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Generation of an Equilibrating Collection of Crystalline Solids from a Dynamic Combinational Library

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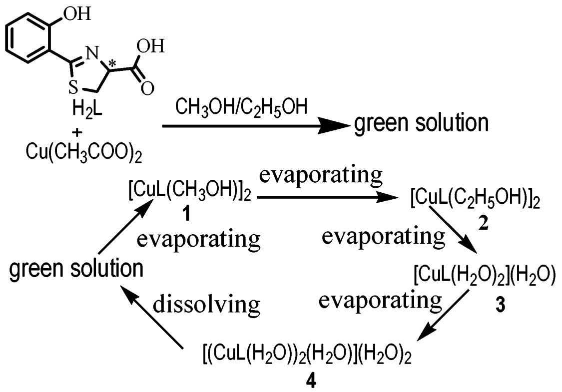
Thermodynamically controlled crystallization of a copper-containing building block [CuL] (H_2L = 2-(2′-hydroxyphenyl)-Δ^2-thiazoline-4-carboxylic acid) from a methanol–ethanol mixture solvent leads to a combinatorial mixture of four crystalline solids, from which each of them is isolated and structurally characterized.

The recent surge in research devoted to designing crystalline solids with molecules that encode well-defined noncovalent motifs is spawned by a fundamental interest in the development of new approaches to the prediction of crystal structures and has subsequently been fueled by the practical opportunities that are offered by new classes of functional materials.[1−3] In order to design species of crystalline solids presenting specific structural and functional features, it is of great importance to establish rules by which control of the molecular packing process can be achieved through chemical programming. Crystallization of compounds from mixed solvent, containing preferentially one out of a wide range of possible crystalline solids, provides an opportunity for studying how the solvent influences the product distribution and thus the molecular packing pathway.

Scheme 1



On the other hand, crystallization of compounds from mixed solvent may yield a mixture of crystalline solids resulting from the reversible combination of different constituents. Such a situation represents a process of dynamic combinatorial chemistry (DCC) of crystal engineering, making potentially available a wide variety of combinations representing the members of a virtual combinatorial library (VCL).[4,5] Of special interest is then the possibility to select and express a given member of the VCL for specific purposes, by means of changing the external factors such as evaporating the solvent. We present here the crystallization of a copper-containing building block [CuL] (H_2L = 2-(2′-hydroxyphenyl)-Δ^2-thiazoline-4-carboxylic acid[6]) in methanol−ethanol (1:1) solvent. From this solution were generated four crystalline solids, and all of them were isolated in the solid state by careful evaporation of the solution in air.

Reaction of the ligand H_2L with $Cu(OAc)_2\cdot 4H_2O$ in methanol−ethanol (1:1) solvent gives a green solution (Scheme 1). After careful evaporation of the solution in air for a few days, green crystals with a strip shape were formed, **1**. After evaporation of the solution for another few days, the crystalline solids of compound **1** disappeared.

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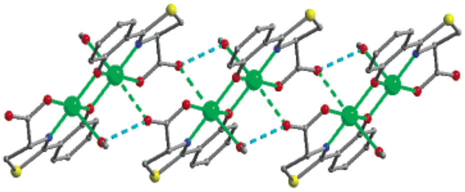

Figure 1. Crystal structure of **1** showing the one-dimensional chain cooperated by weak coordination bonds and hydrogen bonds.

As an alternative, rhomboid crystals were formed, **2**. Elemental[7] and crystal structure analyses[8] clearly indicate that the two kinds of crystals correspond to two different materials.

Compound **1** crystallizes in centrosymmetric space group *Pbca*, and the basic building block for crystal packing is a dicopper $[CuL(MeOH)]_2$ unit. Since the center of the dimeric unit occupies the inversion center, consequently the molecules occur as nonchiral of $\Delta-\Lambda$ configuration for the two copper centers and $R-S$ configuration for the two chiral carbon centers. The copper atom is coordinated in a pyramidal manner with the NO_2 tridentate donors of the ligand and a phenyl oxygen atom from another ligand of the dimer forming the equatorial plane, while the oxygen atom of the methanol molecule occupies the apical position. The uncoordinated carboxyl oxygen atom from another dimeric unit contacts the copper atom with a weak coordination bond connecting the dimeric units into a one-dimensional chain (Figure 1). Hydrogen bonds between the oxygen atoms in methanol molecules and the oxygen atoms are also found to stabilize the molecular aggregation.

Compound **2** is a two-dimensional channel structure (Figure 2) based on the dimeric unit $[CuL(CH_3CH_2OH)]_2$. The copper atom is coordinated in a lengthened octahedral geometry with the NO_2 tridentate donors of the ligand and a phenyl oxygen atom from another ligand of the dimer forming the equatorial plane. The oxygen atom of the ethanol molecule and the carboxyl oxygen atom from another molecule occupy the axial positions, thus the dimeric units are further connected into a two-dimensional network with channels. Ethanol molecules are included in the channels. Classic O−H···O hydrogen bonds between the oxygen atoms of ethanol molecules and the oxygen atoms in carboxyl groups are also found to be important in stabilizing the two-dimensional network.

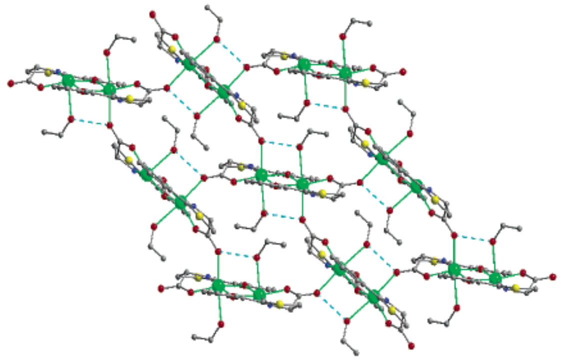

Figure 2. Crystal structure of **2** showing the two-dimensional channeled structure.

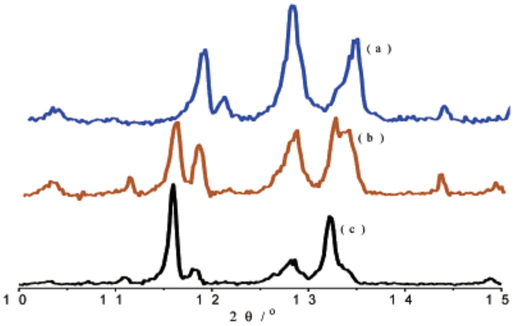

Figure 3. Powder X-ray pattern of the residue formed fresh (a), after standing for a few days (b), and after standing for a month (c).

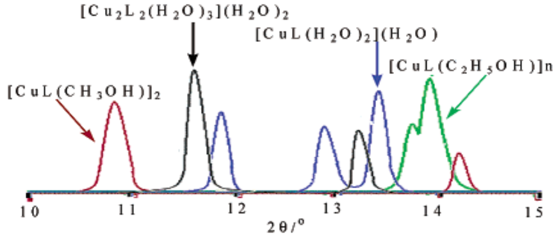

Figure 4. Powder X-ray patterns of the four crystalline solids calculated from the single-crystal structure.

To further evaluate the solvent-dependent crystallization of this system, the solution, with crystals of compound **2** in it, was evaporated until almost dry. The precipitate formed was studied using powder X-ray diffraction analysis (Figure 3a). It is surprising to find that the residue does not exhibit any peak corresponding to either compound **1** or **2** (Figure 4).

Crystal structure and elemental analyses[9] clearly indicate that the residue is a water-coordinated copper compound, **3**. After standing for another few days, powder X-ray diffraction of the residue (Figure 3b) reveals that, in addition to compound **3**, another new compound **4** was formed. One month later, powder X-ray diffraction (Figure 3c) of the last residue clearly reveals that compound **3** disappeared, and compound **4**[10] was isolated. It is also interesting to note that

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(7) For compound **1**, calculated for $(C_{10}H_7NO_3S)Cu(CH_3OH)$: C, 41.7; H, 3.5; N, 4.4. Found: C, 41.1; H, 3.8; N, 4.1. For compound **2**, calculated for $(C_{10}H_7NO_3S)Cu(C_2H_5OH)$: C, 43.6; H, 4.0; N, 4.2. Found: C, 43.3; H, 4.1; N, 3.9.

(8) Crystal structure of **1**, $C_{11}H_{11}NO_4SCu$: M_r = 316.81 g·mol^{-1}, orthorhombic, space group *Pbca*, $a = 16.411(3)$ Å, $b = 7.482(1)$ Å, $c = 19.545(3)$ Å, $V = 2399.7(7)$ Å^3, $Z = 8$, $T = 293$K, $\mu = 1.999$ mm^{-1}, 10969 unique reflections were collected on a Bruker CCD SMART system,[12] R1 = 0.049, and wR2 = 0.082 for 2118 reflections with $I > 2\sigma(I)$. Crystal structure of **2**, $C_{12}H_{13}NO_4SCu$: M_r = 330.83 g·mol^{-1}, monoclinic, space group *C*2/*c*, $a = 23.175(7)$ Å, $b = 7.431(4)$ Å, $c = 14.542(16)$ Å, $\beta = 93.67(2)°$, $V = 2499(3)$ Å^3, $Z = 8$, $T = 293$K, $\mu = 1.923$ mm^{-1}, 5133 unique reflections were collected on a Siemens P4 system,[13] R1 = 0.069, and wR2 = 0.191 for 2212 reflections with $I > 2\sigma(I)$. The structures were solved by direct methods and refined on F^2 using full-matrix least-squares methods using SHELXTL version 5.1.[14] Anisotropic thermal parameters were refined for non-hydrogen atoms. Hydrogen atoms were localized in their calculation positions and refined using a riding model.

(9) For compound **3**. Calculated for $C_{10}H_{13}NO_6SCu$: C, 35.4; H, 3.9; N, 4.1. Found: C, 35.4; H, 4.1; N, 4.1. Crystal structure of **3**, $C_{10}H_{13}NO_6SCu$: M_r = 338.81 g·mol^{-1}, monoclinic, space group $P2_1/c$, $a = 13.876(2)$ Å, $b = 5.543(1)$ Å, $c = 16.389(2)$ Å, $\beta = 97.80(1)°$, $V = 1249.0(3)$ Å^3, $Z = 4$, $T = 293$K, $\mu = 1.938$ mm^{-1}, 5869 unique reflections were collected on a Bruker CCD SMART system, R1 = 0.034, and wR2 = 0.096 for 2203 reflections with $I > 2\sigma(I)$.

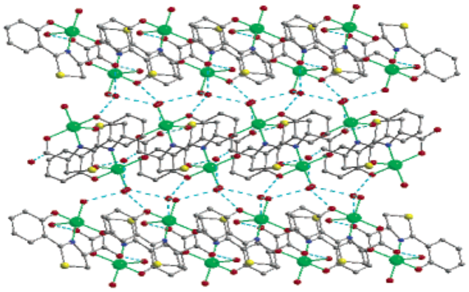

Figure 5. Crystal structure of compound **3** showing the two-dimensional layered structure.

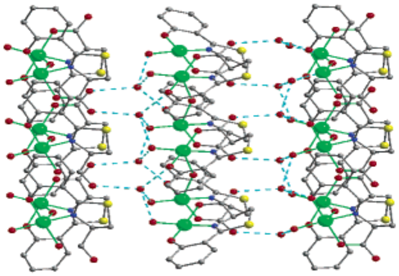

Figure 6. Crystal structure of compound **4** showing the two-dimensional layered structure.

after compound **3** or **4** is dissolved in a methanol–ethanol (1:1) mixture solvent and the solution carefully evaporated again, a new cycle of the crystallization takes place.

Both compounds **3** and **4** have two-dimensional hydrogen-bonded layered structures (Figures 5 and 6). The copper centers in the two compounds have tetragonal pyramidal geometry with the N_2O planar tridentate ligand and one water molecule forming the basal plane and another water molecule occupying the apical position.

In compound **4**, the apical water molecule serves as a bridge to form a dimeric copper unit. Extensive hydrogen bonds are found to link the molecules together, forming a two-dimensional hydrogen-bonding sandwichlike sheet. The inner layer is formed by the $CuNO_4$ units and water molecules linked through hydrogen bonds, and the two outer layers are consist of sulfur atoms and phenyl rings.

Crystal engineering—the planning and construction of crystalline supramolecular architectures from modular building blocks—permits the rational design of functional molecular materials that exhibit technologically useful behavior[11] such as conductivity, superconductivity, ferromagnetism, and nonlinear optical properties. Crystallization of a copper-containing compound in methanol–ethanol (1:1) solvents generates in an equilibrating mixture of four crystalline solids, from which each of them is isolated. These features represent an alternative illustration of a dynamic combinatorial chemistry process. Such a result is quite interesting with respect to crystal engineering and the investigation of the factors that dictate the solid-state selection process.

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Supporting Information Available: Complete synthetic procedure and tables of crystal structure data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) For compound **4**. Calculated for $C_{20}H_{24}N_2O_{11}S_2Cu_2$: C, 36.4; H, 3.7; N, 4.2. Found: C, 36.5; H, 3.8; N, 4.2. Crystal structure of **4**, $C_{20}H_{24}N_2O_{11}S_2Cu_2$: $M_r = 659.61$ g·mol^{-1}, orthorhombic, space group *Pbcn*, $a = 5.635(1)$ Å, $b = 15.872(2)$ Å, $c = 26.691(3)$ Å, $V = 2387.0(4)$ Å^3, $Z = 4$, $T = 293$K, $\mu = 2.022$ mm^{-1}, 10185 unique reflections were collected on a Bruker CCD SMART system, R1 = 0.037, and wR2 = 0.084 for 2107 reflections with $I > 2\sigma(I)$.

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