Inorg. Chem. **1993,** *32,* 5981-5989

Hydrogen-Bond-Directed Assembly of One-Dimensional and Two-Dimensional Polymeric Copper(II) Complexes with Trifluoroacetate and Hydroxypyridine as Ligands: Syntheses and Structural Investigations

Steven R. Breeze and Suning Wang*

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada

Received July 16, 1993●

The assembly of copper(II) complexes through hydrogen-bonding interactions between trifluoroacetate and hydroxypyridine ligands has been investigated. Copper(II) complexes with trifluoroacetate and hydroxypyridine (PyOH) as ligands display various structural features in the solid state. Four members of this family of molecules have been synthesized and characterized structurally. Compound **1** has the formula of $[Cu^{II}(O_2CCF_3)_2(HO_2CCF_3)_2(2\text{-PyOH})]_2[Cu^{II}(2\text{-PyOH})_6]Cl_2$, and the mononuclear units in this complex are linked together to form a one-dimensional structure through hydrogen bonds in the solid state. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with a = 11.134(4) Å, b = 20.434(6) Å, c = 17.112(5) Å, β = 102.45(3)°, and Z = 2. The chloride ion in **1** appears to play an important role in linking the mononuclear units together through hydrogen-bond interactions. The elimination of the chloride from compound **1** resulted in the formation of compound **2** with the formula of $[Cu^{II}(O_2CCF_3)_2(2\text{-PyOH})_3](2\text{-PyOH})(THF)$. Two uncoordinated 2-PyOH ligands link two molecules of **2** together through the formation of hydrogen bonds with the coordinated 2-hydroxypyridine ligands. This dimer is further linked to the other dimer through hydrogen-bonding interactions between the trifluoroacetate ligand and the 2-PyOH ligand to form a one-dimensional structure. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with a = 12.380(5) Å, b = 13.635(5) Å, c = 11.126(6) Å, α = 107.65(4), β = 96.45(4), γ = 111.91(3)°, and Z = 2. In the absence of excess 2-PyOH ligands, compound **3** with the formula of $Cu^{II}_2(O_2CCF_3)_4(2\text{-PyOH})_4$ was obtained. Intermolecular hydrogen bonds between the trifluoroacetate and the 2-PyOH ligand link the dimers together to form a one-dimensional array. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with a = 10.117(2) Å, b = 11.486(2) Å, c = 8.137(1) Å, α = 103.34(1), β = 104.01(1), γ = 87.13(2)°, and Z = 1. Compound **4** with the formula of $Cu^{II}(O_2CCF_3)_2(3\text{-PyOH})_2(THF)_2$ was obtained when the 2-PyOH ligand was replaced by the 3-PyOH ligand. In contrast to the one-dimensional structures of **1**–**3**, compound **4** has a two-dimensional network linked by hydrogen bonds between the trifluoroacetate ligand and the 3-PyOH ligand. Compound **4** crystallizes in the monoclinic space group $P2_1/n$ with a = 9.868(9) Å, b = 8.035(5) Å, c = 16.86(1) Å, β = 93.81(7)°, and Z = 2. The structural features observed in these complexes are attributed to the specific hydrogen-bonding interactions between the ligands.

Introduction

The discovery of high-temperature superconductors has prompted intense research in the development of chemical precursors for ceramic materials.[1] We have been interested in developing synthetic strategies for multicomponent molecular precursor compounds, which could be used directly in the synthesis of ceramic materials. One of the frequently used strategies for the synthesis of multicomponent complexes is to bring metal ions together through bridging ligands.[2] Bifunctional ligands have been particularly useful in such applications.[3] By using bifunctional ligands, several polynuclear metal complexes have been synthesized successfully and employed in the production of superconductors by our group.[3] However, the assembly of metal ions by this method is highly dependent on the coordination geometry and electronic properties of the metal ions and the nature of the ligands. Unless a very elaborate and coordination-specific ligand is used, often one has little control over the composition and the structure of the final product. In contrast, hydrogen-bonding interactions between ligands are specific and directional and have little dependence on the properties of metal ions,[4] although we have found recently that hydrogen-bonding interactions can influence the coordination environment of certain metal ions.[5] Hydrogen-bonding interactions play a critical role in the structures and functions of bimolecules.[6] Hydrogen bonds have also been used widely in the construction of supramolecules.[7] Despite the fact that hydrogen bonds have been frequently observed in inorganic molecules, their applications in the synthesis of inorganic materials have not been well investigated. As part of our continuing efforts to develop synthetic strategies for the systematic synthesis of molecular precursor compounds, we have

---

● Abstract published in *Advance ACS Abstracts,* November 15, 1993.

(1) (a) Segal, D. *Chemical Synthesis of Advanced Ceramic Materials*; Cambridge University Press: Cambridge, U.K., 1989. (b) Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds. *Better Ceramics through Chemistry*; *Mater. Res. Soc. Symp. Proc.*, Pittsburg, PA, 1988; Vol. 121. Zelinski, B. J. J., Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds. *Ibid.* 1990; Vol. 180.

(2) (a) Bidell, W.; Döring, J.; Bosch, H. M.; Hund, H.-U.; Plappert, E.; Berke, H. *Inorg. Chem.* **1993**, *32*, 502. (b) Samuel, J. A.; Vaartstra, B. A.; Huffman, J. C.; Trojan, K. L.; Hatfield, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 9623. (c) Murray, H. H.; Briggs, D. A.; Garzon, G.; Raptis, R. G.; Porter, L. C.; Fackler, J. P., Jr. *Organometallics* **1987**, *6*, 1992.

(3) (a) Wang, S. *Inorg. Chem.* **1991**, *30*, 2252. (b) Wang, S.; Pang, Z.; Wagner, M. J. *Inorg. Chem.* **1992**, *31*, 5381. (c) Wang, S.; Trepanier, S. J.; Wagner, M. J. *Inorg. Chem.* **1993**, *32*, 833. (d) Wang, S.; Trepanier, S. J.; Zheng, J. C.; Pang, Z.; Wagner, M. J. *Inorg. Chem.* **1992**, *31*, 2118. (e) Wang, S.; Smith, K. D. L.; Pang, Z.; Wagner, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1594. (f) Wang, S.; Pang, Z.; Smith, K. D. L.; Wagner, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, in press.

(4) (a) Hamilton, W. C.; Iber, J. A. *Hydrogen Bonding in Solids*; Benjamin: New York, 1968. (b) Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Clarendon: Oxford, U.K., 1975. (c) Vinogradov, S. N.; Linnell, R. H. *Hydrogen Bonding*; Van Nostrand Reinhold Co.: New York, 1971.

(5) Breeze, S. R.; Wang, S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 589.

(6) (a) Jeffery, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer: Berlin, 1991. (b) Thuong, N. T.; Hélène, C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 660.

(7) (a) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304 and references therein. (b) Geib, S. J.; Vicent, C.; Fan, E.; Hamilton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 119.

0020-1669/93/1332-5981$04.00/0

Table I. Crystallographic Data

	1	**2**	**3**	**4**
formula	$C_{56}H_{44}Cu_3Cl_2F_{24}O_{24}N_8$	$C_{28}H_{28}CuF_6O_9N_4$	$C_{28}H_{20}Cu_2F_{12}O_{12}N_4$	$C_{22}H_{26}F_6O_8N_2$
fw	1930.5	742.09	959.42	623.54
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	11.134(4)	12.380(5)	10.117(2)	9.868(9)
b, Å	20.434(6)	13.635(5)	11.486(2)	8.035(5)
c, Å	17.112(5)	11.126(6)	8.137(1)	16.86(1)
α, deg	90	107.65(4)	103.34(1)	90
β, deg	102.45(3)	96.45(4)	104.01(1)	93.81(7)
γ, deg	90	111.91(3)	87.13(2)	90
V, Å^3	3801(1)	1605(1)	892.7(3)	1333(1)
Z	2	2	1	2
ρ_{calc}, g cm^{-3}	1.69	1.50	1.79	1.55
μ	10.4	7.7	13.18	9.1
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69
R^a	0.087	0.049	0.063	0.073
$R_w{}^b$	0.069	0.037	0.060	0.063

[a] $R = (\sum_{i=1}^{n}(|F_o|_i - |F_o|_i))/(\sum_{i=1}^{n}|F_o|_i)$. [b] $R_w = ((\sum_{i=1}^{n}W_i(|F_o|_i - |F_c|_i)^2)/(\sum_{i=1}^{n}W_i|F_o|_i^2))^{1/2}$; $W = 1/\sigma^2(F_o)$.

been investigating the synthesis and structures of hetero- and homonuclear metal complexes linked by hydrogen bonds. In our preliminary study, trifluoroacetic acid and hydroxypyridine have been employed as the ligands because both ligands are not only capable of binding to metal centers but also can form hydrogen bonds by functioning as both hydrogen donor and acceptor. In this report, the syntheses and structures of several copper(II) complexes with one-dimensional and two-dimensional networks linked by hydrogen bonds are described.

Experimental Section

All reactions were carried out under nitrogen atmosphere. $Cu(OCH_3)_2$, hydroxypyridine, and trifluoroacetic acid were purchased from Aldrich Chemical Co., Inc. $Ag(O_2CCF_3)$ was obtained from the Strem Chemical Co. Solvents were freshly distilled prior to use. Elemental analyses were performed at Desert Analytics, Tucson, AZ.

Synthesis of $[Cu^{II}(O_2CCF_3)_2(HO_2CCF_3)_2(2\text{-}PyOH)]_2[Cu^{II}(2\text{-}PyOH)_6]Cl_2$ (1). Compound 1 can be synthesized by several methods. The procedure described here produced this compound in best yield. HO_2CCF_3 (100 mg, 0.88 mmol) was placed in 10 mL of THF. Sodium metal (26 mg, 0.70 mmol) was added to the solution. After the sodium reacted with the acid completely, 160 mg of 2-PyOH (1.68 mmol), 160 mg of $Ag(O_2CCF_3)$ (0.72 mmol), and 75 mg of $CuCl_2$ (0.56 mmol) were added. The mixture was stirred for 12 h at 23 °C. After filtration, a blue-green solution was obtained. Addition of hexane resulted in the formation of the blue-green crystals of the product (205 mg, 0.11 mmol, 20% yield, based on copper). Mp: 129 °C. Anal. Calcd for $C_{56}H_{44}Cu_3Cl_2F_{24}O_{24}N_8$: C, 34.80; H, 2.28; N, 5.80. Found: C, 34.57; H, 2.06; N, 5.50.

Synthesis of $[Cu^{II}(O_2CCF_3)_2(2\text{-}PyOH)_3](2\text{-}PyOH)(THF)$ (2). $Cu(OCH_3)_2$ (100 mg, 0.80 mmol) and 306 mg of 2-PyOH (3.22 mmol) were mixed in 20 mL of THF at 23 °C. HO_2CCF_3 (181 mg, 1.59 mmol) and $Ag(O_2CCF_3)$ (9 mg, 0.04 mmol) were added. (The addition of $Ag(O_2CCF_3)$ was to remove the chloride impurity (approximately 3%) present in the starting material $Cu(OCH_3)_2$.) After being stirred for about 20 h, the solution was filtered and concentrated to about 10 mL. The addition of hexane resulted in the formation of blue-green crystals of the product (363 mg, 0.49 mmol, yield 61%). Mp: 79 °C. Anal. Calcd for $C_{28}H_{28}CuF_6O_9N_4$: C, 45.32; H, 3.78; N, 7.55. Found: C, 45.00; H, 3.45; N, 7.45.

Synthesis of $Cu^{II}_2(O_2CCF_3)_4(2\text{-}PyOH)_4$ (3). $Cu(OCH_3)_2$ (200 mg, 1.60 mmol) and 2-PyOH (450 mg, 4.26 mmol) were mixed in 20 mL of THF at 23 °C. HO_2CCF_3 (486 mg, 4.26 mmol) and $Ag(O_2CCF_3)$ (18 mg, 0.08 mmol) were added to the solution. After being stirred for 20 h, the solution was filtered and concentrated to about 10 mL. The addition of hexane (approximately 3 mL) resulted in the formation light green crystals of the product (199 mg, 0.21 mmol, yield 26%). Mp: 135–140 °C. Anal. Calcd for $C_{28}H_{20}Cu_2F_{12}O_{12}N_4$: C, 35.05; H, 2.10; N, 5.84. Found: C, 35.52; H, 2.15; N, 6.09.

Synthesis of $Cu^{II}(O_2CCF_3)_2(3\text{-}PyOH)_2(THF)_2$ (4). $Cu(OH)_2$ (100 mg, 1.03 mmol) and 3-PyOH (197 mg, 2.07 mmol) were mixed in 20 mL of THF. HO_2CCF_3 (234 mg, 2.05 mmol) was added. After being stirred overnight, the solution was filtered and concentrated to about 10 mL. Hexane (approximately 3 mL) was added. Dark blue crystals were obtained (243 mg, 0.39 mmol, yield 38%). Compound 4 decomposes rapidly upon isolation from the solution due to the loss of THF molecules. Elemental analysis was therefore not performed.

X-ray Crystallographic Analysis. Single crystals of 1–4 were obtained from THF/hexane solutions. All crystals were mounted on glass fibers and sealed by epoxy glue. Data were collected over the range $3 < 2\theta < 50°$ for compounds 1–3 and $3 < 2\theta < 47°$ for compound 4 at 23 °C on a Rigaku four-circle AFC6-S diffractometer with graphite-monochromated Mo Kα radiation operated at 50 kV, 35 mA. Three standard reflections were measured every 150 reflections. No significant decay was observed during the period of data collection for all crystals. All data processing was performed on a Silica Graphic computer using the TEXSAN crystallographic package. Data were corrected for Lorentz-polarization effects and absorptions. Neutral-atom scattering factors were taken from Cromer and Waber.[8]

Crystals of 2 and 3 belong to the triclinic crystal system. Crystals of 1 and 4 belong to the monoclinic crystal system. The space group $P2_1/c$ and $P2_1/n$ were uniquely determined by the systematic absences for 1 and 4, respectively. Molecules of 1, 3, and 4 possess an inversion center of symmetry. The positions of metal atoms in all structures were determined by direct methods (MITHRIL). The remaining non-hydrogen atoms were located by difference Fourier syntheses. The positions of hydrogen atoms bonded to carbon atoms on the hydroxypyridine ligands and the THF molecules were calculated. Their contribution in the structure factor calculation was included. Two of the CF_3 groups in 1 displayed a 2-fold rotation disorder. Two sets of fluorine atoms were located and refined successfully for each of the disordered CF_3 groups. Copper atoms, nondisordered fluorine atoms, and oxygen atoms in 1 were refined anisotropically. The hydrogen atoms bonded to the nitrogen atom of the 2-PyOH ligand in 1 could not be located directly from the difference Fourier maps. Their positions were therefore calculated as well. One of the CF_3 groups in 2 displayed a 2-fold rotation disorder. Two sets of fluorine atoms were located and refined successfully for this group. A THF solvent molecule was located in the lattice of 2 and refined successfully. The hydrogen atoms bonded to the nitrogen atoms of the 2-PyOH ligands in 2 and 3 were located by difference Fourier syntheses. Their positions were not refined. Atoms heavier than the nitrogen atom in 2 and 3 were refined anisotropically. The copper atom, fluorine atoms, oxygen atoms, the nitrogen atom, and some of the carbon atoms in 4 were refined anisotropically. The proton bonded to the oxygen atom of the 3-PyOH ligand in 4 was located directly from the difference Fourier map, and its position was not refined. The crystallographic analysis data are given in Table I.

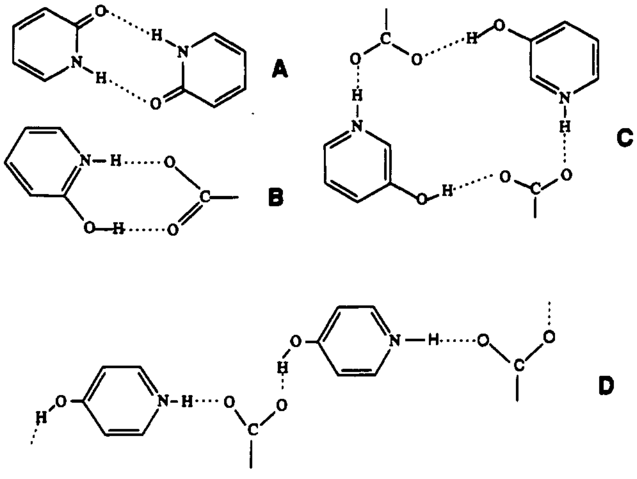
Results and Discussion

Hydroxypyridine and carboxylic acids form hydrogen-bonded aggregates readily in solution and solid state. We chose trifluoroacetic acid in our synthesis, instead of the ordinary acetic acid, because the product with trifluoroacetate is usually more soluble in organic solvents, hence, can be more readily crystallized

---

[8] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 A.

Chart I



than the corresponding acetate products. The structures and the sizes of the hydrogen-bonded aggregates between hydroxypyridine and carboxylic acid are dependent on the position of the hydroxy group on the pyridine ring. For example, 2-hydroxypyridine forms the dimer (**A**) (Chart I) with itself and the dimer (**B**) with carboxylic acids in the solid state.[9a] While 3-hydroxypyridine forms a cyclic tetramer (**C**) with trifluoroacetic acid, 4-hydroxypyridine forms a one-dimensional polymer (**D**) with the trifluoroacetic acid in the solid state.[9b] The hydrogen bonds in these structures are highly directional and specific. Incorporation of metal ions into these hydrogen-bonded systems by partially removing the protons could result in the formation of ordered arrays of metal complexes. The structures of these complexes could then be modified readily by adjusting the hydrogen-bonding components. Indeed, when copper(II) ions are included in these systems, various structures were observed.

Synthesis and Crystal Structure of $[Cu^{II}(O_2CCF_3)_2(HO_2CCF_3)_2(2\text{-}PyOH)]_2[Cu^{II}(2\text{-}PyOH)_6]Cl_2$ (1). Compound **1** was initially isolated from the reaction of $Cu(OCH_3)_2$ with trifluoroacetic acid and 2-PyOH in low yield. The chlorine component was from the starting material $Cu(OCH_3)_2$, which typically contains about 3% chlorine impurity. The yield of compound **1** was improved when $CuCl_2$ was included in the starting materials.

The molecule of **1** consists of three unusual monomeric copper(II) components, one monomer unit with the formula of $[Cu^{II}(2\text{-}PyOH)_6]Cl_2$, sandwiched by two monomer units with the formula of $Cu^{II}(O_2CCF_3)_2(HO_2CCF_3)_2(2\text{-}PyOH)$. This molecule contains an inversion center. An ORTEP diagram showing the structure of the $Cu(O_2CCF_3)_2(HO_2CCF_3)_2(2\text{-}PyOH)$ unit, the $[Cu(2\text{-}PyOH)_6]^{2+}$ cation, and the location of the chloride is given in Figure 1. Positional and thermal parameters are given in Table II. Selected bond distances and angles are given in Table III. All 2-PyOH ligands in **1** are coordinated to the copper(II) centers in the tautomer form of 2-pyridone as evidenced by the characteristic C–O double-bond distances: C(1)–O(1) = 1.26(2), C(6)–O(2) = 1.23(2), C(11)–O(3) = 1.21(2), and C(16)–O(4) = 1.23(2) Å. The proton on the 2-PyOH ligand is therefore believed to bond to the nitrogen atom. The positions of these protons could not be directly determined by X-ray crystallographic analysis. The idealized positions of these protons were calculated and shown in Figure 1. The $[Cu(2\text{-}PyOH)_6]^{2+}$ cation has a elongated octahedral geometry with two of the 2-PyOH ligands occupying the axial position and the Cu(2)–O(2) distance of 2.29(1) Å. This cation was previously unknown, although the compound $[Cu(PyNO)_6]X_2$, PyNO = pyridine *N*-oxide, X = BF_4^- and ClO_4^-, with a regular octahedral geometry has been reported previously,[10] where the PyNO ligand is isoelectronic with the 2-pyridone ligand.

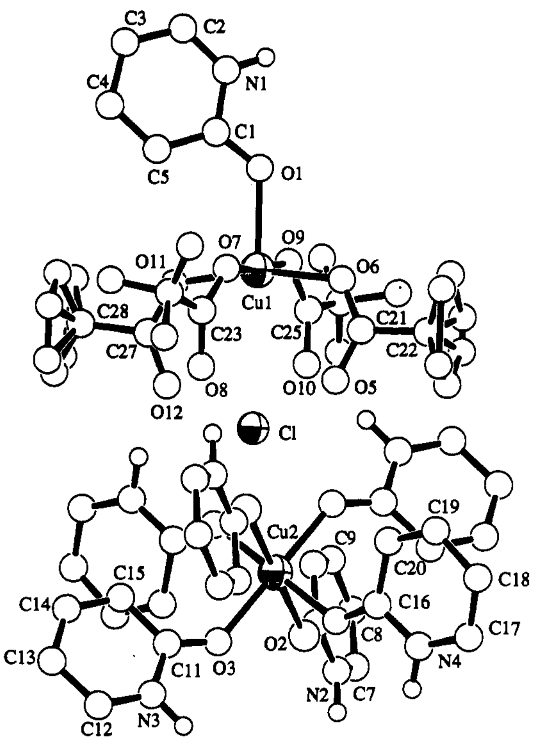


Figure 1. ORTEP diagram for the $Cu(O_2CCF_3)_2(HO_2CCF_3)_2(2\text{-}PyOH)$ unit, the $[Cu(2\text{-}PyOH)_6]^{2+}$ cation, and the chlorine atom in compound **1** with labeling scheme. For clarity, all non-metal atoms are shown by using idealized spheres.

The $Cu(O_2CCF_3)_2(HO_2CCF_3)_2(2\text{-}PyOH)$ unit has a square-pyramidal geometry with the 2-PyOH ligand occupying the axial position and the Cu(1)–O(1) distance of 2.24(1) Å. The distances between the noncoordinating oxygen atoms of the trifluoroacetate ligands and the copper center are more than 3 Å. Therefore, we believe that there is no significant bonding interactions between these oxygen atoms and the copper center. Although square-pyramidal and elongated octahedral geometries have been frequently observed in copper(II) complexes,[11] the "cup" shape structure of the $Cu(O_2CCF_3)_2(HO_2CCF_3)_2(2\text{-}PyOH)$ unit is unusual. It is well-known that the carboxylate groups usually tend to either chelate the metal ion or to bridge two metal centers together to form a Cu_2 dimer compound. The cup structure observed in **1** is therefore usually unstable unless a stabilization force is present. For example, a similar cup structure as that in **1** has been observed in the $[CaCu^{II}(O_2CCH_2OC_6H_4Cl\text{-}2)_4(H_2O)_5]$ compound,[12] where the copper(II) center has a square-pyramidal geometry with a H_2O molecule occupying the axial position and the cup structure is stabilized by a $[Ca(H_2O)_4]^{2+}$ cation which is bonded by the four oxygen atoms of the carboxylate ligands in the copper(II) complex. Recently, we have reported the structure of the $[Bi^{III}(O_2CCF_3)_4Ph][(CH_3)_2NHCH_2CH_2CH_2NH(CH_3)_2]$ complex,[5] where the anionic bismuth complex has a cup structure similar to that observed in **1**. Crystallographic analysis for the bismuth system established that the cup structure is stabilized by selective hydrogen-bonding interactions between the diammonium cation and the oxygen atoms of the anion. Although the protons bonded to oxygen atoms in **1** could not be determined, we believe that the cup structure in **1** is also stabilized by the hydrogen-bonding interactions between the oxygen atoms

---

(9) (a) Gallant, M.; Viet, M. T. P.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 721 and references therein. (b) Wang, S.; Breeze, S. R. Unpublished results.

(10) Keizzers, C. P.; McMullan, R. K.; Wood, J. S.; van Kalkeren, G.; Srinivasan, R.; De Boer, E. *Inorg. Chem.* **1982**, *21*, 4275.

(11) *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McClerverty, J. A., Ed.; Vol. 5, chap. 53, Pergamon Press: Oxford, U.K., 1987; Vol. 5, Chapter 53.

(12) Smith, G.; O'Reilly, E. J. *J. Chem. Soc., Dalton Trans.* **1985**, 243.

Table II. Positional and Thermal Parameters (B_{eq}) for Compound 1

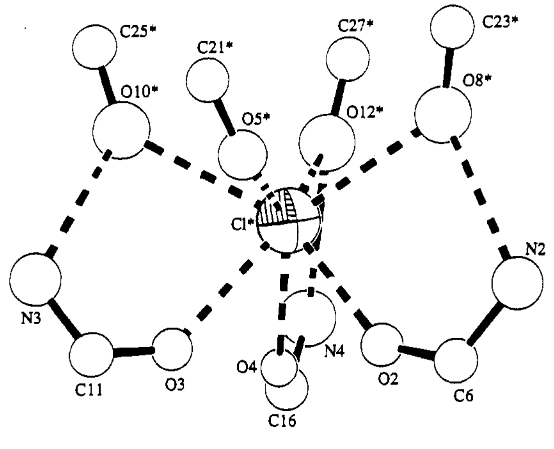
atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Cu(1)	0.4246(2)	0.17870(9)	0.0029(1)	2.65(5)
Cu(2)	0.5000	0.5000	0.0000	3.01(8)
Cl	0.4362(7)	0.3476(3)	0.0038(4)	8.7(2)
O(1)	0.415(1)	0.0692(5)	0.0024(7)	3.4(3)
O(2)	0.658(1)	0.5613(5)	0.0721(7)	3.2(3)
O(3)	0.389(1)	0.5786(5)	0.0078(7)	3.5(3)
O(4)	0.537(1)	0.5497(5)	–0.0926(7)	3.7(3)
O(5)	0.496(1)	0.2932(5)	–0.0999(7)	4.6(4)
O(6)	0.513(1)	0.1847(5)	–0.0867(7)	3.7(3)
O(7)	0.268(1)	0.1827(5)	–0.0716(6)	3.2(3)
O(8)	0.225(1)	0.2899(6)	–0.0702(7)	4.2(4)
O(9)	0.583(1)	0.1642(6)	0.0791(7)	3.9(4)
O(10)	0.632(1)	0.2715(6)	0.0749(8)	5.0(4)
O(11)	0.340(1)	0.1967(6)	0.0907(7)	3.8(4)
O(12)	0.361(1)	0.3046(5)	0.1123(7)	3.7(3)
N(1)	0.355(1)	–0.0327(7)	0.0268(8)	3.3(3)
N(2)	0.836(1)	0.5920(7)	0.1573(8)	3.3(3)
N(3)	0.227(2)	0.6410(8)	–0.0087(9)	4.9(4)
N(4)	0.595(1)	0.5746(7)	–0.2064(9)	3.5(3)
C(1)	0.334(2)	0.0340(9)	0.022(1)	2.9(4)
C(2)	0.278(2)	–0.074(1)	0.049(1)	5.2(5)
C(3)	0.171(2)	–0.055(1)	0.068(1)	5.7(5)
C(4)	0.142(2)	0.014(1)	0.066(1)	6.4(6)
C(5)	0.227(2)	0.0566(9)	0.043(1)	4.2(5)
C(6)	0.746(2)	0.5447(9)	0.125(1)	3.6(4)
C(7)	0.939(2)	0.584(1)	0.212(1)	6.8(6)
C(8)	0.966(2)	0.522(1)	0.247(1)	7.0(6)
C(9)	0.878(2)	0.472(1)	0.218(1)	6.3(6)
C(10)	0.774(2)	0.4809(9)	0.162(1)	4.8(5)
C(11)	0.284(2)	0.5849(10)	0.016(1)	3.7(4)
C(12)	0.112(2)	0.657(1)	–0.005(1)	6.6(6)
C(13)	0.045(2)	0.613(1)	0.031(1)	6.9(6)
C(14)	0.097(2)	0.555(1)	0.054(1)	6.0(6)
C(15)	0.208(2)	0.5387(9)	0.047(1)	4.4(5)
C(16)	0.550(2)	0.5320(9)	–0.159(1)	3.3(4)
C(17)	0.621(2)	0.5634(10)	–0.279(1)	4.8(5)
C(18)	0.596(2)	0.501(1)	–0.310(1)	5.1(5)
C(19)	0.547(2)	0.4523(9)	–0.267(1)	4.5(5)
C(20)	0.525(2)	0.4647(9)	–0.195(1)	3.8(4)
C(21)	0.531(2)	0.2384(10)	–0.114(1)	3.0(4)
C(22)	0.610(2)	0.237(1)	–0.175(1)	5.7(5)
C(23)	0.200(2)	0.231(1)	–0.087(1)	3.1(4)
C(24)	0.071(2)	0.217(1)	–0.132(1)	5.1(5)
C(25)	0.651(2)	0.2129(10)	0.093(1)	3.4(4)
C(26)	0.778(3)	0.199(1)	0.142(2)	6.4(6)
C(27)	0.320(2)	0.251(1)	0.120(1)	3.6(4)
C(28)	0.240(2)	0.244(1)	0.181(2)	8.1(7)

[a] $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(bb^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{22}bb^*cc^* \cos\alpha)$.

Table III. Selected Bond Lengths (Å) and Angles (deg) for Compound 1

	Distances		
Cu(1)–O(1)	2.239(10)	Cu(1)–O(6)	2.00(1)
Cu(1)–O(7)	1.93(1)	Cu(1)–O(9)	1.97(1)
Cu(1)–O(11)	1.97(1)	Cu(2)–O(3)	2.05(1)
Cu(2)–O(3)	2.05(1)	Cu(2)–O(4)	2.00(1)
Cu(2)–O(4)	2.00(1)	O(1)–C(1)	1.26(2)
O(2)–C(6)	1.23(2)	O(3)–C(11)	1.21(2)
O(4)–C(16)	1.23(2)	O(5)–C(21)	1.23(2)
O(6)–C(21)	1.23(2)	O(7)–C(23)	1.24(2)
O(8)–C(23)	1.25(2)	O(9)–C(25)	1.24(2)
O(10)–C(25)	1.24(2)	O(11)–C(27)	1.25(2)
O(12)–C(27)	1.21(2)	N(1)–C(1)	1.38(2)
N(1)–C(2)	1.32(3)	N(2)–C(6)	1.41(2)
N(2)–C(7)	1.33(2)	N(3)–C(11)	1.34(3)
N(3)–C(12)	1.33(3)	N(4)–C(16)	1.35(2)
N(4)–C(17)	1.35(3)	C(1)–C(5)	1.39(3)
C(2)–C(3)	1.35(3)	C(3)–C(4)	1.43(3)
C(4)–C(5)	1.41(3)	C(6)–C(10)	1.46(3)
C(7)–C(8)	1.39(3)	C(8)–C(9)	1.44(3)
C(9)–C(10)	1.34(3)	C(11)–C(15)	1.44(3)
C(12)–C(13)	1.40(4)	C(13)–C(14)	1.34(3)
C(14)–C(15)	1.31(3)	C(16)–C(20)	1.51(3)
C(17)–C(18)	1.39(3)	C(18)–C(19)	1.42(3)
C(19)–C(20)	1.32(3)	C(21)–C(22)	1.50(3)
C(23)–C(24)	1.51(3)	C(25)–C(26)	1.51(3)
C(27)–C(28)	1.53(4)		
	Angles		
O(1)–Cu(1)–O(6)	95.0(5)	O(1)–Cu(1)–O(7)	90.3(4)
O(1)–Cu(1)–O(9)	83.5(4)	O(1)–Cu(1)–O(11)	99.2(5)
O(6)–Cu(1)–O(7)	90.9(5)	O(6)–Cu(1)–O(9)	89.9(5)
O(6)–Cu(1)–O(11)	165.7(5)	O(7)–Cu(1)–O(9)	173.8(5)
O(7)–Cu(1)–O(11)	89.0(5)	O(9)–Cu(1)–O(11)	91.8(5)
O(3)–Cu(2)–O(3)	180.0	O(3)–Cu(2)–O(4)	83.3(5)
O(3)–Cu(2)–O(4)	96.7(5)	O(3)–Cu(2)–O(4)	96.7(5)
O(3)–Cu(2)–O(4)	83.3(5)	O(4)–Cu(2)–O(4)	180.0
Cu(1)–O(1)–C(1)	127(1)	Cu(2)–O(3)–C(11)	134(1)
Cu(2)–O(4)–C(16)	131(1)	Cu(1)–O(6)–C(21)	120(1)
Cu(1)–O(7)–C(23)	126(1)	Cu(1)–O(9)–C(25)	115(1)
Cu(1)–O(11)–C(27)	128(1)		

of the trifluoroacetate ligands, the chlorine atom, and the nitrogen and oxygen atoms of the 2-PyOH ligands. The distances between the chlorine atom and the oxygen atoms of the trifluoroacetate ligands are significantly shorter than the sum of van der Waals radii of the chlorine ion and the oxygen atom (3.21 Å),[16] Cl–O(5) = 2.31(2), Cl–O(8) = 2.69(1), Cl–O(10) = 2.74(1), and Cl–O(12) = 2.36(1) Å, suggesting the presence of very strong hydrogen bonds[13] between Cl, O(5), and O(12) and possible hydrogen bonds between Cl, O(8), and O(10). The very short separations of Cl–O(2) = 2.38(1), Cl–O(4) = 2.57(1), and Cl–O(3) = 2.51(1) Å also suggest the presence of possible strong hydrogen bonds between the chlorine atom and the oxygen atoms of the 2-PyOH ligands. In addition to the hydrogen bonds between oxygen atoms and the chlorine atom, it also appears that there are additional hydrogen-bonding interactions between three of the oxygen atoms of the trifluoroacetate ligands and the nitrogen atoms of pyridone ligands, which could be called the second-sphere hydrogen-bonding interactions. The distances and geometries of the atoms involved in hydrogen bonds surrounding the chlorine ion are shown in Figure 2. On the basis of the charges of the metal ions and ligands, there are a total of five protons available for hydrogen bonds between the two copper monomers and the chlorine ion, two from the trifluoroacetic acid ligands and three from the 2-PyOH ligands. However, as shown in Figure 2, there are at least 10 possible hydrogen bonds. Although the



Cl - O2	2.38(1)	Cl - O3	2.51(1)
Cl - O4	2.57(1)	Cl - O8	2.69(1)
Cl - O10	2.74(1)	Cl - O12	2.36(1)
Cl - O5	2.31(2)	N2 - O8	2.84(2)
N3 - O10	2.78(2)	N4 - O12	2.93(2)

Figure 2. Diagram showing the geometric features and parameters of the chlorine atom and the neighbor atoms which may be involved in hydrogen bonds with the chlorine atom in compound **1**. The dashed lines indicate the possible hydrogen bonds.

---

(13) (a) Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91. (b) Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320.

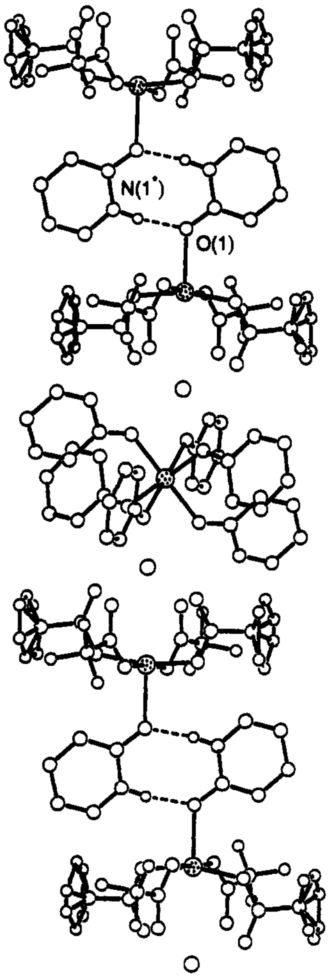


Figure 3. Diagram showing the extended one-dimensional structure and intermolecular hydrogen bonds of compound 1.

sharing of one proton by more than two atoms is a possible explanation, it is more likely that this may be caused by the occupancy disorder of the protons in the crystal lattice, leading to a statistically random distribution of the protons between atoms with comparable electron negativity. To our knowledge, such a hydrogen-bonded cage or trap for the chlorine ion is unprecedented. A better crystallographic study, especially neutron diffraction analysis, will no doubt provide valuable information for hydrogen-bonding interactions in this copper system. Unfortunately, due to the limitation of our X-ray diffraction facilities, we have not been able to conduct such a study. The tricopper units are further linked to each other through intermolecular hydrogen bonds between the 2-PyOH ligands (O(1)–N(1*) = 2.81(2) Å) to form a one-dimensional hydrogen-bonded chain as shown in Figure 3. The Cu(1)–Cu(2) separation is 6.621(3) Å, while the Cu(1)–Cu(1*) separation is 7.499(4) Å, which excludes any significant Cu–Cu interactions.

It appears that the first-sphere hydrogen-bonding interactions between the chlorine and the oxygen atoms play a critical role in the formation and the stability of the trimer structure because our attempts to eliminate the chlorine ion from this system by the addition of silver(I) or thallium(I) salt lead to either decomposition or the formation of new species such as compound 2. The stability of the $[Cu(2\text{-}PyOH)_6]^{2+}$ cation also appears to be dependent on the hydrogen-bonding force in this system because our attempt to synthesize this cationic complex independently by using anions such as PF_6^- as the counterion was unsuccessful.

Table IV. Positional and Thermal Parameters (B_{eq}) for Compound 2

atom	x	y	z	B_{eq},[a] Å^2
Cu(1)	0.82769(7)	0.11370(7)	0.31288(8)	3.03(2)
F(1)	0.891(3)	0.500(2)	0.492(6)	11(1)
F(2)	0.876(2)	0.503(2)	0.608(2)	10.0(6)
F(3)	0.803(5)	0.454(3)	0.627(3)	10(1)
F(4)	0.699(2)	0.402(2)	0.500(3)	10.0(8)
F(5)	0.708(3)	0.405(3)	0.443(4)	9.1(10)
F(6)	0.827(3)	0.465(2)	0.408(2)	8.0(6)
F(7)	1.2908(4)	0.3153(5)	0.3588(5)	12.4(2)
F(8)	1.1694(4)	0.3104(4)	0.2092(4)	7.4(1)
F(9)	1.1973(5)	0.1665(4)	0.1952(5)	9.9(2)
O(1)	0.8070(3)	0.2556(3)	0.3504(4)	3.7(1)
O(2)	0.8582(4)	0.2895(4)	0.5630(4)	6.2(1)
O(3)	0.9845(3)	0.1902(3)	0.2803(4)	3.7(1)
O(4)	1.1154(4)	0.1932(4)	0.4421(4)	6.0(1)
O(5)	0.8588(3)	−0.0101(3)	0.3379(4)	3.8(1)
O(6)	0.7554(3)	0.0488(3)	0.0910(3)	3.5(1)
O(7)	0.6615(3)	0.0379(3)	0.3277(4)	3.4(1)
O(8)	0.6605(4)	0.1513(3)	−0.1373(4)	4.2(1)
O(9)	0.4994(6)	0.3863(6)	0.8242(7)	11.1(2)
N(1)	0.8103(4)	0.2540(4)	0.0480(5)	3.2(1)
N(2)	0.9340(4)	−0.1361(4)	0.3407(4)	3.0(1)
N(3)	0.5874(4)	−0.0447(4)	−0.0793(4)	3.1(1)
N(4)	0.5157(4)	−0.1032(4)	0.3580(4)	3.4(1)
C(1)	0.8287(6)	0.3112(5)	0.4713(7)	3.5(1)
C(2)	0.8081(8)	0.4192(7)	0.4990(8)	4.4(2)
C(3)	1.0848(6)	0.2076(5)	0.3430(7)	3.7(1)
C(4)	1.1875(7)	0.2528(7)	0.2781(8)	4.8(2)
C(5)	0.7369(5)	0.2471(5)	−0.0585(6)	3.3(1)
C(6)	0.7557(6)	0.3532(6)	−0.0702(6)	4.6(2)
C(7)	0.8412(6)	0.4514(6)	0.0199(7)	5.5(2)
C(8)	0.9151(6)	0.4529(6)	0.1269(7)	5.1(2)
C(9)	0.8973(6)	0.3522(6)	0.1374(6)	4.1(1)
C(10)	0.9103(5)	−0.0695(5)	0.2817(5)	2.8(1)
C(11)	0.9416(5)	−0.0751(5)	0.1625(6)	3.5(1)
C(12)	0.9948(6)	−0.1449(6)	0.1131(6)	4.6(2)
C(13)	1.0162(6)	−0.2124(6)	0.1774(7)	4.7(2)
C(14)	0.9853(5)	−0.2070(5)	0.2889(6)	3.9(1)
C(15)	0.6629(5)	−0.0414(5)	0.0248(6)	3.1(1)
C(16)	0.6243(5)	−0.1451(5)	0.0473(6)	3.8(1)
C(17)	0.5212(6)	−0.2378(5)	−0.0277(6)	4.0(1)
C(18)	0.4489(5)	−0.2339(5)	−0.1330(6)	3.7(1)
C(19)	0.4839(5)	−0.1368(5)	−0.1554(6)	3.6(1)
C(20)	0.6302(5)	−0.0190(5)	0.4001(6)	3.0(1)
C(21)	0.7003(5)	−0.0036(5)	0.5192(6)	4.0(1)
C(22)	0.6554(6)	−0.0740(6)	0.5841(6)	4.6(2)
C(23)	0.5389(6)	−0.1597(5)	0.5366(6)	4.4(2)
C(24)	0.4706(6)	−0.1717(5)	0.4257(6)	4.3(1)
C(25)	0.3744(9)	0.3463(8)	0.7810(9)	9.4(3)
C(26)	0.3516(8)	0.4243(8)	0.7242(8)	8.4(2)
C(27)	0.4684(8)	0.4793(7)	0.6892(8)	8.1(2)
C(28)	0.5595(8)	0.4775(8)	0.7879(9)	8.8(3)

[a] $B_{eq} = (8/3)\pi^2(u_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(bb^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha)$.

Synthesis and Crystal Structure of $[Cu^{II}(O_2CCF_3)_2(2\text{-}PyOH)_3]$-(2-PyOH)(THF) (2). Compound 2 was isolated readily from the reaction of $Cu(OCH_3)_2$, trifluoroacetic acid, and 2-PyOH in a 1:2:4 ratio in the presence of $Ag(O_2CCF_3)$ in THF. The structure of 2 was determined by X-ray diffraction analysis. Positional and thermal parameters are given in Table IV. Selected bond distances and angles are given in Table V. An ORTEP diagram for the molecule of 2 is shown in Figure 4. The copper ion in 2 has a square-pyramidal geometry with two 2-PyOH ligands and two trifluoroacetate ligands occupying the equatorial positions and one 2-PyOH ligand occupying the axial position, Cu(1)–O(6) = 2.293(4) Å. Again, as found in 1, the 2-PyOH ligands in 2 coordinate to the copper center in the form of pyridone through the oxygen atoms only. The C–O bond distances in the 2-PyOH ligands range from 1.250(6) to 1.274(6) Å. The protons bonded to the nitrogen atoms of the 2-PyOH ligands were located directly from the X-ray crystallographic analysis.

The most interesting feature of this molecule is the presence of an uncoordinated 2-PyOH ligand which attaches itself to the copper complex through the formation of two intramolecular hydrogen bonds with a coordinated 2-PyOH ligand between the oxygen atom and the nitrogen atom, N(1)–O(6) = 2.826(6) and N(3)–O(8) = 2.784(6) Å. This 2-PyOH ligand is further

Table V. Selected Bond Lengths (Å) and Angles (deg) for Compound 2

	Distances		
Cu(1)–O(1)	1.971(4)	Cu(1)–O(3)	1.965(4)
Cu(1)–O(5)	1.956(4)	Cu(1)–O(6)	2.295(4)
Cu(1)–O(7)	1.980(4)	O(2)–C(1)	1.201(7)
O(1)–C(1)	1.267(7)	O(4)–C(3)	1.221(7)
O(3)–C(3)	1.253(7)	O(6)–C(15)	1.256(6)
O(5)–C(10)	1.273(6)	O(8)–C(5)	1.251(6)
O(7)–C(20)	1.275(6)	N(1)–C(9)	1.348(7)
N(1)–C(5)	1.365(7)	N(2)–C(14)	1.368(7)
N(2)–C(10)	1.363(6)	N(3)–C(19)	1.359(7)
N(3)–C(15)	1.382(6)	N(4)–C(24)	1.373(7)
N(4)–C(20)	1.362(6)	C(3)–C(4)	1.552(9)
C(1)–C(2)	1.533(8)	C(6)–C(7)	1.344(8)
C(5)–C(6)	1.427(8)	C(8)–C(9)	1.350(8)
C(7)–C(8)	1.408(8)	C(11)–C(12)	1.368(8)
C(10)–C(11)	1.411(7)	C(13)–C(14)	1.328(8)
C(12)–C(13)	1.403(8)	C(16)–C(17)	1.356(8)
C(15)–C(16)	1.423(7)	C(18)–C(19)	1.341(7)
C(17)–C(18)	1.420(7)	C(21)–C(22)	1.364(8)
C(20)–C(21)	1.411(7)	C(23)–C(24)	1.342(8)
	Angles		
O(1)–Cu(1)–O(3)	89.3(2)	O(1)–Cu(1)–O(5)	161.1(2)
O(1)–Cu(1)–O(6)	95.3(2)	O(1)–Cu(1)–O(7)	88.3(2)
O(3)–Cu(1)–O(5)	95.4(2)	O(3)–Cu(1)–O(6)	84.8(2)
O(3)–Cu(1)–O(7)	173.6(2)	O(5)–Cu(1)–O(6)	103.3(2)
O(5)–Cu(1)–O(7)	88.8(2)	O(6)–Cu(1)–O(7)	89.5(1)
Cu(1)–O(1)–C(1)	113.1(4)	Cu(1)–O(3)–C(3)	126.2(4)
Cu(1)–O(5)–C(10)	133.4(4)	Cu(1)–O(6)–C(15)	124.5(4)
Cu(1)–O(7)–C(20)	125.7(4)		

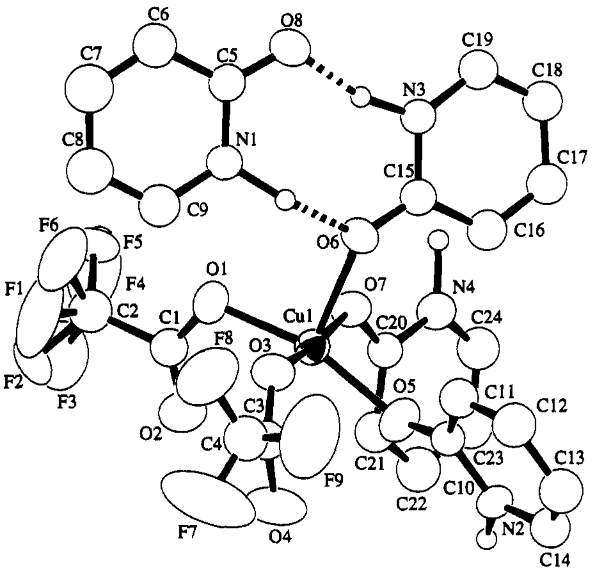


Figure 4. ORTEP diagram showing the molecular structure of compound 2 with labeling scheme and 50% thermal ellipsoids. The THF solvent molecule was omitted for clarity.

connected to another coordinated 2-PyOH ligand of a neighboring molecule through the formation of an intermolecular hydrogen bond, N(4*)–O(8) = 2.823(6) Å. In compound 1, the chlorine atom functions not only as a hydrogen-bond bridge but also as a counterion to balance the charge of the trimer complex. In contrast, in compound 2, the neutral uncoordinated 2-PyOH ligand functions solely as a hydrogen-bond bridge to bring two $Cu(O_2CCF_3)_2(2\text{-PyOH})_2$ units together (Figure 5). Although hydrogen bonds between coordinated ligands and counterions have been frequently observed in inorganic complexes, a neutral uncoordinated ligand as a hydrogen-bond bridge between molecules such as that observed in 2 has rarely been reported. One exception is the water molecule, which has been found previously to function as a neutral hydrogen-bond-bridge in certain inorganic complexes.[14] Recently, Zaworoko and co-workers have reported the construction of a three-dimensional network consisting of the $[M(CO)_3(\mu_3\text{-}OH)]_4$ units, M = Mn and Re, interlinked by propanediamine or 4,4-bipyridine ligands through hydrogen bonds only.[15]

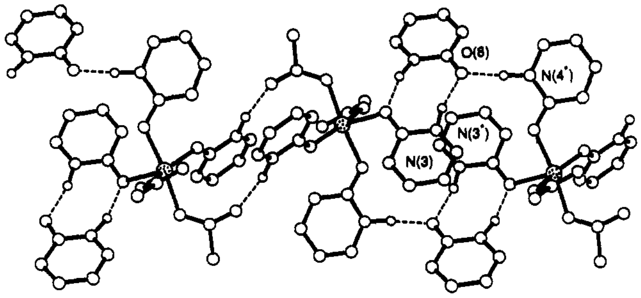


Figure 5. Diagram showing the one-dimensional hydrogen-bonded network of compound 2. The fluorine atoms were not shown for clarity.

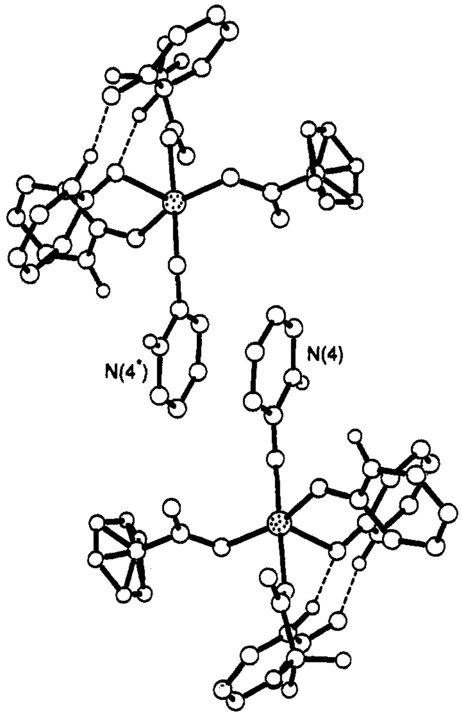


Figure 6. Diagram showing the stacking of two pyridine rings from two neighboring polymer chains in the crystal lattice of 2.

The 2-PyOH-linked dimer of 2 is further linked to the other dimer through the formation of two intermolecular hydrogen bonds between the trifluoroacetate ligand and a coordinated 2-PyOH ligand, N(2)–O(4) = 2.817(6) Å. The Cu–Cu separation between this linkage is the shortest in the structure, 7.672(2) Å. As a result of hydrogen bonds, a one-dimensional array was achieved as shown in Figure 5. The O(2) atom of the trifluoroacetate ligand appears to occupy the sixth position of the copper center with a Cu(1)–O(2) separation of 2.946(5) Å. There are extensive stackings of the aromatic rings in this system. The N(3) and N(3*) rings are parallel to each other with an average separation distance of 4.39 Å. The most significant stacking is between the N(4) and N(4*) pyridine rings from two neighboring chains. These two rings are completely eclipsed (Figure 6), and the atomic distances between these two rings range from 3.71 to 3.73 Å, which are comparable with the sum[16] of van der Waals radii of the carbon atom (3.70 Å).

The uncoordinated 2-PyOH hydrogen-bond linkage is believed to play an important role in the formation of the compound 2 and

---

(14) (a) Sletten, J. *Acta Chem. Scand. Sect. A* **1983**, *37*, 569. (b) Wang, S.; Smith, K. D. L.; Pang, Z.; Wagner, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, *1594*.

(15) Copp, S. B.; Subramanian, S.; Zaworoko, M. J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 706.

(16) Emsley, J. *The Elements*, 2nd ed.; Clarendon Press: Oxford, U.K., 1991.

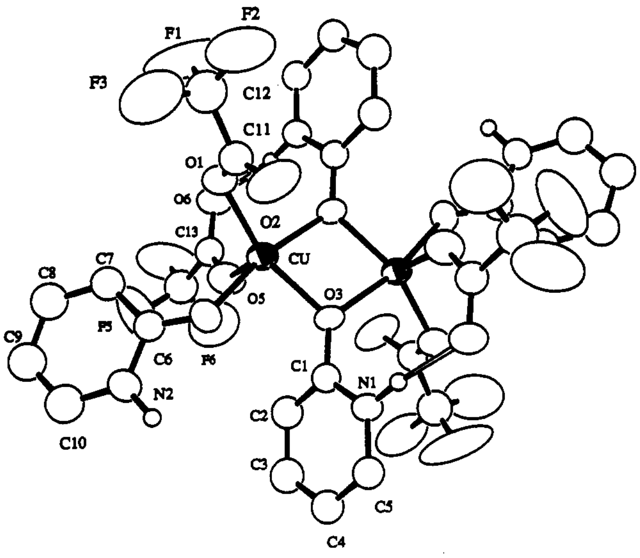


Figure 7. ORTEP diagram showing the dimeric structure of **3** with labeling scheme and 50% thermal ellipsoids.

Table VI. Positional and Thermal Parameters (B_{eq}) for Compound **3**

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Cu	0.0176(1)	0.13902(8)	0.0725(1)	3.50(4)
F(1)	0.3720(6)	0.3333(9)	−0.005(1)	13.9(5)
F(2)	0.5059(6)	0.2500(7)	0.155(1)	12.6(5)
F(3)	0.408(1)	0.3939(8)	0.249(1)	17.9(7)
F(4)	−0.3827(6)	0.3023(7)	−0.4120(8)	11.0(4)
F(5)	−0.3705(7)	0.3547(6)	−0.1433(8)	10.7(4)
F(6)	−0.4324(6)	0.1856(7)	−0.277(1)	11.0(4)
O(1)	0.1590(5)	0.2435(4)	0.0562(6)	4.1(2)
O(2)	0.3029(6)	0.1588(6)	0.2473(8)	7.5(3)
O(3)	−0.0603(5)	−0.0071(4)	0.1124(6)	3.9(2)
O(4)	−0.0251(5)	0.2372(4)	0.2822(6)	3.9(2)
O(5)	−0.1688(5)	0.1881(5)	−0.0874(6)	4.9(2)
O(6)	−0.1275(5)	0.2283(5)	−0.3271(6)	4.6(2)
N(1)	−0.1040(6)	−0.0857(5)	0.3250(7)	3.3(1)
N(2)	−0.1562(6)	0.3697(5)	0.4133(7)	3.9(1)
C(1)	−0.1437(7)	−0.0144(6)	0.2103(9)	3.2(1)
C(2)	−0.2660(8)	0.0437(7)	0.205(1)	4.1(2)
C(3)	−0.3475(8)	0.0295(7)	0.313(1)	4.7(2)
C(4)	−0.3014(8)	−0.0433(6)	0.431(1)	3.9(2)
C(5)	−0.1829(7)	−0.1004(6)	0.4333(9)	3.6(1)
C(6)	−0.0797(7)	0.3384(6)	0.2945(9)	3.4(1)
C(7)	−0.0696(8)	0.4262(7)	0.202(1)	4.2(2)
C(8)	−0.1351(9)	0.5317(7)	0.228(1)	5.1(2)
C(9)	−0.2162(9)	0.5572(8)	0.348(1)	5.4(2)
C(10)	−0.2235(9)	0.4751(8)	0.440(1)	5.3(2)
C(11)	0.2748(8)	0.2260(7)	0.151(1)	3.9(2)
C(12)	0.388(1)	0.2971(1)	0.133(1)	5.7(2)
C(13)	−0.1984(8)	0.2250(6)	−0.223(1)	3.7(1)
C(14)	−0.343(1)	0.2706(9)	−0.264(1)	5.4(2)

[a] $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(bb^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

the one-dimensional solid-state structure. To test this hypothesis, we repeated the synthesis of compound **2** with a reduced Cu$(OCH_3)_2$/2-PyOH ratio (approximately 1:2.5). Not surprisingly, instead of compound **2**, a new compound **3** was isolated.

Synthesis and Crystal Structure of $Cu^{II}_2(O_2CCF_3)_4(2\text{-PyOH})_4$ (3). Compound **3** was obtained from the reaction of $Cu(OCH_3)_2$, trifluoroacetic acid, and 2-PyOH in a 1:2.66:2.66 ratio in the presence of $Ag(O_2CCF_3)$ in THF. Compound **3** is a dimeric copper(II) complex. The molecular structure of **3** is shown in Figure 7. Positional and thermal parameters are given in Table VI. Selected bond distances and angles are given in Table VII. The two copper(II) ions in **3** are bridged by two oxygen atoms of the 2-PyOH ligands with a Cu–Cu separation of 3.145(2) Å. The geometry of the copper center can be best described as a distorted square-pyramid with a trifluoroacetate ligand occupying the axial position, Cu–O(5) = 2.147(5) Å. The O(2) atom of the other trifluoroacetate ligand appears to occupy the sixth position, Cu–O(2) = 2.888(6) Å. The hydrogen atoms bonded to the nitrogen atoms of the 2-PyOH ligands have been located directly from X-ray diffraction analysis, and their positions could not be refined. The C(1)–O(3) distance, 1.310(7) Å, of the bridging 2-PyOH ligand is significantly longer than the C(6)–O(4) distance, 1.256(8) Å, of the nonbridging 2-PyOH ligand, indicative of an increased C–O single-bond character on the bridging 2-PyOH, which could be attributed to the coordination to the copper centers. The bridging 2-PyOH ligand forms an intramolecular hydrogen bond with the O(6) atom of the trifluoroacetate ligand, N(1)–O(6) = 2.790(8) Å. The O(6) atom of the trifluoroacetate ligand also forms an intermolecular hydrogen bond with a 2-PyOH ligand from the other dimer, N(2*)–O(6) = 2.905(8) Å. As a result, the dicopper units are linked together through hydrogen bonds to form a one-dimensional array. The two bridging 2-PyOH ligands from the two dimers are stacked. The atomic distances between these two aromatic rings are from 4.72 to 4.79 Å. If the solid-state structures of compounds **1** and **2** can be described as one-dimensional chains in term of the arrangement of the copper ions, the structure of **3** could be described as a one-dimensional band as shown in Figure 8.

Table VII. Selected Bond Lengths (Å) and angles (deg) for Compound 3

	Distances		
Cu–O(1)	1.960(5)	N(1)–C(5)	1.366(8)
Cu–O(3)	2.013(5)	N(2)–C(6)	1.355(8)
Cu–O(3)	1.986(5)	N(2)–C(10)	1.358(9)
Cu–O(4)	1.946(5)	C(1)–C(2)	1.372(9)
Cu–O(5)	2.147(5)	C(2)–C(3)	1.39(1)
O(1)–C(11)	1.272(8)	C(3)–C(4)	1.39(1)
O(2)–C(11)	1.200(8)	C(4)–C(5)	1.336(9)
O(3)–C(1)	1.310(7)	C(6)–C(7)	1.412(9)
O(4)–C(6)	1.256(8)	C(7)–C(8)	1.35(1)
O(5)–C(13)	1.233(8)	C(8)–C(9)	1.39(1)
O(6)–C(13)	1.246(8)	C(9)–C(10)	1.35(1)
N(1)–C(1)	1.357(8)	C(11)–C(12)	1.50(1)
		C(13)–C(14)	1.52(1)
	Angles		
O(1)–Cu–O(3)	157.0(2)	O(3)–Cu–O(5)	94.9(2)
O(1)–Cu–O(3)	92.6(2)	O(4)–Cu–O(5)	91.8(2)
O(1)–Cu–O(4)	97.2(2)	Cu–O(1)–C(11)	112.2(5)
O(1)–Cu–O(5)	105.9(2)	Cu–O(3)–Cu	103.7(2)
O(3)–Cu–O(3)	76.3(2)	Cu–O(3)–C(1)	129.3(4)
O(3)–Cu–O(4)	91.1(2)	Cu–O(3)–C(1)	125.7(4)
O(3)–Cu–O(5)	95.2(2)	Cu–O(4)–C(6)	125.5(4)
O(3)–Cu–O(4)	166.2(2)	Cu–O(5)–C(13)	134.6(5)

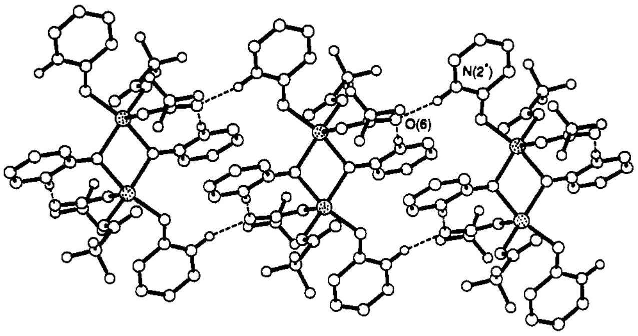


Figure 8. Diagram showing the polymeric structure of compound **3** linked by hydrogen bonds.

The various structures of copper(II) complexes with 2-PyOH and trifluoroacetate ligands demonstrate that hydrogen-bonding interaction patterns in this system are complex and can be readily modified by introducing heteroatoms such as chlorine or neutral hydrogen-bond bridging ligands such as the 2-PyOH ligand. However, all three structures with the 2-PyOH ligand described here are limited to one-dimensional hydrogen-bonded arrays only in the solid state. The geometric factor of the 2-PyOH ligand

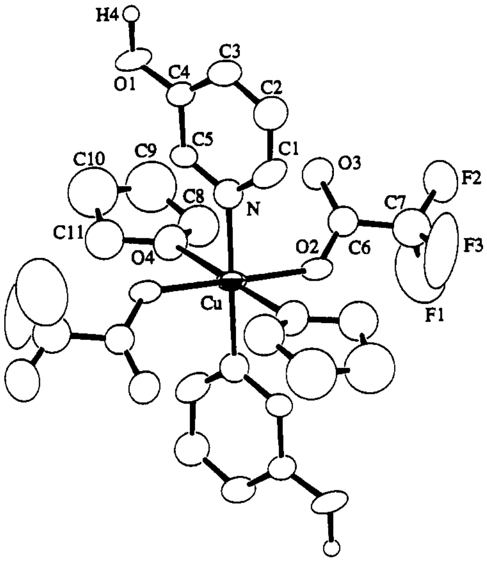


Figure 9. ORTEP diagram showing the molecular structure of compound **4** with labeling scheme and 50% thermal ellipsoids.

where the nitrogen and oxygen atoms are separated by one carbon atom only is believed to be responsible for this limitation. In contrast, the nitrogen and oxygen atoms in the 3-PyOH and 4-PyOH ligands are separated by more than one carbon atom and the geometries of these molecules are in favor of the formation of polymeric hydrogen-bonded species with trifluoroacetic acid, as shown by the structures **C** and **D**. In order to extend the dimensionality of the hydrogen-bonded network of the copper(II) complex, we therefore investigated the synthesis and structures of copper(II) complexes with trifluoroacetate and 3-PyOH and 4-PyOH ligands.

Synthesis and Crystal Structure of $\mathbf{Cu^{II}(O_2CCF_3)_2(3\text{-}PyOH)_2(THF)_2}$ (4). Compound **4** was isolated readily as the major product from the reaction of $Cu(OH)_2$, HO_2CCF_3, and 3-PyOH in a 1:2:2 ratio in THF. This compound loses THF molecules rapidly upon isolation from the solution. Nevertheless, we have been able to determine the structure of this compound by X-ray diffraction analysis. A similar reaction was carried out for the 4-PyOH ligand. However, the structure of the 4-PyOH complex has not been determined due to the lack of suitable crystals for X-ray diffraction analysis.

An ORTEP diagram for **4** is shown in Figure 9. Positional and thermal parameters are given in Table VIII. Selected bond distances and angles are listed in Table IX. Compound **4** has the same number of hydroxypyridine and trifluoroacetate ligands as compound **3** does. However, the structure of compound **3** is dramatically different from that of **3**. Compound **4** is a mononuclear complex with an inversion center and an elongated octahedral geometry. Two THF molecules occupy the axial positions with a long Cu–O(4) bond length, 2.684(6) Å. Copper(II) complexes with ether ligands are uncommon due to their poor nucleophilicity. A few copper(II) complexes with coordinated dioxane ligands have been reported previously.[17] In contrast to the 2-PyOH ligand which coordinates to the copper(II) center through the oxygen atom in compounds **1**–**3**, the 3-PyOH ligand in **4** is coordinated to the copper(II) center through the nitrogen atom only. This difference is believed to be caused by the electronic properties of these ligands. It has been well established that the 2-pyridone resonance form of the 2-PyOH ligand is dominant in polar solvents[18a,b] and in solids.[18c,d] The 2-pyridone tautomer form increases the nucleophilicity of the oxygen atom and enables the oxygen atom to coordinate to one or two copper centers. The 3-PyOH ligand, however, does not have the corresponding 3-pyridone tautomer. As a result, the nitrogen center of the 3-PyOH ligand becomes a preferred binding site for the Cu(II) ion. The C(4)–O(1) bond length of the 3-PyOH, 1.358(9) Å, is significantly longer than those of 2-PyOH observed in **1**–**3**, which is in agreement with the hydroxypyridine form of the 3-PyOH. Hydrogen-bonding interaction is perhaps the other factor that prevents the oxygen atom of the 3-PyOH ligand from being bonded to the copper(II) center. The proton on the oxygen atom O(1) was located from X-ray diffraction analysis, and its position was not refined. This proton is hydrogen-bonded to the oxygen atom of the trifluoroacetate ligand of a neighbor molecule, O(1)–O(3*) = 2.681(8) Å. Consequently, compound **4** has a two-dimensional structure with a cross-linked hydrogen-bonded network as shown in Figure 10. The shortest Cu–Cu separation in this network is 8.04(1) Å.

Table VIII. Positional and Thermal Parameters (B_{eq}) for Compound 4

atom	x	y	z	B_{eq},[a] Å^2
Cu	0.5000	0.0000	1.0000	3.78(4)
F(1)	0.8466(9)	0.367(2)	0.9378(8)	18.1(5)
F(2)	0.9829(7)	0.281(1)	1.0200(4)	11.9(3)
F(3)	0.9189(9)	0.143(1)	0.9240(5)	14.5(4)
O(1)	0.5597(6)	−0.1785(8)	1.2978(3)	4.7(2)
O(2)	0.6681(5)	0.1103(7)	0.9738(3)	3.8(2)
O(3)	0.7673(6)	0.1836(9)	1.0918(3)	5.4(2)
O(4)	0.4092(6)	0.2215(7)	1.1033(3)	4.3(2)
N(1)	0.5950(7)	−0.1329(9)	1.0878(4)	3.3(2)
C(1)	0.7024(10)	−0.223(1)	1.0782(5)	4.4(3)
C(2)	0.7734(10)	−0.307(1)	1.1393(6)	4.8(3)
C(3)	0.7270(9)	−0.295(1)	1.2153(5)	3.8(2)
C(4)	0.6140(8)	−0.201(1)	1.2266(5)	2.9(2)
C(5)	0.5495(8)	−0.123(1)	1.1599(5)	3.0(2)
C(6)	0.7632(8)	0.172(1)	1.0196(5)	3.2(2)
C(7)	0.881(1)	0.238(2)	0.9786(7)	5.5(3)
C(8)	0.471(1)	0.381(2)	1.1225(7)	6.4(3)
C(9)	0.419(1)	0.431(2)	1.2025(8)	9.6(4)
C(10)	0.311(1)	0.307(2)	1.2188(9)	9.4(4)
C(11)	0.289(1)	0.215(1)	1.1464(6)	5.6(2)

[a] $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(bb^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

Table IX. Selected Bond Lengths (Å) and Angles (deg) for Compound 4

	Distances		
Cu–O(2)	1.957(5)	Cu–O(2)	1.957(5)
Cu–N(1)	2.006(7)	Cu–N(1)	2.006(7)
F(1)–C(7)	1.28(1)	F(2)–C(7)	1.24(1)
F(3)–C(7)	1.27(1)	O(1)–C(4)	1.358(9)
O(2)–C(6)	1.275(9)	O(3)–C(6)	1.218(9)
O(4)–C(8)	1.45(1)	O(4)–C(11)	1.44(1)
N(1)–C(1)	1.30(1)	N(1)–C(5)	1.325(9)
C(1)–C(2)	1.38(1)	C(2)–C(3)	1.39(1)
C(3)–C(4)	1.37(1)	C(4)–C(5)	1.40(1)
C(6)–C(7)	1.49(1)	C(8)–C(9)	1.53(1)
C(9)–C(10)	1.49(2)	C(10)–C(11)	1.43(2)
	Angles		
O(2)–Cu–O(2)	180.0	O(2)–Cu–N(1)	92.6(3)
O(2)–Cu–N(1)	87.4(3)	O(2)–Cu–N(1)	87.4(3)
O(2)–Cu–N(1)	92.6(3)	N(1)–Cu–N(1)	180.0
Cu–O(2)–C(6)	129.8(5)	C(8)–O(4)–C(11)	105.7(8)
Cu–N(1)–C(1)	123.3(6)	Cu–N(1)–C(5)	118.4(6)

Concluding Remarks. The structures and stability of copper(II) complexes with trifluoroacetate and hydroxypyridine as ligands are dependent on hydrogen-bonding interactions between coordinated and uncoordinated ligands, the geometries and

---

[17] Evenhuis, C. J.; Hitchman, M. A.; McDonald, R. G.; Goodgame, D. M. L.; Kwistowski, E.; Dettloffweglikowska, U.; Pakawatchai, C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 943.

[18] (a) Frank, J.; Katritzky, A. R. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1428. (b) Kuzuya, M.; Noguchi, A.; Okuda, T. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1423. (c) Wheeler, G. L.; Ammon, H. L. *Acta Crystallogr.* **1974**, *B30*, 680. (d) Almof, J.; Kvick, A.; Olovsson, I. *Acta Crystallogr.* **1971**, *B27*, 1201.

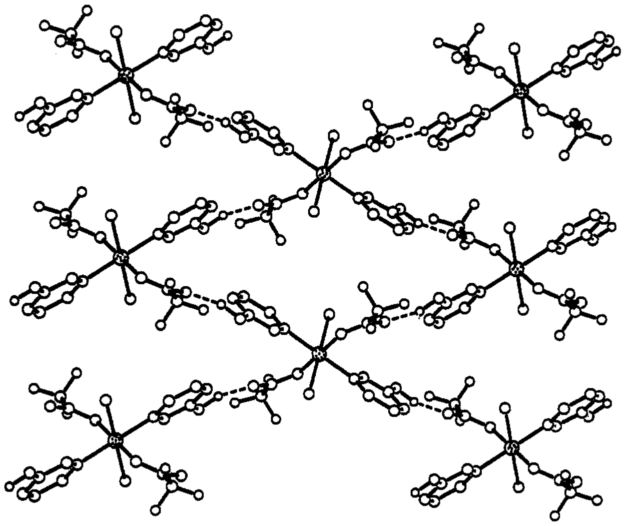


Figure 10. Diagram showing the two-dimensional hydrogen-bonded network of **4**. The carbon atoms of the THF molecule were omitted for clarity.

electronic properties of the hyrdoxypyridine ligand, and solvent molecules. Hydrogen-bond formations between ligands can be used to assemble metal complexes to form extended arrays with various metal–metal separation distances and structural features. The structural variations induced by hydrogen bonds could also have an impact on physical properties such as electronic, magnetic, and thermal properties of the metal compounds. Proper design and choice of ligands with hydrogen-bonding functionality could lead to the formation of useful inorganic materials with desired physical properties. Hydrogen-bonding interactions could also be used in the synthesis of certain heterometallic compounds which may not be obtained readily by conventional synthetic methods. Investigation of physical properties of the copper(II) complexes reported here and further exploration of synthetic applications of hydrogen bondings to inorganic compounds are being conducted by our group.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this research.

Supplementary Material Available: Tables listing details of the crystallographic analyses, complete positional and thermal parameters, anisotropic thermal parameters, and bond distances and angles for compounds **1**–**4** (33 pages). Ordering information is given on any current masthead page.