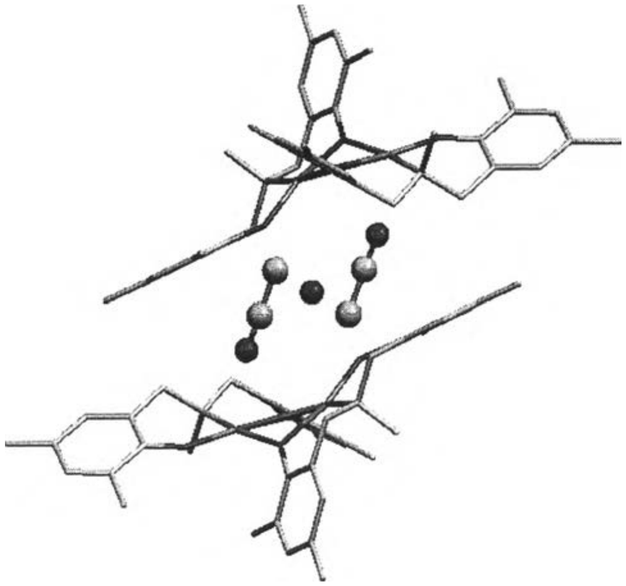


Figure 2. Crystal structure of Type III. (Hydrogen atoms are omitted for clarity.)

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References and Notes

1. Y. Ni, R. R. Puthenkovilakom, and Q. Huo, *Langmuir*, **20**, 2765 (2004).
2. T. H. Bayburt, Y. V. Grinkova, and S. G. Sligar, *Nano Lett.*, **2**, 853 (2002).
3. S. Noro, S. Kitagawa, M. Kondo, and K. Seki, *Angew. Chem. Int. Ed. Engl.*, **39**, 2081 (2000).
4. J. W. Steed, in "Encyclopedia of Supramolecular Chemistry," ed. by J. L. Atwood and J. W. Steed, Marcel Dekker, New York (2004), Vol. 2, p 1401-1426.
5. H. S. Choi, T. Ooya, S. Sasaki, and N. Yui, *Macromolecules*, **36**, 5342 (2003).
6. S. K. Dutta and M. W. Perkovic, *Inorg. Chem.*, **41**, 6938 (2002)..
7. C. Janiak, *J. Chem. Soc., Dalton Trans.*, **21**, 3885 (2000).

8. G. R. Desiraju, in "Encyclopedia of Supramolecular Chemistry," ed. by J. L. Atwood and J. W. Steed, Marcel Dekker, New York (2004), Vol. 1, p 658-665.
9. Z. Jedlinski and M. Sokol, *Pure & Appl. Chem.*, **67**, 587 (1995).
10. N. Funasaki, H. Yamaguchi, S. Ishikawa, and S. Neya, *J. Phys. Chem. B*, **105**, 760 (2001).
11. J.-G. Mao, Z. Wang, and A. Clearfield, *Inorg. Chem.*, **41**, 3713 (2002).
12. A. Shivanyuk, J. C. Friese, S. Doring, J. Rebek, Jr., *J. Org. Chem.*, **68**, 6489 (2003). b) C. Kim, S. J. Lee, I. H. Lee, K. T. Kim, H. H. Song, and H.-J. Jeon, *Chem. Mater.*, **15**, 3638 (2003).
13. S. Phongtamrug, B. Pulpoka, and S. Chirachanchai, *Supra. Chem.*, **16**, 269 (2004).
14. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-261408 for Type I, 258999 for Type II, and 261409 for Type III. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
15. S. M. Malathy Sony, M. Kuppayee, M. N. Ponnuswamy, J. Manonmani, M. Kandasamy, and H.-K. Fun, *Cryst. Res. Technol.*, **2002**, 37, 1360.