J. Am. Chem. Soc. **1996,** *118,* 3117−3124

Construction of Three-Dimensional Supramolecular Coordination Copper(I) Compounds with Channel Structures Hosting a Variety of Anions by Changing the Hydrogen-Bonding Mode and Distances

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Received October 10, 1995[⊗]

Abstract: This paper describes four novel hydrogen-bonded copper(I) supramolecules with channel structures. The reactions of copper(I) salt with 3-cyano-6-methyl-2(1*H*)-pyridinone (Hcmp) in acetone have isolated four polymeric coordination products $[Cu(Hcmp)_4]X$, where X = ClO_4^- (**1**), BF_4^- (**2**), PF_6^- (**3**), and $CF_3SO_3^-$ (**4**). All four compounds crystallized in the tetragonal system. Each structure contains a three-dimensional framework of tetrahedral CuN_4 centers linked by intermolecular hydrogen bonds through pyridone N and O atoms in a head-to-tail mode. The very special structural features of the four compounds are related to the two types of hydrogen-bonding. Complexes **1** and **2** with smaller counteranions involve each Hcmp group hydrogen-bonded to two adjacent others (type A), which generates an open square channel filled with aligned ClO_4^- or BF_4^- ions, whereas **3** and **4** involve 1:1 pairwise hydrogen-bonding of Hcmp (type B) which results in four independent interpenetrating diamond-like frameworks with big cavities to accommodate larger anions of PF_6^- and $CF_3SO_3^-$. Novel insight into the unique role played by the hydrogen-bonding mode and distances on the architecture of the network is discussed. The study indicates that the metal complex supramolecular structures can be rationally designed via hydrogen-bonding interactions.

Introduction

In the last few years there has been a surge of research activity in the development of new solid-state structures which involve the self-assembly of molecules into well-defined supramolecules via noncovalent, multiple intermolecular interactions.[1,2] Strong, selective, and directional hydrogen bonding has been noted as a most powerful organizing force in molecular assembly, and the vast majority of publications and reviews have been devoted to the self-organization of organic molecules into one-, two- or three-dimensional hydrogen-bonded architectures.[3−9] The use of metal cations to link organic molecules is an alternative method for the design of new inorganic and organometallic supramolecules.[10−20] Among several notable examples of supramolecular structures, the one with large internal chambers has received considerable attention in both organic and inorganic chemistry since it shows great promise for a number of applications such as selective enclathration, microporosity, and catalytic activity.[4] Wuest recently demonstrated that self-association of di- and tetrapyridone through hydrogen bonding can produce a two- and three-dimensional organic diamondoid network with large internal rectangular channels similar to the behavior of zeolites.[7] Robson and co-workers have described a 3-D $[Cd(CN)_2]_n$ framework with a honeycomb structure containing a hexagonal channel.[10] By means of controlling the

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

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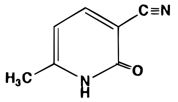
Table 1. Crystallographic Data and Data Collection Parameters for Hcmp and Complexes **1**−**4**

	Hcmp	**1**	**2**	**3**	**4**
empirical formula	$C_7H_6N_2O$	$C_{28}H_{24}N_8C_uClO_8$	$C_{28}H_{24}N_8CuBF_4O_4$	$C_{28}H_{24}N_8CuPF_6O_4$	$C_{29}H_{24}N_8CuSF_3O_7$
fw	134.14	699.55	686.90	745.06	749.16
cryst color, habit	colorless, brick	colorless, cubic	colorless, brick	colorless, cubic	colorless, brick
cryst dimens, mm	0.50 × 0.50 × 0.55	0.28 × 0.29 × 0.42	0.10 × 0.10 × 0.40	0.40 × 0.30 × 0.40	0.25 × 0.25 × 0.25
crystal system	triclinic	tetragonal	tetragonal	tetragonal	tetragonal
space group	$P\bar{1}$	$I\bar{4}$	$I\bar{4}$	$P4/n$	$P\bar{4}$
a, Å	7.447(1)	17.082(3)	17.044(2)	17.686(3)	17.684(2)
b, Å	11.489(2)	17.082(3)	17.044(2)	17.686(3)	17.684(2)
c, Å	3.931(1)	5.228(5)	5.203(3)	5.181(3)	5.250(3)
α, deg	91.50(2)	90.0	90.0	90.0	90.0
β, deg	91.1(2)	90.0	90.0	90.0	90.0
γ, deg	72.77(1)	90.0	90.0	90.0	90.0
V, Å^3	321.1(1)	1525.6(8)	1511.5(5)	1620.6(6)	1641(1)
Z	2	2	2	2	2
d(calcd), g cm^{-3}	1.387	1.523	1.509	1.527	1.515
F(000)	140	716	700	756	764
μ, cm^{-1}	0.91	8.67	7.96	8.05	8.04
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan rate, deg min^{-1}	8.0	2.0	8.0	4.0	8.0
$2\theta_{max}$, deg	55.0	55.0	55.0	55.0	55.0
no. of reflns. measd	1572	1031	1021	2195	2219
no. of unique data	1458	969	960	2068	2093
R_{int}	0.011	0.026	0.033	0.016	0.033
no. of obsd data ($I > 3.00\sigma(I)$)	911	783	753	1153	1262
no. of parameters	91	104	104	107	196
R^a	0.040	0.033	0.051	0.056	0.072
$R_w{}^b$	0.045	0.036	0.056	0.069	0.093
goodness of fit	1.69	1.23	1.79	2.65	3.05

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

direction of hydrogen-bonding, Hamilton constructed an extended helical channel structure from a simple monomeric subunit.[3b] Moreover, various examples of interpenetrating superdiamond frames generating a large cavity have been found in the supramolecular chemistry of hydrogen-bonded organic molecules,[9] and some intercalating diamondoid polymeric complexes up to 7-fold have been described.[11,12,19]

An important goal in this developing field has been the rationalization of the structures of supramolecular crystals based on the structures of their component molecules.[6] Many research groups have attempted the strategy using hydrogen-bonding to control molecular aggregation in organic chemistry, and some success has been achieved.[1b,3−6] By contrast, considerably less is known about hydrogen-bonding control of self-assembly of coordination compounds and few hydrogen-bonded supramolecular coordination compounds are reported.[17] With the major interest in the rational design and synthesis of coordination polymers exhibiting novel frameworks, we have reported a number of one-, two-, and three-dimensional polymeric metal complexes connected through $\pi-\pi$ interactions,[21−24] hydrogen-bonding,[25] or S···S contacts[26] as well as coordination bonds,[22−28] which possess unique bookshelf,[26a] graphite,[22] or diamond-like structures.[28] Here we report a new type of hydrogen-bonded self-assembly of three-dimensional copper(I) complexes of 3-cyano-6-methyl-2(1*H*)-pyridinone (Hcmp) having channels the size of which can be adapted to take in a variety of anions by changing the hydrogen-bonding mode and distances. The reason to choose Hcmp as the building block was 2-fold: firstly this molecule is small which would reinforce the unidentate coordination of each ligand to the tetrahedral copper(I) ion without steric hindrance; secondly Hcmp possesses both a coordination group (CN) and a hydrogen-bonding group[8] (pyridone), and it would be a proper strong and versatile binding motif for formation of hydrogen-bonded metal complex supramolecules.



3-cyano-6-methyl-2(1H)-pyridinone (Hcmp)

Experimental Section

General Methods. All operations were conducted under an argon or ethylene atmosphere by using the standard Schlenk vacuum line technique. The compound $[Cu(CH_3CN)_4]PF_6$ was synthesized according to literature procedures.[29] Acetone treated with $KMnO_4$ was dried over K_2CO_3 from 4 Å molecular sieves. Reagent grade 3-cyano-6-methyl-2(1*H*)-pyridinone was obtained from Aldrich Chemicals. All other chemicals were purchased from Wako Pure Chemical, Inc., and used without further purification. IR spectra were recorded as KBr disks on a JASCO 8000 FT-IR spectrometer. The elemental analyses were carried out in the Department of Chemistry, Tokyo Metropolitan University of Japan.

The ligand Hcmp forms air-stable complexes with each of the copper(I) metal salts. The single crystals of all four complexes were

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Hcmp and Complexes **1**−**3**

	Hcmp	1	2	3
Cu−N(1)		1.978(4)	1.974(6)	1.976(4)
N(1)−C(6)	1.147(3)	1.136(6)	1.136(9)	1.129(6)
C(1)−O(1)	1.247(3)	1.234(5)	1.242(8)	1.240(6)
C(1)−C(2)	1.436(2)	1.452(5)	1.448(8)	1.438(6)
C(1)−N(2)	1.378(2)	1.374(5)	1.388(9)	1.370(6)
C(2)−C(3)	1.371(3)	1.366(6)	1.370(9)	1.357(6)
C(3)−C(4)	1.393(3)	1.386(6)	1.384(9)	1.388(7)
C(4)−C(5)	1.362(3)	1.361(6)	1.368(9)	1.365(7)
C(5)−C(7)	1.490(3)	1.486(6)	1.494(9)	1.488(7)
C(5)−N(2)	1.365(3)	1.360(5)	1.341(8)	1.354(6)
N(1)−Cu−N(1′)		106.2(2)	106.0(3)	105.2(2)
N(1)−Cu−N(1″)		111.1(1)	111.2(2)	111.6(1)
Cu−N(1)−C(6)		172.6(4)	172.7(6)	172.4(4)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **4**

Cu(1)−N(1)	1.98(1)	Cu(2)−N(3)	1.98(1)
N(1)−C(6)	1.09(2)	N(3)−C(13)	1.18(2)
C(1)−O(1)	1.19(2)	C(8)−O(2)	1.26(2)
C(1)−C(2)	1.46(2)	C(8)−C(9)	1.44(2)
C(2)−C(3)	1.36(2)	C(9)−C(10)	1.36(2)
C(3)−C(4)	1.38(2)	C(10)−C(11)	1.41(2)
C(4)−C(5)	1.34(2)	C(11)−C(12)	1.38(2)
C(5)−C(7)	1.50(2)	C(12)−C(14)	1.51(2)
C(5)−N(2)	1.31(2)	C(12)−N(4)	1.34(2)
N(1)−Cu(1)−N(1′)	104.1(7)	N(3)−Cu(2) -N(3′)	110.7(4)
N(1)−Cu(1)−N(1″)	112.2(4)	N(3)−Cu(2) -N(3″)	107.0(8)
Cu(1)−N(1)−C(6)	173.0(1)	Cu(2)−N(3)−C(13)	170.1(1)

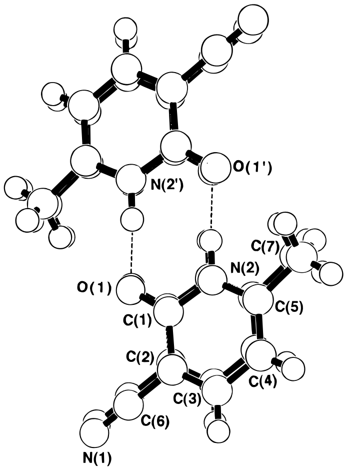

Figure 1. Molecular packing diagram of a free Hcmp molecule on the *ab* plane showing intermolecular hydrogen-bonding (broken lines) and pyridone ring stacking. The same atom numbering scheme is used for other compounds.

grown by slow diffusion of acetone solution of the ligand and metal salt in a sealed glass tube using a 1:1 molar ratio. A number of experiments have also been conducted by varying the metal:ligand ratio as 1:2 or 1:4, but the main products obtained are found to be the same as those from the reactions with a 1:1 molar ratio. **CAUTION:** One of the following preparations uses $Cu(ClO_4)_2 \cdot 6H_2O$, which is potentially explosive.

Synthesis of [Cu(Hcmp)$_4$]ClO$_4$ (1). Copper(II) perchlorate hexahydrate (0.10 mmol, 37.1 mg) and copper plates (3 × 3 × 1 mm, five pieces) were stirred in 5.0 mL of acetone under an ethylene atmosphere for 1 h, and to the resultant colorless solution was added an acetone solution (5.0 mL) containing Hcmp (0.20 mmol, 26.8 mg) under argon. The mixture was stirred and filtered, and the colorless filtrate was transferred to a 10 mm diameter glass tube and layered with 1.0 mL of *n*-pentane as a diffusion solvent. After standing for one week at ambient temperature colorless cubic crystals were isolated at the interface between the two solutions together with a small amount of white precipitate. No other byproducts were obtained. Anal. Calcd for $C_{28}H_{24}N_8CuClO_8$: C, 48.08; H, 3.46; N, 16.02. Found: C, 47.22; H, 3.31; N, 15.19.

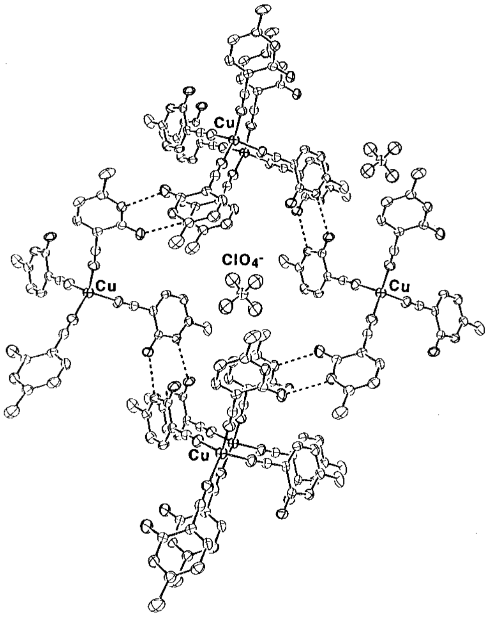

Figure 2. Perspective view of the molecular structure of **1** showing that four [Cu(Hcmp)$_4$]ClO$_4$ monomers are interlinked by hydrogen bonds to form a cavity.

Synthesis of [Cu(Hcmp)$_4$]BF$_4$ (2). The colorless brick crystals of **2** were prepared in the same way as **1** using $Cu(BF_4)_2 \cdot 10H_2O$ (0.10 mmol, 41.7 mg) instead of copper(II) perchlorate hexahydrate.

Synthesis of [Cu(Hcmp)$_4$]PF$_6$ (3). A 16.4 mg sample of [Cu(CH$_3$CN)$_4$]PF$_6$ (0.05 mmol) was added to an acetone solution (5.0 mL) containing Hcmp (6.7 mg, 0.05 mmol) under an argon atmosphere. The solution was stirred and filtered, and the colorless filtrate was transferred to a 10 mm diameter glass tube and layered with 1.0 mL of *n*-pentane as a diffusion solvent. After standing for two weeks at ambient temperature colorless cubic crystals were isolated. Anal. Calcd for $C_{28}H_{24}N_8CuPF_6O_4$: C, 45.14; H, 3.25; N, 15.04. Found: C, 43.74; H, 3.34; N, 14.51.

Synthesis of [Cu(Hcmp)$_4$]CF$_3$SO$_3$ (4). The colorless brick crystals of **4** were prepared in the same way as **1** using $Cu(CF_3SO_3)_2$ (0.10 mmol, 36.1 mg) instead of copper(II) perchlorate hexahydrate. Anal. Calcd for $C_{29}H_{24}N_8CuSF_3O_7$: C, 46.50; H, 3.23; N, 14.96. Found: C, 46.22; H, 3.09; N, 14.68.

X-ray Data Collection, Structure Solution, and Refinement. All the single-crystal X-ray diffraction experiments were performed at room temperature on a Rigaku AFC-5R or Rigaku AFC-6S four-circle diffractometer equipped with a 12 kW rotating anode Mo X-ray source ($\lambda(K_\alpha) = 0.710\,69$ Å). In each case, a suitable single crystal was mounted on a glass fiber. Unit cell parameters were obtained from a least-squares analysis of the setting angles of 25 high-angle reflections in which the appropriate cell angles were constrained to their ideal values. Intensity data were collected by using standard scan techniques ($\omega-2\theta$). In all cases the intensities of 3 standard reflections, monitored at 150 reflection intervals throughout the data collection, remained constant within experimental error, indicating crystal and electronic stability. Space groups were selected on the basis of systematic absences and intensity statistics which in all cases led to satisfactory refinements.

The diffracted intensities were corrected for Lorentz, polarization, and background effects. An empirical absorption correction, using the program DIFABS,[30a] was applied to Hcmp and complex **3**, which resulted in transmission factors ranging from 0.76 to 1.27 and from 0.96 to 1.00, respectively. The structures were solved by a combination of direct method and difference Fourier methods and refined by a full-

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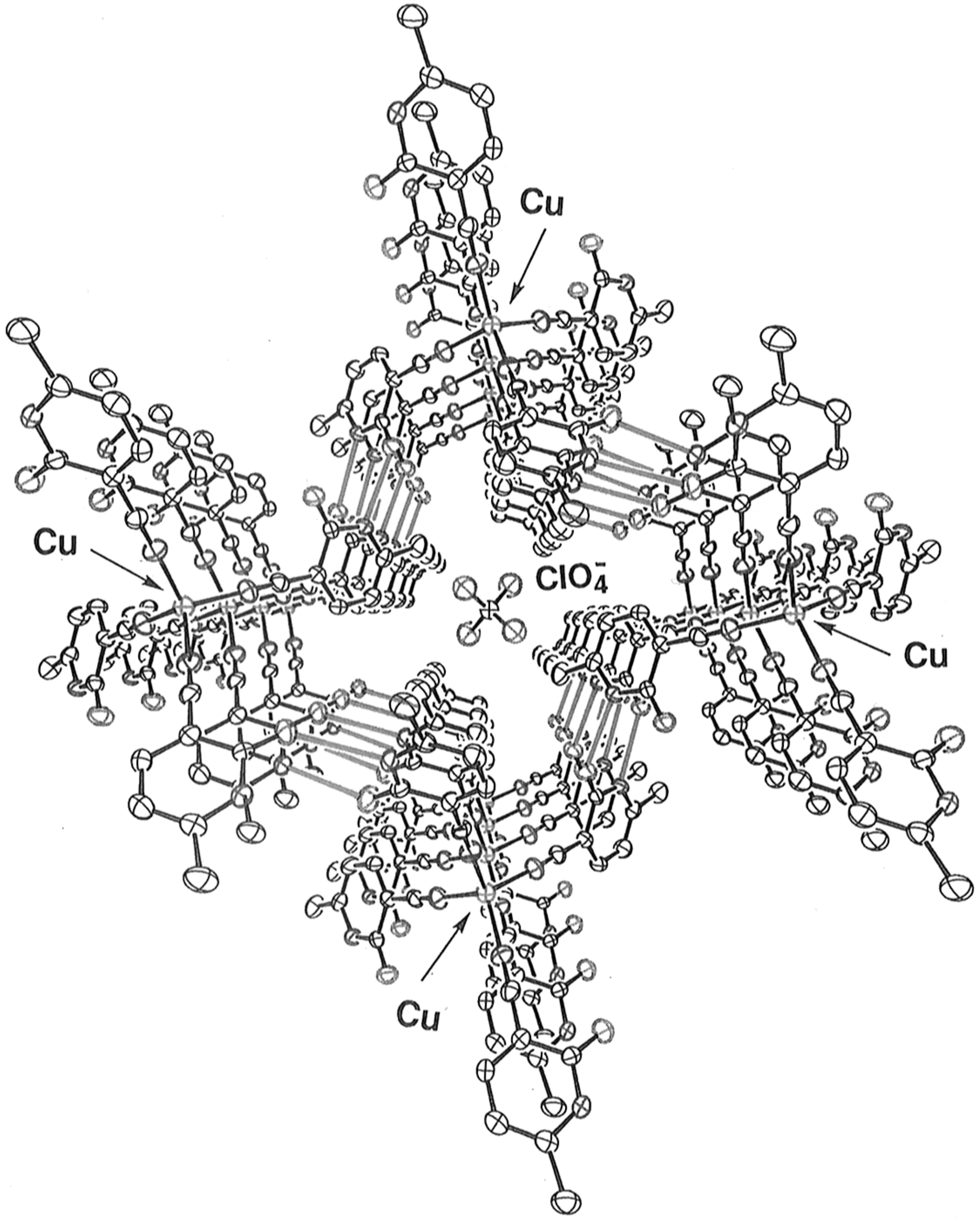

Figure 3. Molecular packing diagram of **1** with open channels along the *c* axis. Hydrogen bonds are shown in red.

matrix least-squares method. The heavy atoms (Cu) were located from an E map calculated by the program MITHRIL.[30b] The remaining non-hydrogen atoms were found by direct-method phase-refinement techniques (DIRDIF).[31] The counteranions ClO_4^-, BF_4^-, PF_6^-, and $CF_3SO_3^-$ were found more or less disordered. The positions of all the hydrogen atoms were determined from difference electron density maps and included in the refinement. Final refinements for all the structures were performed on these data having $I > 3\sigma(I)$ and included anisotropic thermal parameters for all non-hydrogen atoms. Reliability factors are defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[32] Hydrogen atoms were assumed to be isotropic. The final difference maps were flat, showing some peaks not exceeding *ca.* 0.70 $e^-/Å^3$ in any of the structures except for $[Cu(Hcmp)_4]CF_3SO_3$, in which several peaks of *ca.* 1 $e^-/Å^3$ were located on special positions in the center of the large channels in the structure. All crystallographic computations were performed on a VAX computer by using the program system TEXSAN.[33] Details of the X-ray experiments and crystal data for the four complexes together with a free Hcmp molecule are summarized in Table 1. Final atomic coordinates for all structures are given in the supporting information. The selected bond lengths and bond angles are given in Tables 2 and 3.

Results

Crystal Structure of Free Hcmp. The single crystals of Hcmp were obtained by recrystallization of the compound in acetone through slow evaporation. Figure 1 illustrates the molecular packing diagram with atom numbering scheme used throughout this paper. We do not deal with any detailed

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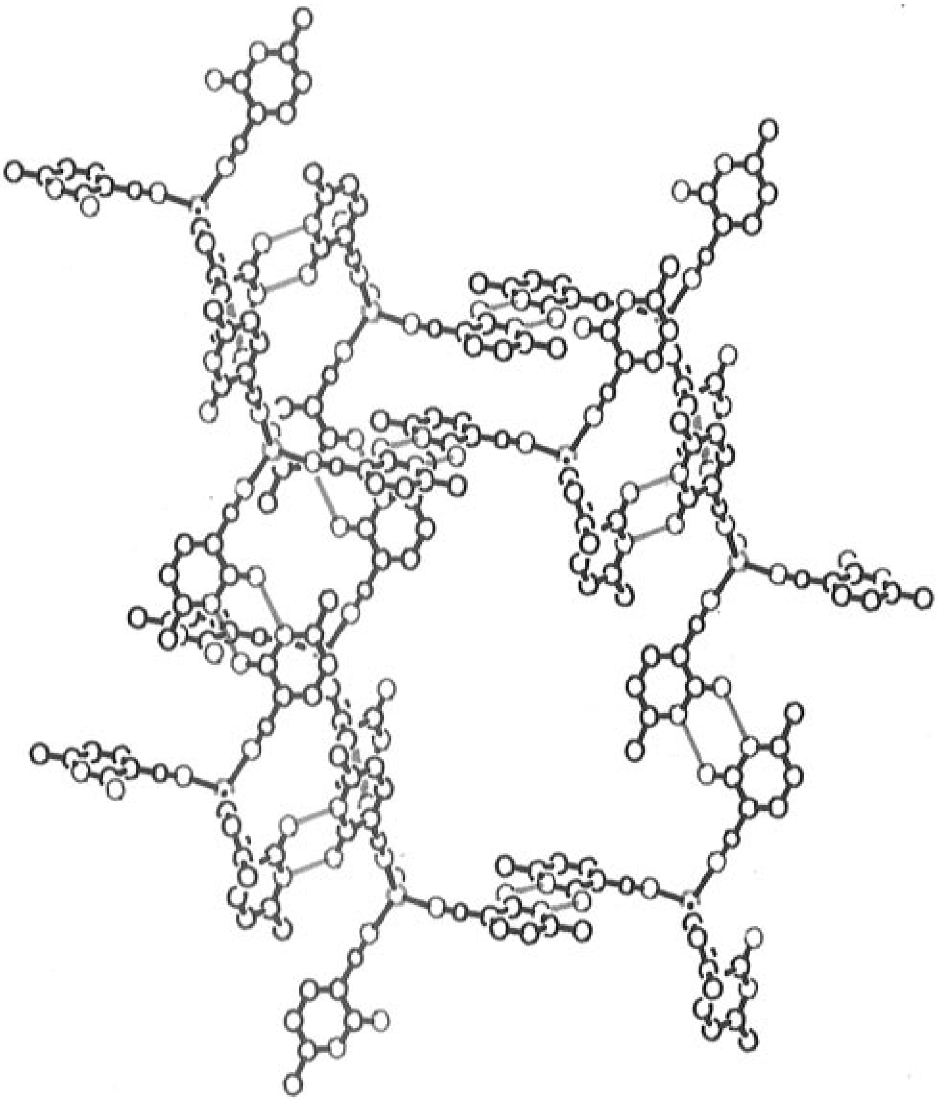

Figure 4. Perspective view of the adamantoid framework in **3** formed by 10 hydrogen-bonded [Cu(Hcmp)$_4$]PF$_6$ subunits. Hydrogen bonds are shown by red lines and Cu atoms by red circles.

structure here, but it should be noted that there are two typical features about this molecule: one is that this molecule forms head-to-tail intermolecular hydrogen bonds through N and O atoms of the pyridone ring[8] with an N···O distance of 2.802 Å; the other is that there is a strong $\pi-\pi$ interaction of pyridone rings with an interplane spacing of 3.39 Å. These features are crucial in determining the overall structure of its complexes with copper(I) ion as presented below.

Crystal Structures of [Cu(Hcmp)$_4$]X (X = ClO$_4^-$, BF$_4^-$). Complexes with Small Anions. X-ray single-crystal structure determinations of the perchlorate salt **1** and tetrafluoroborate salt **2** of Hcmp revealed that they are isomorphous with similar conformations of the molecules. Since the structure of the perchlorate is somewhat more precise than that of the tetrafluoborate, all figures concerned are based on the results of **1**.

In the polymeric structure each copper(I) ion is tetrahedrally coordinated to four cyano groups of symmetry-related Hcmp ligands with N−Cu−N angles of 106.2(2)° and 111.1(1)° for **1** and 106.0(3)° and 111.2(2)° for **2**. The metal centers occupy crystallographic $\bar{4}$ positions, and hence all Cu−N bonds are identical, being 1.978(4) and 1.974(6) Å for **1** and **2**, respectively. Each Hcmp molecule is hydrogen-bonded to two adjacent others through pyridone N and O atoms; i.e., each [Cu(Hcmp)$_4$]X entity is connected to eight neighboring counterparts. The dihedral angle between the hydrogen-bonded Hcmp groups is 83.44° and 84.98° for **1** and **2**, respectively. This results in four [Cu(Hcmp)$_4$]X monomers interconnected through hydrogen bonds, forming a layer with an open cavity occupied by the counteranion as illustrated in Figure 2. The overall structure is made of such layers, each consisting of an infinite square array of copper atoms coordinated with Hcmp groups and bridged by hydrogen bonds leading to the cross-linking of a given layer with those immediately above and below it. The closest interlayer Cu···Cu separation is 5.23 and 5.20 Å for **1** and **2**, respectively. The three-dimensional frames of **1** and **2** contain 4-connected (the Cu atoms) and 3-connected (the ligands) centers in the ratio 1:4. The topological type can be evidenced by placing a nodal point at the centers of the ligands and correctly connecting all the metallic and organic centers. The resulting frame can be related to the uniform 3-D net $(8, {}^{3}_{4})$ described by A. F. Wells,[34] where 4 and 3 are the numbers of links meeting at each point for M and L, respectively, and 8 is the number of points in the smallest circuits. The salient aspect of the structure is that such connectivity generates infinite channels of constant diameter running parallel to the *c* axis, Figure 3, which are filled with the aligned counteranions.

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[34] Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1993; pp 86−93.

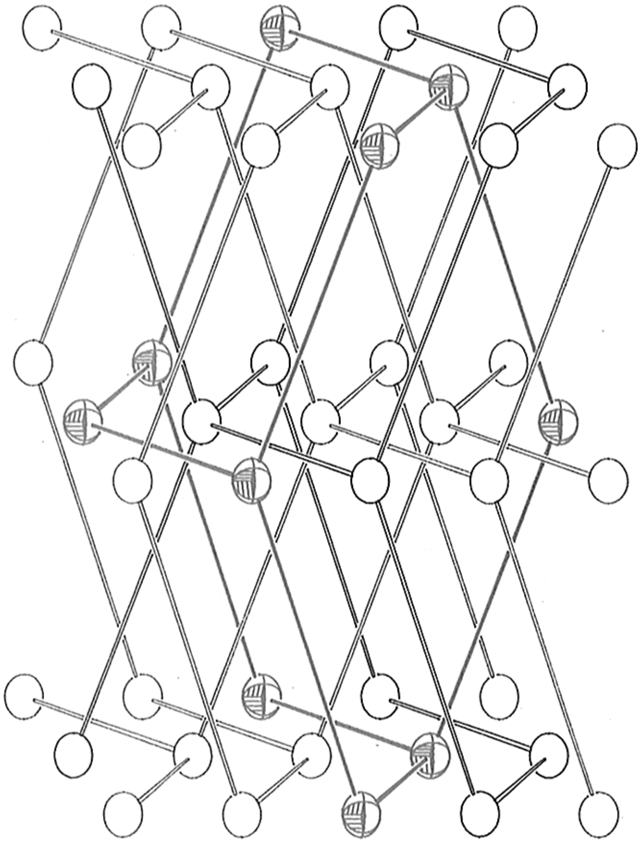

Figure 5. Part of the 4-fold diamondoid superstructure in the crystal lattice of **3** shown in four different colors, formed by the intercalation of four adamantane Cu_{10} frameworks from Figure 4 where only copper atoms are shown.

Crystal Structures of $[Cu(Hcmp)_4]X$ ($X = PF_6^-$, $CF_3SO_3^-$). Complexes with Large Anions. The hexafluorophosphate salt **3** and trifluoromethanesulfonate salt **4** of Hcmp have similar conformations of the molecules although they crystallize in different space groups. All figures concerned in this section are based on the results of **3** as it has more precise structural data. The molecular structure of both complexes consists of $[Cu(Hcmp)_4]X$ entities in which each copper(I) ion, as in **1** and **2**, takes a tetrahedral configuration shared by four Hcmp molecules with N−Cu−N angles of 105.2(2)° and 111.6(1)° for **3** and 104.1(7)°, 112.2(4)°, 107.0(8)°, and 110.7(4)° for **4**. Each Hcmp moiety in the monomeric unit of $[Cu(Hcmp)_4]X$ is head-to-tail hydrogen-bonded to only one adjacent Hcmp molecule, rather than two as in **1** and **2**, with rather smaller dihedral angles of 0° and 11.43° for **3** and **4**, respectively. Thus, one $[Cu(Hcmp)_4]X$ entity is connected to four adjacent others and these repeating units form a three-dimensional adamantane or diamond-like architecture of metal atoms as shown in Figure 4. The structure exists as four independent interpenetrating adamantane networks with intraframe Cu⋯Cu separations of 12.50 Å in both cases, Figure 5. This type of diamondoid architecture has been observed in another copper(I) complex, $[Cu(bipy)_2]PF_6$, with Cu⋯Cu separations of 11.16 Å.[13] Between these frameworks there are no bonds since the closest metal−metal contact is 5.18 and 5.25 Å for **3** and **4**, respectively. The diamondoid frameworks in both complexes are stacked with each other in such way that all the copper centers are found on lines parallel to the *c* axis, which defines enormous linear chambers, Figure 6, similar to the square channel lattice observed in **1** and **2**. The counteranions PF_6^- and $CF_3SO_3^-$ occupy channels which run along the 4-fold crystallographic axes. The anions are disordered on 4-fold axes in both cases, and this in particular may account for the large deviations of the internal bonding parameters and high *R* value in **4**.

Close interplane separations of 3.38 and 3.39 Å between adjacent Hcmp molecules in **3** and **4**, respectively, similar to the corresponding spacing of 3.39 Å for the free Hcmp shown in Figure 1, suggest the presence of strong $\pi-\pi$ interactions between pyridone rings in this type of compound. These separations are essentially the same or even slightly shorter than 3.40 and 3.43 Å for copper(I) complexes of phenazine[23] and 1-aminopyrene,[21] respectively.

Discussion

The most remarkable feature of this study is that different patterns of hydrogen-bonding in the above four copper(I) complexes of Hcmp give rise to two types of different frameworks, namely, a square channel architecture for **1** and **2** and superadamantane networks for **3** and **4.** The IR spectra of the four complexes show weak broad bands at *ca*. 3450 cm^{-1} corresponding to ν_{O-H}, indicative of an enolic contribution. Accordingly, the ν_{N-H} and $\nu_{C=O}$ stretches are also affected to a certain extent. The frequencies observed for the free ligand at 2885 and 3000 cm^{-1} and 1625 and 1680 cm^{-1} corresponding to the N−H and C=O stretching bands, respectively, shifted to *ca*. 3070 and 3200 cm^{-1} and 1600 and 1640 cm^{-1}. Table 4 lists hydrogen bond distances and angles for four compounds. These data, together with IR spectroscopy, confirm the presence of hydrogen bonds.

As described earlier, in **1** and **2** each Hcmp group is hydrogen-bonded to two adjacent Hcmp molecules through pyridone N and O atoms, and this results in each $[Cu(Hcmp)_4]X$ entity being connected to eight others (herein called type A hydrogen bonds). In contrast, each Hcmp molecule in **3** and **4** is head-to-tail hydrogen-bonded to only one neighboring Hcmp group (herein called type B hydrogen bonds), Figure 7. Type A hydrogen bonds link the tetrahedral CuN_4 subunits, resulting in a square channel framework with a relatively small size of cavities (*ca*. 12.1 Å in diameter) filled with small guest anions ClO_4^- and BF_4^-. The hydrogen bond distance N⋯O of 2.876 Å for **1** is slightly longer than 2.845 Å for **2**, consistent with the larger cavity to accommodate the larger size of the perchlorate anion, which leads to the best crystal packing.

When the small anion is changed to the drastically larger PF_6^- or $CF_3SO_3^-$ the cavities in the square channel lattice for complexes **1** and **2** cannot be effectively adapted for large guest ions only by elongating the hydrogen bond distances. If the stoichiometry is to remain the same, one way for the system to respond and avoid this destabilizing repulsion is to rearrange the hydrogen-bonding mode from type A to type B. The type B hydrogen-bonding connects the tetrahedral metal centers, giving a superdiamond network with larger open cavities (*ca*. 13.3 Å in diameter) that just fit the large anions although hydrogen bond distances are slightly shorter than those of type A, Table 4. This suggests that both the H-bonding mode and distances play an important role in crystal engineering of coordination polymers. This finding is in line with previous results of using H-bonding to control organic molecular aggregation for designed structures.[5,35,36]

Although there is a large body of literature available for three-dimensional diamondoid networks formed by hydrogen-bonded organic subunits or by metal cations linked through organic molecules, complexes **3** and **4** presented in this work are novel

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(36) Ghadiri, M. R.; Granja, J. R.; Milligan, R. A.; McRee, D. E.; Khazanovich, N. *Nature* **1993**, *366*, 324.

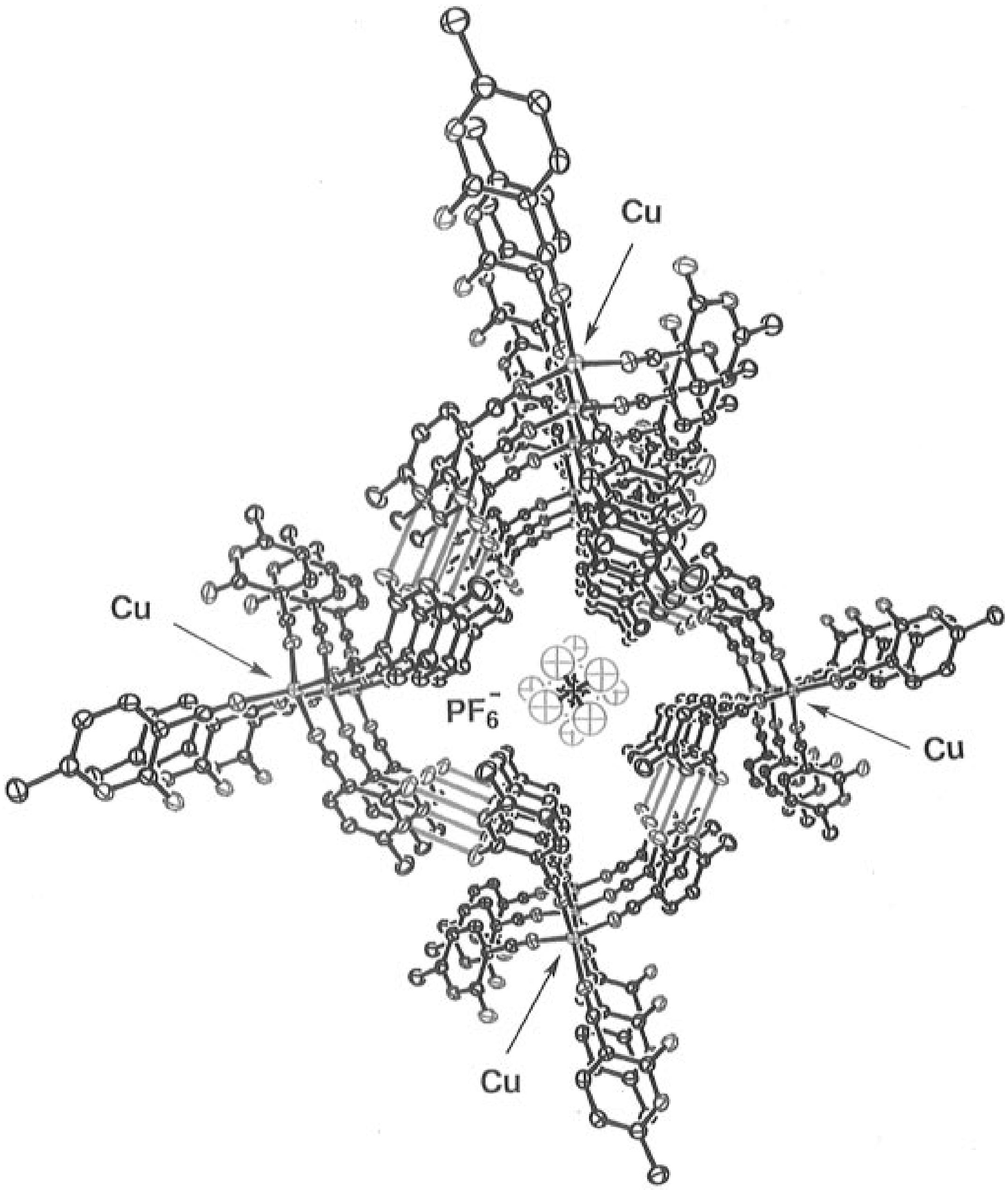

Figure 6. Superdiamond structure in **3** which generates a large channel. Hydrogen bonds are shown in red.

Table 4. Selected Hydrogen Bond Distances (Å) and Angles (deg) for Hcmp and Complexes **1**−**4**

	Hcmp	**1**	**2**	**3**	**4**
		Distances			
N···O	2.802	2.876	2.845	2.785	2.81 2.75
N−H···O	1.816	2.028	1.789	1.815	1.854 1.825
		Angles			
N−H···O	174.73	171.81	173.89	176.91	160.57 174.45

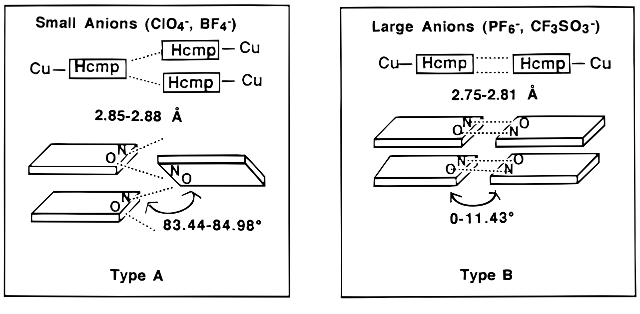

Figure 7. Schematic presentation of two types of hydrogen bonds in **1**−**4**.

members of the limited family of hydrogen-bonded supramolecular coordination compounds having such a framework. A few relevant examples of Cu(I) and Ag(I) complexes are known to have interwoven diamondoid frameworks made up of tetrahedral metal centers connected by bidentate linear ligands such as pyrazine in $[Cu(2,5\text{-}Mepz)_2]PF_6$,[14] 4,4′-bipyridyl in $[Cu(bipy)_2]PF_6$,[13] and $[Ag(bipy)_2]CF_3SO_3$.[20] A unique previous example of the hydrogen-bonded diamondoid framework based on metal centers was reported for $[Mn(CO)_3(\mu_3\text{-}OH)]_4$.[17] However, there exists an obvious difference in assembly between this compound and those of the present work, which can be defined as self-assembly for complexes **3** and **4** and modular or strict self-assembly for the organomanganese complex.[1a] Another relevant aspect of this work that is particularly noticeable is that both **1** and **2** involve a rarely seen square channel network rather than frequently observed honeycomb frameworks as in cadmium cyanide,[10] silver(I) phenazine,[24b] copper(I) benzothiadiazole,[22] and copper(I) pyrazine[13,27a] systems or the helical channel structure as in the hydrogen-bonded pimelic acid polymeric compound.[3b] To the best our knowledge, the structures of copper(I) perchlorate and tetrafluoborate salts of Hcmp represent the first examples of the three-dimensional square channel lattice linked with hydrogen bonds. These square channel solids, like those with honeycomb structures, can also be viewed as composed of host frameworks and might have potential properties in the area of host−guest chemistry.[2,4]

Concluding Remarks

We have undertaken the X-ray structural determination of 3-cyano-6-methyl-2(1*H*)-pyridinone (Hcmp). Since this very simple organic molecule possesses a unique feature of strong intermolecular hydrogen-bonding and $\pi-\pi$ interaction, we have prepared four polymeric copper(I) complexes of this ligand by hydrogen bonds. The structures described in this paper demonstrate that intermolecular hydrogen-bonding interactions have enormous potential for assembling multicomponent systems in which the subunits are metal complexes. Modification of the hydrogen-bonding mode and distances as well as the direction of H-bonding sites[3] can effectively facilitate transition of one framework to the other. This contribution adds several new features to the fast developing field of hydrogen-bonded supramolecular chemistry and aids in the fundamental understanding of molecular recognition and systematic rationalization of molecular aggregation in inorganic crystal engineering. We are currently using basic information we have collected from this preliminary study in an attempt to design numerous other systems and processes.

Acknowledgment. This work was partially supported by a Grant-in Aid for Scientific Research (Nos. 0723226 and 07241260) from the Ministry of Education, Science and Culture in Japan. The authors are also grateful to Kinki University for financial support (Grant GG 1100).

Supporting Information Available: Tables of complete fractional atomic coordinates, anisotropic thermal parameters, bond lengths and angles, hydrogen bond distances and angles, and least-squares plane calculations (31 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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