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Structural Control of Copper(I) Coordination Polymers: Construction of One-, Two-, and Three-Dimensional Frameworks of Tetrahedral Copper(I) Ions Bridged by Dicyanobenzene Derivatives

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With the use of three dicyanobenzene derivatives as bridging ligands, four copper(I) coordination polymers, $[Cu(dchq)_2](ClO_4)(Me_2CO)_2$ (**1**; dchq = 1,2-dicyanohydroquinone), $[Cu(ipn)_2](PF_6)(Me_2CO)$ (**2**; ipn = 1,3-dicyanobenzene), and $[Cu(dmtpn)_2](X)(dmtpn)(THF)$ (**3a** ($X = BF_4$), **3b** ($X = ClO_4$); dmtpn = 2,5-dimethylterephthalonitrile) were synthesized and characterized. Single-crystal X-ray analyses revealed that all copper(I) ions in these complexes have tetrahedral geometry and are coordinated by four ligands which also coordinate to the next copper ions, resulting in the formation of coordination polymer compounds. The polymer framework of **1** consists of one-dimensional chains that run along the *a*-axis direction and weakly interact with each other through $\pi-\pi$ interactions between the dchq molecules and through hydrogen bonding. **2** has a two-dimensional sheet with a square arrangement of copper(I) ions. Stacking of the square lattice in the *c*-axis direction forms cavities in which the acetone molecules and PF_6^- anions are incorporated. Both **3a** and **3b** are isostructural and have triply interpenetrated three-dimensional diamond-like frameworks with $\pi-\pi$ stacking columns of alternately coordinated and uncoordinated dmtpn molecules. It is demonstrated that the dimensionality of the polymer structures can be successfully controlled by the relative positions of two CN groups in the bridging ligands. Crystallographic data are as follows. **1**: $C_{22}H_{20}CuClN_4O_{10}$, monoclinic, $C2/c$, $a = 19.514(2)$ Å, $b = 10.526(2)$ Å, $c = 12.276(1)$ Å, $\beta = 96.839(8)°$, $Z = 4$. **2**: $C_{19}H_{14}CuF_6N_4OP$, orthorhombic, $P2_12_12_1$, $a = 12.743(2)$ Å, $b = 15.026(3)$ Å, $c = 11.362(2)$ Å, $Z = 4$. **3a**: $C_{34}H_{32}BCuF_4N_6O$, monoclinic, Cc, $a = 9.599(3)$ Å, $b = 27.298(5)$ Å, $c = 13.367(3)$ Å, $\beta = 105.45(2)°$, $Z = 4$. **3b**: $C_{34}H_{32}ClCuN_6O_5$, monoclinic, Cc, $a = 9.590(7)$ Å, $b = 27.429(3)$ Å, $c = 13.416(4)$ Å, $\beta = 105.80(3)°$, $Z = 4$.

Introduction

Recently, much research interest has been focused on coordination polymer compounds because of their possibility of offering new functional materials by hybridizing or fusing organic and inorganic components.[1−3] Their advantageous characteristics are a variety of combinations of transition metal ions and organic bridging ligands, which lead to a variety of structures and functionalities.[4−6] When a linear bidentate molecule is used as a bridging ligand, the dimensionality of the resultant polymeric structure can be varied with the geometry of metal ion. Two-coordination around a metal ion leads to a one-dimensional chain structure,[7−10] a trigonal three- or a square planar four-coordination corresponds to formation of a hexagonal (honeycomb)[10,11] or a square lattice,[12−15] respectively, and a tetrahedral four- or an octahedral six-coordination around a metal ion corresponds to a three-dimensional diamond-like[2,11,16−21] or a cubic-type structure,[22,23] respectively.

On the other hand, if we use nonlinear bridging ligands, what kind of structures can we obtain? The systematic work of Kinoshita et al.[16,24,25] using the aliphatic bridging ligands $NC(CH_2)_nCN$ shows that combining tetrahedral copper(I) ions with

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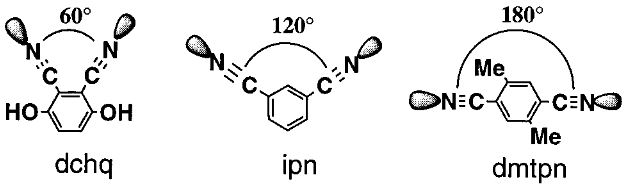

Figure 1. The three dicyanobenzene derivatives used as bridging ligands and their bridging angles.

those ligands having $n = 2$, 3, and 4 leads to one-, two-, and three-dimensional structures, respectively. However, since the relative positions of the CN groups in these aliphatic ligands are not fixed *a priori*, it is difficult to predict their bridging angles in different systems. Predicting polymeric structures before X-ray structural determinations is very important in the design of new functional coordination polymer compounds. The simplest series of bridging ligands having fixed bridging angles is a family of diazines: pyridazine, pyrimidine, and pyrazine, and their derivatives. Pyrazine and 2,5-dimethylpyrazine have been known to form diamond-like structures with tetrahedral silver(I)[8] and copper(I)[19] ions, respectively. However, probably because of a steric conjestion around a metal ion, two- or three-coordination rather than four-coordination sometimes occurs together with coordination of a solvent molecule or a counterion. Although some pyridazine-bridged coordination polymers have been known,[26-28] they usually have additional coordination or bridging of counterions. In order to simplify the discussion, we focus on a "binary" polymer framework. This is a polymer framework composed of one kind of metal ion and one kind of bridging ligand, and all of the metal coordination sites are occupied by the bridging ligand, not by solvent molecules or counterions. Pyridazine- or pyrimidine-bridged binary polymers with tetrahedral metal ions are rare. Only one example, so far as we know,[29] of a binary polymer has been reported: [Cu(pyrimidine)$_2$]BF$_4$,[30] which has a complex three-dimensional polymer network.

As another series of bridging ligands with fixed bridging angles, we chose dicyanobenzene and its derivatives: 1,2-dicyanohydroquinone (dchq), isophthalonitrile (ipn ≡ 1,3-dicyanobenzene), and 2,5-dimethylterephthalonitrile (dmtpn) (Figure 1). These species seem to create less steric hindrance than diazines when coordinated to a metal ion, which will ensure four-coordination of the ligands to a tetrahedral metal ion and the formation of "binary" polymer frameworks. We report here the syntheses and crystal structures of their coordination polymer compounds with the tetrahedral copper(I) ion. One-dimensional chain, two-dimensional sheet, and three-dimensional diamond-like structures[20] can be formed selectively by varying the bridging ligands.

Experimental Section

General Methods. All operations were carried out under argon or ethylene by using standard Schlenk or vacuum line techniques. Tetrakis(acetonitrile)copper(I) hexafluorophosphate was synthesized and purified by a literature method.[31] Acetone treated with potassium permanganate was dried over potassium carbonate and distilled immediately before use. Benzene was distilled from sodium/benzophenone under argon immediately before use. Methanol was dehydrated on magnesium cake and distilled immediately before use. All other chemicals of reagent grade were purchased from the Wako Pure Chemical Co., Inc., and were used without further purification. Infrared spectra (400−4000 cm^{-1}) were recorded on a JASCO FT/IR-8000 spectrophotometer using KBr disks.

Safety Note. *Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared, and these should be handled with great caution.*

Synthesis of [Cu(dchq)$_2$](ClO$_4$)(Me$_2$CO)$_2$ (1). A colorless solution of copper(I) perchlorate in acetone (4 mL) obtained by reaction of copper(II) perchlorate hexahydrate (18.5 mg, 0.05 mmol) and copper metal under ethylene was mixed with a brown solution of dchq (32.0 mg, 0.2 mmol) dissolved in 6 mL of acetone. The resultant solution was transferred to a glass tube under argon, and 5 mL of *n*-pentane was added slowly. The glass tube was sealed and kept at room temperature. After the sample was allowed to stand for 1 week, brown columnar crystals were obtained. A slight difference between calculated and observed values in the following elemental analysis data may be due to gradual loss of acetone incorporated in the crystal (*vide infra*). Anal. Calcd for $C_{22}H_{20}CuClN_4O_{10}$: C, 44.08; H, 3.36; N, 9.35. Found: C, 43.01; H, 3.14; N, 9.34. Main IR bands (cm^{-1}): 3578 (s), 3499 (m), 3291 (s, sh), 3250 (s), 2236 (s), 1495 (s), 1410 (m), 1304 (s), 1144 (s), 1113 (s), 1088 (s), 953 (m), 829 (m), 748 (w), 629 (m), 550 (w), 471 (w).

Synthesis of [Cu(ipn)$_2$](PF$_6$)(Me$_2$CO) (2). A solution of tetrakis(acetonitrile)copper(I) hexafluorophosphate (37.7 mg, 0.1 mmol) in acetone (10 mL) was poured into a reaction vessel containing 12.9 mg of ipn (0.1 mmol). The resultant colorless solution was transferred to a glass tube, and 5 mL of *n*-pentane was added slowly. The glass tube was sealed and kept at room temperature. After the sample was allowed to stand for 1 week, colorless prismatic crystals were obtained. The crystal loses its clarity upon drying in argon, probably due to the loss of the acetone molecule incorporated in the crystal. Anal. Calcd for $C_{16}H_8CuF_6N_4P$ (**2** without acetone): C, 41.35; H, 1.74; N, 12.05. Found: C, 41.03; H, 1.75; N, 12.19. Main IR bands (cm^{-1}): 3058 (m), 2236 (s), 1500 (m), 1434 (m), 837 (s), 713 (m), 541 (m), 505 (m).

Synthesis of [Cu(dmtpn)$_2$](X)(dmtpn)(THF) (3a, X = BF$_4$; 3b, X = ClO$_4$). A colorless solution of copper(I) tetrafluoroborate or copper(I) perchlorate (0.036 mmol) in THF (1.2 mL) was poured to the bottom of a glass tube. Then THF (0.6 mL) and a colorless solution of dmtpn (11.2 mg, 0.07 mmol) dissolved in THF (0.6 mL) were added slowly in sequence. The glass tube was sealed under argon and kept at room temperature. After 3 days, pale yellow, platelike crystals were obtained for both anions corresponding to **3a** and **3b**. Anal. Calcd for $C_{34}H_{32}BCuF_4N_6O$ (**3a**): C, 59.10; H, 4.67; N, 12.16. Found: C, 58.81; H, 4.77; N, 12.09. A low yield of **3b** and the existence of byproducts with less clarity prevent a precise determination of analytical data for **3b**. Main IR bands are as follows (cm^{-1}). **3a**: 3040 (m), 2230 (m), 1808 (w), 1705 (w), 1495 (m), 1447 (m), 1393 (m), 1285 (m), 1040 (s), 907 (m), 521 (w), 464 (m). **3b**: 3042 (m), 2232 (m), 1808 (w), 1707 (w), 1493 (m), 1451 (m), 1393 (m), 1285 (m), 1065 (s), 907 (m), 521 (w), 465 (m).

X-ray Data Collections and Structure Solutions and Refinements. Crystals suited for X-ray measurements were mounted on glass fibers using adhesives. In the case of **2**, the crystal was coated by the adhesive to avoid loss of its clarity. Diffraction data for all compounds were collected at ambient temperature on a Rigaku AFC5R, AFC6S, or AFC7R four-circle diffractometer using graphite-monochromated Mo Kα radiation. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards for **1** and **2** decreased by 3.5% and 5.4%, respectively. Linear correction factors were applied to these data. Those for the other compounds remained constant throughout data collection, indicating crystal and electronic stability. Azimuthal scans of several reflections for each compound indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. Crystal data and details of measurements for the obtained copper(I) complexes, [Cu(dchq)$_2$](ClO$_4$)(Me$_2$CO)$_2$ (**1**), [Cu(ipn)$_2$](PF$_6$)(Me$_2$CO) (**2**), and [Cu(dmtpn)$_2$](X)(dmtpn)(THF) (**3a**, X = BF$_4$; **3b**, X = ClO$_4$), are summarized in Table 1.

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Table 1. Crystal Data for [Cu(dchq)$_2$](ClO$_4$)(Me$_2$CO)$_2$ (**1**), [Cu(ipn)$_2$](PF$_6$)(Me$_2$CO) (**2**), and [Cu(dmtpn)$_2$](X)(dmtpn)(THF) (**3a**, X = BF$_4$; **3b**, X = ClO$_4$)

	1	**2**	**3a**	**3b**
formula	$C_{22}H_{20}CuClN_4O_{10}$	$C_{19}H_{14}CuF_6N_4OP$	$C_{34}H_{32}BCuF_4N_6O$	$C_{34}H_{32}ClCuN_6O_5$
M	599.42	522.86	691.02	703.67
space group	$C2/c$ (No. 15)	$P2_12_12_1$ (No. 19)	Cc (No. 9)	Cc (No. 9)
T, °C	23	20	23	23
a, Å	19.514(2)	12.743(2)	9.599(3)	9.590(7)
b, Å	10.526(2)	15.026(3)	27.298(5)	27.429(3)
c, Å	12.276(1)	11.362(2)	13.367(3)	13.416(4)
α, deg	90.000	90.000	90.000	90.000
β, deg	96.839(8)	90.000	105.45(2)	105.80(3)
γ, deg	90.000	90.000	90.000	90.000
V, Å^3	2503.6(5)	2175.6(6)	3376(1)	3396(2)
Z	4	4	4	4
ρ_{calcd}, g cm^{-3}	1.590	1.596	1.359	1.376
radiation (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
μ, cm^{-1}	10.43	11.47	7.03	7.72
R,[a] R_w[b]	0.048, 0.058	0.069, 0.097	0.062, 0.076	0.056, 0.064

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

Table 2. Selected Atomic Coordinates and Isotropic Temperature Factors for [Cu(dchq)$_2$](ClO$_4$)(Me$_2$CO)$_2$

atom	x	y	z	B_{eq},[a] Å^2
Cu(1)	1.0000	0.06139(6)	0.2500	2.42(1)
Cl(1)	0.5000	0.0446(1)	0.2500	3.94(3)
O(1)	0.7935(1)	−0.2205(3)	0.1999(2)	4.03(7)
O(2)	0.8254(2)	−0.4243(3)	0.6167(2)	4.10(7)
O(3)	0.5442(3)	0.1154(6)	0.2003(6)	14.2(2)
O(4)	0.5375(2)	−0.0383(6)	0.3221(5)	12.2(2)
O(5)	0.1938(1)	0.1693(3)	0.0641(2)	4.33(7)
N(1)	0.9312(1)	−0.0492(3)	0.3171(2)	2.62(6)
N(2)	0.9445(1)	−0.1631(3)	0.6343(2)	2.63(6)
C(1)	0.8001(2)	−0.2711(3)	0.3004(3)	2.63(7)
C(2)	0.8503(2)	−0.2217(3)	0.3782(2)	2.19(6)
C(3)	0.8599(2)	−0.2713(3)	0.4866(2)	2.14(6)
C(4)	0.8197(2)	−0.3729(3)	0.5149(3)	2.59(7)
C(5)	0.7691(2)	−0.4211(3)	0.4348(3)	2.94(7)
C(6)	0.7592(2)	−0.3720(4)	0.3314(3)	3.07(8)
C(7)	0.8951(2)	−0.1241(3)	0.3450(2)	2.23(6)
C(8)	0.9083(2)	−0.2130(3)	0.5681(3)	2.28(6)
C(9)	0.1368(2)	0.2145(3)	0.0421(3)	2.79(7)
C(10)	0.1137(3)	0.3252(5)	0.1021(5)	5.8(1)
C(11)	0.0863(2)	0.1565(5)	−0.0431(4)	4.3(1)

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

Table 3. Selected Atomic Coordinates and Isotropic Temperature Factors for [Cu(ipn)$_2$](PF$_6$)(Me$_2$CO)

atom	x	y	z	B_{eq},[a] Å^2
Cu(1)	0.25438(9)	0.51132(6)	0.2292(1)	4.40(2)
P(1)	0.1317(2)	0.8927(2)	0.1640(3)	4.80(6)
F(1)	0.1624	0.8052	0.2396	9.8(3)
F(2)	0.1013	0.7922	0.1533	7.4(6)
F(3)	0.0111	0.8699	0.1848	8.0(3)
F(4)	0.0275	0.9015	0.2516	8.6(4)
F(5)	0.0333	0.9183	0.0787	14.9(7)
F(6)	0.1628	0.9308	0.2833	14.5(5)
F(7)	0.1261	1.0006	0.1567	7.7(3)
F(8)	0.1092	0.9725	0.0823	7.0(4)
F(9)	0.2383	0.9041	0.0925	8.4(5)
F(10)	0.2559	0.8977	0.1487	6.3(2)
F(11)	0.1273	0.8622	0.0254	13.7(8)
F(12)	0.1343	0.8122	0.0689	6.9(5)
O(1)	0.3409(8)	0.2194(6)	0.198(1)	8.4(3)
N(1)	0.3244(7)	0.6019(6)	0.1260(8)	5.1(2)
N(2)	0.1933(7)	0.4166(5)	0.1313(9)	5.3(2)
N(3)	0.6466(6)	0.9533(6)	0.1556(8)	5.1(2)
N(4)	−0.1497(7)	0.0751(5)	0.1752(8)	4.9(2)
C(1)	0.3562(7)	0.6627(6)	0.082(1)	4.4(2)
C(2)	0.3961(7)	0.7424(6)	0.0264(8)	3.8(2)
C(3)	0.3528(8)	0.7764(7)	−0.077(1)	4.6(2)
C(4)	0.3947(9)	0.8532(7)	−0.1227(8)	4.8(2)
C(5)	0.4734(8)	0.8982(6)	−0.0742(9)	4.5(2)
C(6)	0.5115(8)	0.8659(6)	0.0334(8)	4.2(2)
C(7)	0.4758(8)	0.7868(6)	0.0831(8)	4.3(2)
C(8)	0.5905(8)	0.9147(6)	0.1016(9)	4.2(2)
C(9)	0.1574(8)	0.3562(6)	0.0819(9)	4.2(2)
C(10)	0.1094(7)	0.2774(6)	0.0364(8)	3.9(2)
C(11)	0.1424(8)	0.2462(7)	−0.0766(9)	4.6(2)
C(12)	0.1007(8)	0.1693(7)	−0.123(1)	5.3(3)
C(13)	0.0238(9)	0.1251(7)	−0.0542(7)	4.4(2)
C(14)	−0.0097(7)	0.1579(5)	0.0516(8)	3.5(2)
C(15)	0.0335(7)	0.2340(6)	0.0991(7)	3.6(2)
C(16)	−0.0854(7)	0.1111(6)	0.1191(9)	4.1(2)
C(17)	0.3592(8)	0.1433(8)	0.1762(9)	4.8(2)
C(18)	0.350(1)	0.111(1)	0.056(1)	7.7(4)
C(19)	0.392(1)	0.0801(9)	0.264(2)	9.4(4)

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

The structures were solved by direct methods[32] and expanded using Fourier techniques. The non-hydrogen atoms were refined either anisotropically or isotropically by full-matrix least-squares calculations. Hydrogen atoms were included but not refined. Reliability factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[33] All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp. The final R and R_w values were 0.048 and 0.058 for **1**, 0.069 and 0.097 for **2**, 0.062 and 0.076 for **3a**, and 0.056 and 0.064 for **3b**, respectively. The slightly greater R values for **2** are caused by disordering of hexafluorophosphate anions. The final parameters for non-hydrogen atoms for **1**-**3b** are given in Tables 2−5, respectively, and selected bond distances and angles are listed in Table 6. Dihedral angles and distances from the least-square planes are listed in Tables 7 and 8.

Results and Discussion

Structure of [Cu(dchq)$_2$](ClO$_4$)(Me$_2$CO)$_2$ (1). An ORTEP drawing of a part of the one-dimensional chain structure in **1** is shown in Figure 2, which also provides the atom-numbering scheme. The asymmetric unit consists of a copper(I) ion, two dchq ligands, a perchlorate ion, and two acetone molecules. Both Cu(1) and Cl(1) atoms are sitting on special positions, (0, y, $^1/_4$) and ($^1/_2$, y', $^1/_4$), respectively, having a 2-fold rotation axis parallel to the b axis. Four cyano nitrogen atoms of four dchq ligands coordinate to a copper(I) ion with slightly distorted tetrahedral geometry. Four Cu−N bond lengths vary from 1.993(3) to 2.025(3) Å and six N−Cu−N′ angles vary from 105.0(1) to 115.0(2)° (Table 6). Each two of the four dchq ligands which bridge the adjacent copper(I) ions are on the same

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(32) For **1**, MITHRIL90: Gilmore, C. J. An integrated direct methods computer program. University of Glasgow, Scotland, 1990. For **2**, SIR88: Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389. For **3a** and **3b**, MITHRIL: Gilmore, C. J. An integrated direct methods computer program. *J. Appl. Crystallogr.* **1984**, *17*, 42.

(33) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table 4. Selected Atomic Coordinates and Isotropic Temperature Factors for $[\mathrm{Cu(dmtpn)_2}](\mathrm{BF_4})(\mathrm{dmtpn})(\mathrm{THF})$

atom	x	y	z	B_{eq},[a] Å^2
Cu(1)	1.4291	0.61339(3)	0.9815	2.56(2)
F(1)	0.959(2)	0.3489(5)	0.996(2)	16.2(5)
F(2)	1.039(1)	0.2773(4)	1.0486(8)	8.7(2)
F(3)	1.045(1)	0.3410(4)	1.152(1)	11.5(3)
F(4)	1.182(1)	0.3405(5)	1.038(1)	11.8(3)
O(1)	1.846(2)	0.9781(9)	0.681(2)	13.8(6)
O(2)	2.045(2)	1.0294(8)	0.777(2)	14.1(6)
N(1)	1.261(1)	0.5757(4)	0.8966(9)	3.0(2)
N(2)	0.596(1)	0.4279(4)	0.5566(8)	3.2(3)
N(3)	1.501(1)	0.6579(5)	0.887(1)	4.4(3)
N(4)	1.870(1)	0.8430(4)	0.5836(8)	3.2(3)
N(5)	0.934(3)	0.5803(4)	0.993(2)	6.5(3)
N(6)	1.029(2)	0.8635(6)	0.923(2)	11.5(5)
C(1)	1.171(1)	0.5550(5)	0.854(1)	2.9(3)
C(2)	1.044(1)	0.5260(5)	0.788(1)	2.3(3)
C(3)	0.970(1)	0.5467(5)	0.698(1)	3.2(3)
C(4)	0.852(2)	0.5211(5)	0.631(1)	3.3(3)
C(5)	0.814(1)	0.4763(6)	0.668(1)	3.2(3)
C(6)	0.891(2)	0.4584(5)	0.770(1)	2.8(3)
C(7)	1.010(1)	0.4832(5)	0.8272(8)	2.6(3)
C(8)	0.700(2)	0.4498(5)	0.610(1)	3.0(3)
C(9)	0.770(2)	0.5404(6)	0.529(1)	5.1(4)
C(10)	1.091(1)	0.4631(5)	0.934(1)	4.0(3)
C(11)	1.551(1)	0.6859(5)	0.840(1)	2.8(3)
C(12)	1.625(1)	0.7200(5)	0.788(1)	2.3(2)
C(13)	1.606(2)	0.7703(7)	0.802(1)	4.0(4)
C(14)	1.671(1)	0.8045(5)	0.753(1)	2.5(2)
C(15)	1.759(1)	0.7847(6)	0.691(1)	3.5(3)
C(16)	1.767(2)	0.7351(5)	0.673(1)	3.0(3)
C(17)	1.697(2)	0.7034(6)	0.724(1)	4.0(3)
C(18)	1.822(2)	0.8191(6)	0.629(1)	4.0(4)
C(19)	1.668(2)	0.8557(6)	0.769(1)	5.0(4)
C(20)	1.718(2)	0.6457(6)	0.703(1)	5.2(4)
C(21)	0.954(2)	0.6210(4)	0.988(2)	4.2(3)
C(22)	0.965(1)	0.6743(4)	0.974(1)	4.2(3)
C(23)	1.052(2)	0.6897(6)	0.908(1)	5.1(4)
C(24)	1.075(1)	0.7397(5)	0.899(1)	5.2(3)
C(25)	1.001(2)	0.7719(5)	0.947(1)	5.7(4)
C(26)	0.914(1)	0.7557(5)	1.010(1)	4.6(3)
C(27)	0.895(1)	0.7060(5)	1.0241(9)	4.4(3)
C(28)	1.017(2)	0.8246(6)	0.934(1)	7.0(4)
C(29)	1.172(2)	0.7574(7)	0.835(1)	8.4(5)
C(30)	0.805(2)	0.6893(7)	1.092(1)	5.5(4)
C(31)	1.823(3)	0.9656(9)	0.779(2)	11.0(6)
C(32)	1.975(2)	0.9820(7)	0.809(1)	6.9(3)
C(33)	1.792(3)	1.024(1)	0.670(2)	11.7(6)
C(34)	1.919(3)	1.0436(9)	0.674(2)	10.5(6)
B(1)	1.065(2)	0.3269(8)	1.061(2)	7.3(4)

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

Table 5. Selected Atomic Coordinates and Isotropic Temperature Factors for $[\mathrm{Cu(dmtpn)_2}](\mathrm{ClO_4})(\mathrm{dmtpn})(\mathrm{THF})$

atom	x	y	z	B_{eq},[a] Å^2
Cu(1)	0.8236	0.11447(3)	0.2254	2.45(2)
Cl(1)	0.4654(4)	0.1730(1)	0.8090(3)	6.3(1)
O(1)	0.444(1)	0.2236(4)	0.7957(8)	7.4(2)
O(2)	0.450(1)	0.1595(5)	0.908(1)	10.7(3)
O(3)	0.348(2)	0.1495(5)	0.737(2)	14.0(4)
O(4)	0.588(1)	0.1580(4)	0.785(1)	9.8(3)
O(5)	0.938(2)	−0.0364(8)	0.433(2)	6.4(5)
O(6)	0.808(3)	−0.045(1)	0.413(2)	7.2(6)
O(7)	0.814(8)	0.035(3)	0.510(6)	9(2)
N(1)	0.6580(8)	0.0756(3)	0.1419(8)	2.7(2)
N(2)	−0.007(1)	−0.0741(4)	−0.1981(8)	3.6(3)
N(3)	0.895(1)	0.1599(4)	0.1291(8)	3.8(3)
N(4)	1.265(1)	0.3431(4)	−0.1733(8)	3.2(3)
N(5)	0.332(2)	0.0799(3)	0.232(1)	7.2(3)
N(6)	0.425(2)	0.3626(5)	0.168(1)	11.5(5)
C(1)	0.565(1)	0.0544(4)	0.096(1)	3.0(3)
C(2)	0.444(1)	0.0265(4)	0.0343(9)	2.4(3)
C(3)	0.362(1)	0.0455(5)	−0.061(1)	3.2(3)
C(4)	0.243(1)	0.0209(4)	−0.126(1)	3.2(3)
C(5)	0.212(1)	−0.0242(5)	−0.086(1)	2.9(3)
C(6)	0.286(1)	−0.0419(4)	0.013(1)	2.5(3)
C(7)	0.402(1)	−0.0163(4)	0.0715(8)	2.4(2)
C(8)	0.092(1)	−0.0512(4)	−0.1469(9)	3.0(3)
C(9)	0.160(1)	0.0381(5)	−0.228(1)	4.0(3)
C(10)	0.486(1)	−0.0370(5)	0.177(1)	4.2(3)
C(11)	0.949(1)	0.1867(4)	0.087(1)	2.7(2)
C(12)	1.019(1)	0.2196(4)	0.0330(9)	2.7(2)
C(13)	1.003(1)	0.2701(5)	0.048(1)	3.4(3)
C(14)	1.067(1)	0.3037(5)	−0.0032(9)	2.8(2)
C(15)	1.152(1)	0.2836(4)	−0.064(1)	3.0(2)
C(16)	1.162(1)	0.2357(5)	−0.0806(9)	3.1(3)
C(17)	1.091(2)	0.2011(5)	−0.032(1)	3.6(3)
C(18)	1.222(1)	0.3179(5)	−0.124(1)	3.4(3)
C(19)	1.065(2)	0.3578(5)	0.014(1)	5.4(4)
C(20)	1.109(2)	0.1474(5)	−0.049(1)	4.4(3)
C(21)	0.348(2)	0.1201(4)	0.233(1)	4.5(3)
C(22)	0.365(1)	0.1736(4)	0.2189(9)	4.0(3)
C(23)	0.452(1)	0.1889(5)	0.154(1)	4.4(3)
C(24)	0.471(1)	0.2398(5)	0.145(1)	5.3(3)
C(25)	0.399(1)	0.2704(4)	0.194(1)	4.5(3)
C(26)	0.315(1)	0.2548(5)	0.255(1)	4.9(3)
C(27)	0.293(1)	0.2045(4)	0.2699(9)	4.4(3)
C(28)	0.416(1)	0.3225(5)	0.181(1)	7.1(4)
C(29)	0.575(2)	0.2572(6)	0.083(1)	7.7(4)
C(30)	0.207(1)	0.1877(6)	0.340(1)	5.7(4)
C(31)	0.934(2)	−0.0305(6)	0.522(1)	6.8(4)
C(32)	0.688(2)	−0.0217(9)	0.412(2)	11.1(6)
C(33)	0.872(2)	0.0176(8)	0.549(2)	7.9(4)
C(34)	0.732(2)	0.0208(8)	0.426(2)	8.2(5)

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

plane. The N−Cu−N′ angle lying in the plane is 110.5(1)°. The two planes are almost orthogonal (dihedral angle: 81.2°), and repetition of this unit in the *c*-axis direction forms the one-dimensional chain structure shown in Figure 3a. In the crystal, all chains run parallel along the *c*-axis direction and interact weakly through both $\pi-\pi$ interactions between the dchq molecules (the nearest carbon to carbon distance of 3.456(5) Å) and hydrogen-bonding interactions between the oxygen atoms of the perchlorate ion and dchq (2.721(5) Å). The adjacent copper ions bridged by two dchq ligands are, strictly speaking, not on the plane defined by these dchq ligands: they are ca. 0.7 Å above or beneath the plane (Table 7). This is probably due to these interchain interactions.

In order to construct a one-dimensional chain from ideal tetrahedral metal ions and bridging ligands, we first consider a one-dimensional array of metal ions at regular intervals whose 2-fold rotation axes are coincident with each other (Figure 4a). Since dchq has a planar structure, the neighboring metal ions can be bridged easily when every other metal ion rotates 90° around the 2-fold rotation axis as illustrated in Figure 4b. The required bridging angle of 70.5° in this case is larger than the nominal bridging angle of 60° in dchq. This misfit is easily compensated by nonlinear C−N−Cu bonds (170.4(3) and 173.8(3)°). All copper(I) ions in the one-dimensional chain in **1** are not on the same line but form a zigzag chain structure as shown in Figure 3, making a Cu′···Cu···Cu″ angle of 156.22(2)°.

Similar one-dimensional chains composed of a tetrahedral metal ion and a bridging ligand so far reported are $[\mathrm{Cu(NC(CH_2)_2CN)_2}](\mathrm{NO_3})$[24] and Cu(*cis*-dbe)$_2$(ClO$_4$)[6] where *cis*-dbe = *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene. The bridged Cu···Cu distance of 6.2727(2) Å in **1** is comparable to those of 5.93 and 6.11 Å in the former and the latter compounds, respectively. Copper(I) ions in the one-dimensional chain in the former compound form a zigzag chain with a Cu′···Cu···Cu″ angle of 157.3°, similar to that of **1**. The deviation from an ideal one-dimensional chain structure in the former compound is probably caused by the spatially twisted positions of two bridging CN groups in succinonitrile. On the other hand, copper(I) ions in the latter compound form a completely straight line. The bulky thienyl groups in the bridging ligand may prevent interchain $\pi-\pi$ interactions, resulting in the formation of the straight chain.

Table 6. Selected Bond Distances (Å) and Angles (deg) for **1**−**3**

Distances for **1**			
Cu(1)−N(1)	2.025(3)	Cu(1)−N(1′)[a]	2.025(3)
Cu(1)−N(2′)[b]	1.993(3)	Cu(1)−N(2″)[c]	1.993(3)
O(1)−C(1)	1.335(4)	O(2)−C(4)	1.354(4)
O(1)···O(5′)[d]	2.672(4)	O(2)···O(4′)[e]	2.721(5)
C(3)···C(5′)[e]	3.456(5)	Cu(1)···Cu(1′)[f]	6.2727(2)
(O(4): ClO_4	O(5): acetone)		
Distances for **2**			
Cu(1)−N(1)	2.006(8)	Cu(1)−N(2)	1.968(9)
Cu(1)−N(3′)[g]	2.017(8)	Cu(1)−N(4′)[h]	1.969(9)
C(4)···C(15′)[i]	3.54(1)	C(7)···C(12′)[j]	3.54(1)
Cu(1)···Cu(1′)[k]	9.791(2)	Cu(1)···Cu(1″)[l]	9.935(2)
Distances for **3a**			
Cu(1)−N(1)	1.99(1)	Cu(1)−N(2′)[m]	2.00(1)
Cu(1)−N(3)	2.00(1)	Cu(1)−N(4′)[n]	2.01(1)
C(13)−C(26′)[o]	3.50(2)	C(16)−C(25′)[p]	3.40(2)
C(18)−C(23′)[p]	3.38(2)		
Distances for **3b**			
Cu(1)−N(1)	1.987(8)	Cu(1)−N(2′)[q]	2.00(1)
Cu(1)−N(3)	2.04(1)	Cu(1)−N(4′)[r]	1.98(1)
C(13)−C(26′)[o]	3.51(2)	C(16)−C(25′)[s]	3.37(2)
C(18)−C(23′)[s]	3.38(2)		
Angles for **1**			
N(1)−Cu(1)−N(1′)[a]	109.8(2)	N(1)−Cu(1)−N(2′)[b]	105.6(1)
N(1)−Cu(1)−N(2″)[c]	110.5(1)	N(1′)[a]−Cu(1)−N(2′)[b]	110.5(1)
N(1′)[a]−Cu(1)−N(2″)[c]	105.6(1)	N(2′)[b]−Cu(1)−N(2″)[c]	115.0(2)
C(7)−N(1)−Cu(1)	170.4(3)	C(8)−N(2)−Cu(1′)[c]	173.8(3)
Cu(1″)[f]··Cu(1)··Cu(1′)[c]	156.22(2)		
Angles for **2**			
N(1)−Cu(1)−N(2)	109.7(4)	N(1)−Cu(1)−N(3′)[g]	113.2(3)
N(1)−Cu(1)−N(4′)[h]	107.1(4)	N(2)−Cu(1)−N(3′)[g]	107.6(4)
N(2)−Cu(1)−N(4′)[h]	113.3(4)	N(3′)[g]−Cu(1)−N(4′)[h]	106.1(4)
C(1)−N(1)−Cu(1)	168.0(9)	C(9)−N(2)−Cu(1)	174.2(9)
C(8)−N(3)−Cu(1′)[k]	172.4(9)	Cu(1′)[l]−N(4)−C(14)	179.1(5)
Angles for **3a**			
N(1)−Cu(1)−N(2′)[m]	114.5(5)	N(1)−Cu(1)−N(3)	108.4(5)
N(1)−Cu(1)−N(4′)[n]	111.1(5)	N(2′)[m]−Cu(1)−N(3)	107.1(5)
N(2′)[m]−Cu(1)−N(4′)[n]	109.2(4)	N(3)−Cu(1)−N(4′)[n]	106.1(5)
Cu(1)−N(1)−C(1)	178(1)	Cu(1′)[t]−N(2)−C(8)	173(1)
Cu(1)−N(3)−C(11)	174(1)	Cu(1″)[p]−N(4)−C(18)	171(1)
Angles for **3b**			
N(1)−Cu(1)−N(2′)[q]	113.9(4)	N(1)−Cu(1)−N(3)	109.0(4)
N(1)−Cu(1)−N(4′)[r]	111.7(4)	N(2′)[q]−Cu(1)−N(3)	107.3(4)
N(2′)[q]−Cu(1)−N(4′)[r]	108.3(4)	N(3)−Cu(1)−N(4′)[r]	106.4(4)
Cu(1)−N(1)−C(1)	179(1)	Cu(1′)[u]−N(2)−C(8)	176(1)
Cu(1)−N(3)−C(11)	173.6(9)	Cu(1″)[r]−N(4)−C(18)	170.8(9)

[a] $-x + 2, y, -z + 1/2$. [b] $x, -y, z - 1/2$. [c] $-x + 2, -y, -z + 1$. [d] $x + 1/2, y - 1/2, z$. [e] $-x + 3/2, -y + 3/2, -z + 1$. [f] $-x + 2, -y, -z$. [g] $-x + 1, y - 1/2, -z + 1/2$. [h] $-x, y + 1/2, -z + 1/2$. [i] $-x + 1/2, -y + 1, z - 1/2$. [j] $-x + 1/2, -y + 1, z + 1/2$. [k] $-x + 1, y + 1/2, -z + 1/2$. [l] $-x, y - 1/2, -z + 1/2$. [m] $x + 1, -y + 1, z + 1/2$. [n] $x - 1/2, -y + 3/2, z + 1/2$. [o] $x + 1, y, z$. [p] $x + 1/2, -y + 3/2, z - 1/2$. [q] $x + 1, -y, z + 1/2$. [r] $x - 1/2, -y + 1/2, z + 1/2$. [s] $x + 1/2, -y + 1/2, z - 1/2$. [t] $x - 1, -y + 1, z - 1/2$. [u] $x - 1, -y, z - 1/2$.

Table 7. Dihedral Angles (deg) and Distances from the Least-Squares Planes (Å) for **1** and **2**

compd	plane 1	plane 2	dihedral angle	atom	dist from plane 1
1	C(1)−C(2)−C(3)−C(4)−C(5)−C(6)	C(1′)−C(2′)−C(3′)−C(4′)−C(5′)−C(6′)[a]	81.22	Cu(1)	0.6975
				Cu(1″)[b]	0.7024
2	C(2)−C(3)−C(4)−C(5)−C(6)−C(7)	C(10)−C(11)−C(12)−C(13)−C(14)−C(15)	58.01	Cu(1)	0.3987
	Cu(1′)[c]−Cu(1″)[d]−Cu(1‴)[e]−Cu(1⁗)[f]			Cu(1)	0.4722

[a] $+x, -y, z - 1/2$. [b] $2 - x, -y, 1 - z$. [c] $1 - x, -1/2 + y, 1/2 - z$. [d] $-1 - x, 3/2 + y, 1/2 - z$.[e] $-1 - x, -1/2 + y, 1/2 - z$. [f] $1 - x, 3/2 + y, 1/2 - z$.

Table 8. Dihedral Angles (deg) for **3a** and **3b**

plane 1	plane 2	**3a**	**3b**
C(2)−C(3)−C(4)−C(5)−C(6)−C(7)	C(12)−C(13)−C(14)−C(15)−C(16)−C(17)	81.77	81.01
C(12)−C(13)−C(14)−C(15)−C(16)−C(17)	C(22)−C(23)−C(24)−C(25)−C(26)−C(27)	2.19	2.37
C(2)−C(3)−C(4)−C(5)−C(6)−C(7)	C(22)−C(23)−C(24)−C(25)−C(26)−C(27)	83.95	83.37

Structure of [Cu(ipn)$_2$](PF$_6$)(Me$_2$CO) (2). An ORTEP drawing of the asymmetric unit of this polymer compound is shown in Figure 5. Four ipn ligands coordinate to a copper(I) ion with tetrahedral geometry (Table 6) through the nitrogen atoms of CN groups. The other CN group of each ipn coordinates to four different copper(I) ions, respectively, which

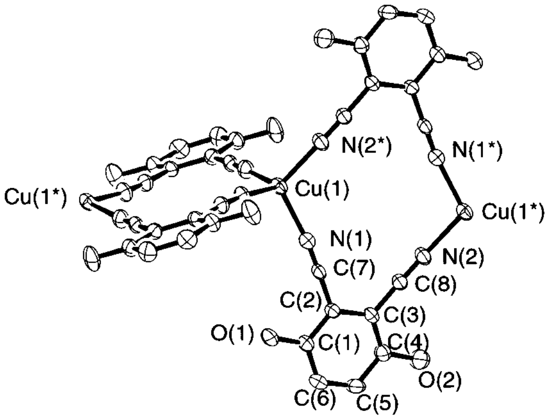

Figure 2. ORTEP drawing of a part of the one-dimensional chain structure in **1** showing 50% probability displacement ellipsoids. Hydrogen atoms, acetone, and ClO_4^- are omitted for clarity.

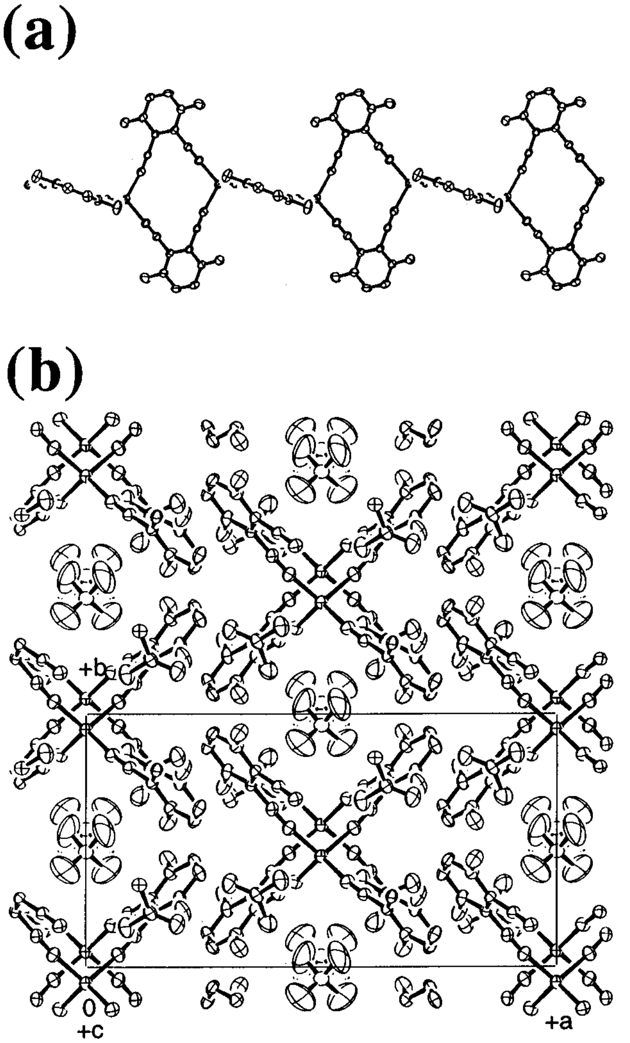

Figure 3. (a) Side view of the one-dimensional chain structure in **1**. (b) Crystal packing of **1** viewed down the *c* axis.

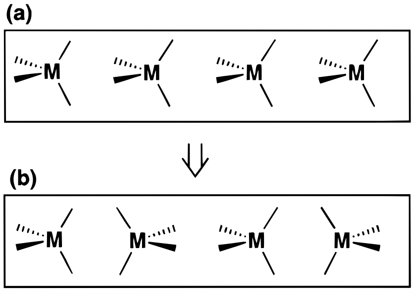

Figure 4. Construction of a one-dimensional chain structure from ideal tetrahedral metal ions and planar bridging ligands. The required bridging angle for the idealized structure is 70.5°.

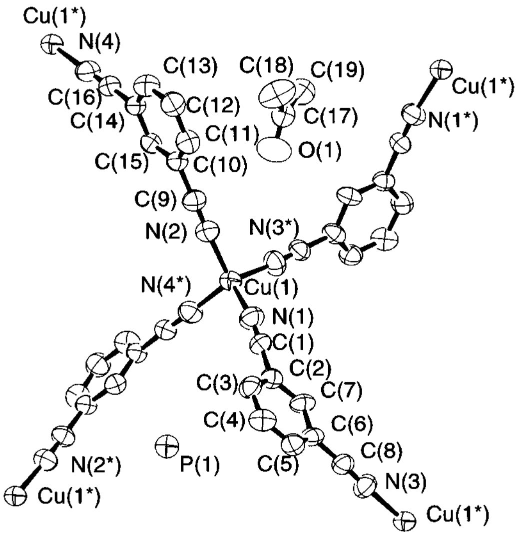

Figure 5. ORTEP drawing of a part of the two-dimensional sheet structure in **2** showing 50% probability displacement ellipsoids. Hydrogen and fluorine atoms are omitted for clarity.

lie on the same plane and form a rectangle with dimensions the same as those of the *a* and *b* axes. The central copper(I) ion is located 0.47 Å above the plane. Two of the four ipn ligands which bridge three copper ions on the diagonal of the rectangle are on the same side of the plane. These two ipn ligands are not parallel to each other but have a dihedral angle of 58.0°. Repetition of this unit in the *a*−*b* plane results in the formation of a two-dimensional sheet structure with Cu···Cu separations of 9.79 and 9.93 Å, as shown in Figure 6. Since successive sheets are stacked in the same manner along the *c*-axis direction, a cavity structure surrounded by four ipn ligands is formed with dimensions of about 6 Å × 11 Å. An acetone molecule and a PF_6 anion are incorporated in the cavity. The acetone molecules are easily removed by drying the crystal in argon, resulting in loss of its clarity, indicating decomposition of the crystal structure.

The two-dimensional structure described here is similar to that of $[Cu(NC(CH_2)_3CN)_2](NO_3)$.[25] Figure 7 shows schematic two-dimensional arrangements of tetrahedral metal ions. In an ideal case, shown in Figure 7a, a ligand with a tetrahedral bridging angle (109.5°) can bridge metal ions without any stress and, if the ligand is planar, the plane will be perpendicular to the metal plane. In the case of compound **2**, shown in Figure 7b, however, the bridging ipn inclines about 30° from the *c* axis, which may relieve stress caused by a misfit of the bridging angle. A nonlinear C−N−Cu angle of 168.0(9)° (Table 6) may also relieve the stress. As a result, the copper(I) ions rotate clockwise and counterclockwise alternately around their 2-fold axis. On the other hand, the bridging ligand in $[Cu(NC(CH_2)_3CN)_2](NO_3)$[25] is not planar or rigid; the arrangement in Figure 7c is realized.

Structure of $[Cu(dmtpn)_2](X)(dmtpn)(THF)$ (3a, X = BF_4; 3b, X = ClO_4). These two compounds have almost same structure.[20] An ORTEP drawing of an asymmetric unit of **3b** together with the atom-numbering scheme is shown in Figure 8. The asymmetric unit of each compound contains one copper(I) ion, two dmtpn ligands coordinating to the copper(I) ion, one tetrafluoroborate or perchlorate counteranion, and one metal-free dmtpn and one THF as guests. As can be seen from Figure

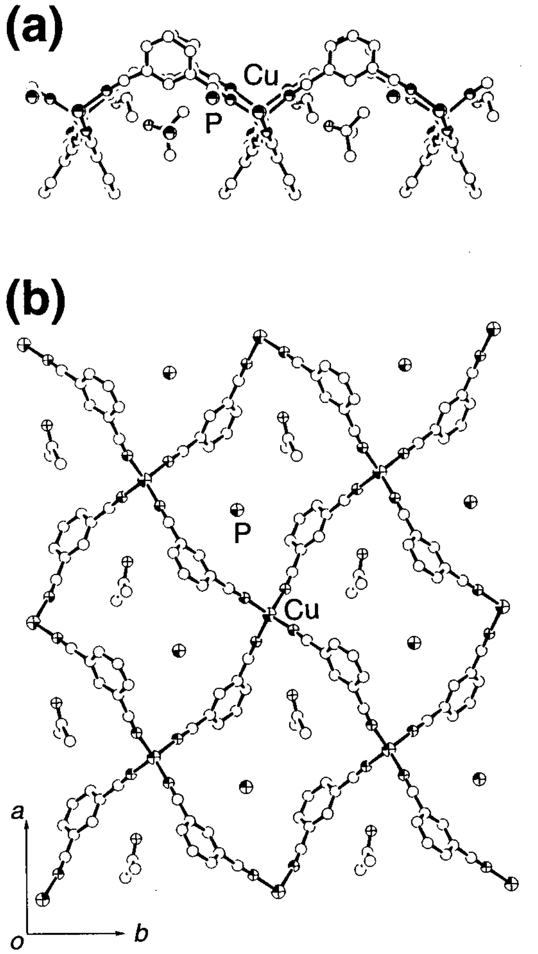

Figure 6. (a) Side view from the [110] direction and (b) top view of the two-dimensional sheet structure in **2**. Hydrogen and fluorine atoms are omitted for clarity.

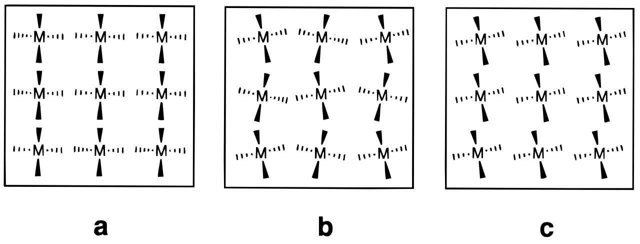

Figure 7. Possible two-dimensional arrangements of tetrahedral metal ions: (a) an ideal arrangement which can be bridged by a ligand with a bridging angle of 109.5°; (b) the arrangement realized in **2**; (c) the arrangement realized in $[Cu(NC(CH_2)_3CN)_2](NO_3)$[25] with a twisted bridging ligand. Boldfaced and dotted lines indicate coordination bonds pointing upward and downward from the metal ions, respectively.

8, the copper(I) ion has a tetrahedral coordination through four nitrogen atoms of four different dmtpn ligands. Table 6 shows Cu−N bond lengths and N−Cu−N′ angles, indicating that both CuN_4 chromophores are almost regular tetrahedra. Two of the four dmtpn ligands around a copper(I) ion and a metal-free dmtpn are almost parallel to each other, while the other two dmtpn ligands are not parallel to each other or to the metal-free dmtpn. The cyano groups at the other end of the four dmtpn ligands, also coordinate to different copper(I) ions, resulting in the formation of a three-dimensional diamond-like framework as shown in Figure 9. It should be noted that there are three independent frameworks interpenetrating each other.

The interpenetration of three-dimensional frameworks is often found in coordination compounds with diamond-like structures. 2-fold to 9-fold interpenetrations of diamondoid networks have been reported.[2,11,16−21] Generally, the degree of interpenetration in a diamond-like structure is strongly correlated with the bridged M···M distance; the longer the M···M distance, the more the degree of interpenetration.[21] The 3-fold interpenetration in compounds **3a** and **3b** should be compared with the 5-fold interpenetration in $[Cu(tpn)_2](BF_4)$[18] (tpn = terephthalonitrile), where these two bridging ligands, dmtpn and tpn, have the same Cu···Cu distance of 11.9 Å. The less interpenetrations in the former compounds are reasonably related to the bulkiness of the methyl groups in dmtpn and the incorporation of guest molecules. Metal-free dmtpn molecules incorporated in the Cu(dmtpn)$_2$ framework participate in the formation of π−π stacking columns (the nearest carbon distances are 3.37(2) and 3.51(2) Å). The pale-yellow color of both **3a** and **3b** is probably induced by the formation of π−π stacking. As can be seen from Figure 9, coordinated and uncoordinated dmtpn molecules stack alternately. The stacking columns run through the diamond-like frameworks along the [101] direction.

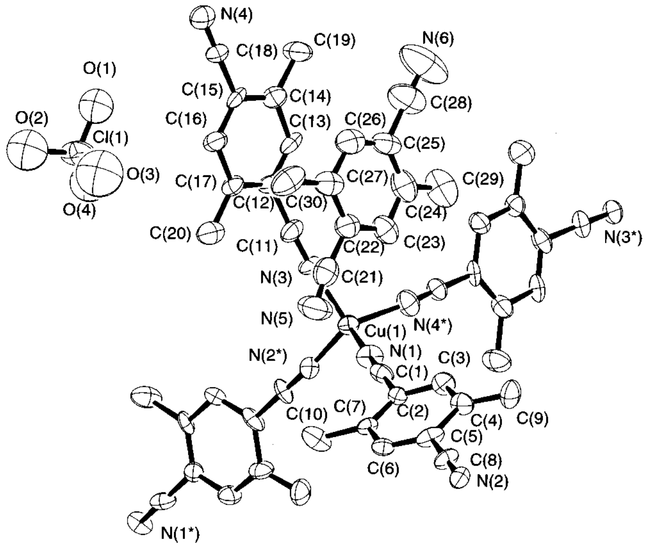

Figure 8. ORTEP drawing of coordinated and uncoordinated dmtpn molecules around a copper(I) ion in **3b** showing 50% probability displacement ellipsoids. Hydrogen atoms and a THF molecule are omitted for clarity.

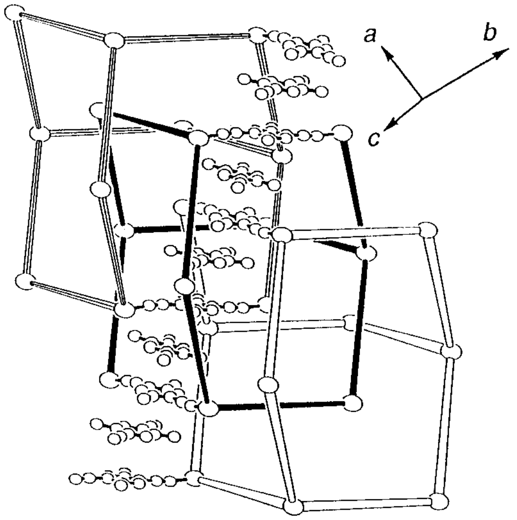

Figure 9. Three independent diamond-like frameworks of copper(I) ions connected by bridging dmtpn ligands in **3b**. Large circles and rods represent copper(I) ions and dmtpn, respectively. Three different types of rods represent independent diamond-like frameworks interpenetrating each other. Also shown is a part of the π−π stacking column composed of alternately coordinated and uncoordinated dmtpn molecules.

Control of Structural Dimensionality in Coordination Polymers. By using three derivatives of dicyanobenzene, dchq, ipn, and dmtpn, as bridging ligands, we could successfully control the dimensionality of copper(I) coordination polymers. Dchq having a bridging angle of 60° forms a one-dimensional chain structure, ipn having one of 120° forms a two-dimensional sheet, and dmtpn having one of 180° forms a three-dimensional diamond-like structure. In each case, a copper(I) ion maintains tetrahedral geometry and the four coordination sites are fully occupied by four bridging ligands, not by solvent molecules or counteranions. This is an important criterion for obtaining "binary" polymer frameworks with tetrahedral metal ions and for controlling their structural dimensionality. To generalize the above findings in different metal−ligand systems will be a topic of our future study.

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Supporting Information Available: Four X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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