Architecture of 2D Sheets with Six-Membered Rings of Coppers Interconnected by 2,1,3-Benzothiadiazoles and a Layered Structure Composed of the 2D Sheets

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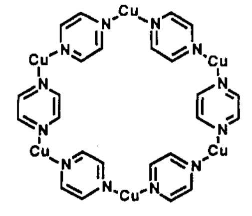
Three Cu(I) complexes and one Ag(I) complex with 2,1,3-benzothiadiazole (btd) and Cu(I) complexes with 5,6-benzopyrimidine (bpm), $\{[Cu_2(btd)_3(ClO_4)](ClO_6)\cdot 2thf\}_\infty$ (**1**), $[Cu(btd)(HPO_3F)]_\infty$ (**2**), $[Cu(btd)(NO_3)]_\infty$ (**3**), $\{[Ag(btd)](ClO_4)\}_\infty$ (**4**), and $\{[Cu_2(bpm)_2(C_2H_4)(Me_2CO)](ClO_4)_2\}_\infty$ (**5**), were synthesized; their molecular structures and packing were determined by using single-crystal X-ray diffraction methods. Complex **1** is a 2D structure composed of six-membered rings of coppers interconnected by six btds, $[Cu_6(btd)_6]^{6+}$. The coppers in the 2D sheet approximately lie in the same plane. The 2D sheet composed of the six-membered rings $[Cu_6(btd)_4(HPO_3F)_4]^{2+}$ is still maintained in **2** although HPO_3F^- anions take part in the interconnecting as well as btd molecules. The Cu framework of the six-membered rings of coppers interconnected by btd and NO_3^-, $[Cu_6(btd)_4(NO_3)_4]^{2+}$, in the 2D complex **3** is in a chair form and makes it possible to stack btd molecules within and between the 2D sheets, forming a layered structure similar to that of graphite. Ag atoms in **4** are coordinated to two nitrogen atoms of interconnecting btd molecules to give a linear chain, and the btd molecules partially overlap between the chains. Cu atoms in **5** are N-coordinated to the interconnecting bpm molecules to form a 1D compound. The roles of metal ion, ligand, and counteranion have been discussed in the construction of 2D sheets with the six-membered rings of metal ions interconnected by aromatic compounds and a layered structure composed of the 2D sheets. Crystal data: **1**, monoclinic $P2_1/a$, $a = 17.817(2)$ Å, $b = 11.220(2)$ Å, $c = 18.186(3)$ Å, $\beta = 110.361(8)°$, $V = 3408(2)$ Å^3, $Z = 4$, 4272 reflections, $R = 0.051$; **2**, monoclinic $P2_1/a$, $a = 16.576(2)$ Å, $b = 10.711(2)$ Å, $c = 11.001(1)$ Å, $\beta = 101.29(1)°$, $V = 1915.4(8)$ Å^3, $Z = 4$, 2645 reflections, $R = 0.045$; **3**, triclinic $P\bar{1}$, $a = 9.757(2)$ Å, $b = 11.593(3)$ Å, $c = 8.124(2)$ Å, $\alpha = 110.23(2)°$, $\beta = 101.20(2)°$, $\gamma = 74.98(2)°$, $V = 827.1(3)$ Å^3, $Z = 2$, 1767 reflections, $R = 0.030$; **4**, monoclinic $C2/c$, $a = 13.483(5)$ Å, $b = 20.384(3)$ Å, $c = 7.278(7)$ Å, $\beta = 98.90(5)°$, $V = 1976(2)$ Å^3, $Z = 8$, 2309 reflections, $R = 0.045$; **5**, monoclinic $C2/c$, $a = 11.099(2)$ Å, $b = 19.106(2)$ Å, $c = 12.558(2)$ Å, $\beta = 104.10(1)°$, $V = 2582.8(5)$ Å^3, $Z = 8$, 2113 reflections, $R = 0.052$.

Introduction

Metal complex polymer chemistry is among the most promising interfaces between synthetically based chemistry and new material chemistry.[1-7] It is providing foundations for the understanding of how molecules can be organized and how functions can be revealed. A particularly high expectation of this field is the genesis of new molecules that have powerful performance capabilities.[7] Huenig et al.[8] have found that an interesting Cu(I) polymer with 2,5-dimethyl-*N*,*N*-dicyanoquinodiimine (ddqd) has a high electric conductivity (powder) of 0.4 S cm^{-1}. Robson et al.[9] have recently constructed three-dimensional cadmium–cyanide complex polymers with a honeycomb structure containing hexagonal channels, which provides a potentially useful model for the future construction of related materials with larger channels and possible catalytic applications.

A number of Cu(I) and Ag(I) complexes with halide, cyanide, and sulfide have been extensively studied, and infinite chains and two and three-dimensional polymers of the metal complexes have been structurally characterized.[10,11] In contrast, there are few reports on the polymers of these metal complexes with organic ligands in the literature.[12-19] The polynuclear Cu(I) complexes with infinite chains (ligand = tetramethylpyrazine,[12] *trans*-1,2-bis(2-pyridyl)ethylene,[13] and 1-(pyrazoyl-1′-ylmethyl)-1,2-diaminoethane[14]), single helical chains (2,6-bis[*N*-{2-(2-pyridyl)ethyl}formimidoyl]-1-methoxybenzene[15]), infinite stairs (thiochrome[16]), two-dimensional networks (ddqd,[8] pyrazine[17]), and three-dimensional networks (phenazine[18] and quinoxaline[19]) have been synthesized and characterized.

We have been interested in two-dimensional polymers consisting of a six-membered ring of metal ions interconnected by aromatic compounds (I)[17,18] that are structurally analogous to sphelands



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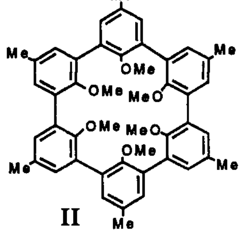

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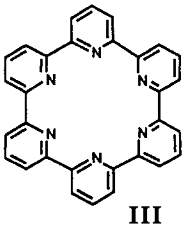

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Table 1. Crystal Data for $\{[Cu_2(btd)_3(ClO_4)]ClO_4{\cdot}2thf\}_\infty$ (**1**), $[Cu(btd)(HPO_3F)]_\infty$ (**2**), $[Cu(btd)(NO_3)]_\infty$ (**3**), $\{[Ag(btd)](ClO_4)\}_\infty$ (**4**), and $\{[Cu_2(bpm)_2(C_2H_4)Me_2CO)](ClO_4)_2\}_\infty$ (**5**)

	1	**2**	**3**	**4**	**5**
chem formula	$Cu_2C_{26}H_{28}N_6O_{10}S_3Cl_2$	$Cu_2Cl_{12}H_{10}N_4O_6F_2P_2S_2$	$CuC_6H_4N_3O_3S$	$AgC_6H_4N_2O_4SCl$	$CuC_{10.5}H_{11}N_2O_{4.5}Cl$
fw	878.75	597.42	261.72	343.49	336.21
color	orange	deep red	red	colorless	yellow
cryst size, mm	0.45 × 0.45 × 0.40	0.40 × 0.20 × 0.25	0.30 × 0.25 × 0.20	0.30 × 0.25 × 0.25	0.25 × 0.35 × 0.25
cryst system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/a$	$P\bar{1}$	$C2/c$	$C2/c$
cell constants					
a, Å	17.817(2)	11.001(1)	9.757(2)	13.483(5)	11.099(2)
b, Å	11.220(2)	10.711(2)	11.593(3)	20.384(3)	19.106(2)
c, Å	18.186(3)	16.576(2)	8.124(2)	7.278(7)	12.558(2)
α, deg	90.00	90.00	110.23(2)	90.00	90.00
β, deg	110.36(1)	101.29(1)	101.20(2)	98.90(5)	104.10(1)
γ, deg	90.00	90.00	74.98(2)	90.00	90.00
V, Å^3	3408(2)	1915.4(4)	827.1(3)	1976(2)	2582.8(5)
Z	4	4	2	8	8
σ_{calcd}, g·cm^{-3}	1.713	2.072	2.102	2.309	1.729
radiation (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Cu Kα (1.154 178)
T, °C	23	23	23	23	23
no. of unique data used ($\|F\| > 3\sigma\|F_o\|$)	4272	2645	1767	1238	2113
R^a	0.051	0.045	0.030	0.045	0.052
$R_w{}^b$	0.060	0.052	0.036	0.048	0.076
F_{000}	1720	1184	520	1328	1360
μ, cm^{-1}	16.45	26.68	28.68	24.89	44.63

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

(**II**)[20] and sexipyridine (**III**),[21] on the basis of our expectation that the incorporation of optically tunable ligands and redox-tunable unsaturated metal centers into the two-dimensional polymer sheets should further augment their physical properties. This has led us to construct molecular assemblies of the metal complexes with linear chains and two-dimensional frameworks, stacking columns, and layer structures.

Although thiadiazoles are readily available ligands, their potential of complex formation has not entirely been explored. Interconnecting N-coordination of thiadiazoles impart to these molecules structural characteristics that can be used for developing unusual metal complex architectures. Especially, 2,1,3-benzothiadiazole (btd) is considered as a potential ligand to bring together Cu and Ag atoms, which can form two-dimensional frameworks. Surprisingly, no metal complexes with thiadiazole have been reported, and subsequently, metal thiadiazole chemistry is not known. Our current interests are focused on the architecture and characterization of new two-dimensional polynuclear complexes composed of six-membered rings of Cu(I) interconnected by btd molecules and a layered structure stacked through π–π interaction of btd molecules between the polymer sheets similar to the layered structure consisting of two-dimensional sheets with six-membered rings of carbons in graphite.

Experimental Section

General Methods. All operations were conducted under argon and ethylene by using the standard Schlenk or vacuum line technique. $[Cu(MeCN)_4]ClO_4$ was prepared according to literature procedures.[22] Acetone treated with $KMnO_4$ was dried over K_2CO_3 from 4-Å molecular sieves. Acetonitrile[23] and tetrahydrofuran (thf)[24] were purified according to literature procedures. Electronic spectra were recorded on a Hitachi spectrometer. Reagent grade 2,1,3-benzothiadiazole and 5,6-benzopyrimidine were obtained from Wako Pure Chemical, Inc. All other chemicals were of reagent grade and were used without further purification.

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 $\{[Cu_2(btd)_3(ClO_4)](ClO_4){\cdot}2thf\}_\infty$ (1). Copper(II) perchlorate hexahydrate (0.16 mM, 59.3 mg) and copper plates (3 × 3 × 1 mm, five pieces) were stirred in thf (8 mL) for 0.5 h under an ethylene atmosphere, and btd (0.32 mM, 43.6 mg) was added. Then, under an argon atmosphere the mixture was stirred and filtered. The yellow filtrate (5 mL) was transferred in a glass tube, and *n*-pentane (5 mL) was added slowly as a diffusion solvent. After standing for 7 days at 25 °C, yellow plate crystals were isolated at the interface between thf and *n*-pentane. Anal. Calcd for $Cu_2C_{26}H_{28}N_6O_{10}S_3Cl_2$: C, 35.53; H, 3.21; N, 9.56. Found: C, 35.27; H, 3.31; N, 9.42.

Synthesis of $[Cu(btd)(HPO_3F)]_\infty$ (2). Tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.5 mM, 186.4 mg) and btd (0.5 mM, 68.1 mg) were stirred in acetone (10 mL) for 10 min under an argon atmosphere, and the mixture was filtered. The yellow filtrate (5 mL) was transferred in a glass tube, and *n*-pentane (5 mL) was added slowly as a diffusion solvent. After standing for 7 days at 25 °C, colorless prism crystals and yellow precipitates were isolated at the interface between acetone and *n*-pentane, and then after standing for 30 days, deep red plate crystals were obtained. Anal. Calcd for $CuC_6H_5N_2O_3SFP$: C, 24.13; H, 1.69; N, 9.38; F, 6.36. Found: C, 23.93; H, 1.69; N, 9.32; F, 6.72.

Synthesis of $[Cu(btd)(NO_3)]_\infty$ (3). Copper(II) nitrate trihydrate (0.112 mM, 27.1 mg) and copper plates (3 × 3 × 1 mm, five pieces) were stirred in thf (8 mL) for 0.5 h under an ethylene atmosphere, and btd (2.24 mM, 30.6 mg) was added. The yellow suspended mixture was stirred for 1 h under an argon atmosphere and then filtered. The yellow filtrate was transferred in a glass tube, and *n*-pentane (5 mL) was added slowly as a diffusion solvent under an argon atmosphere. Yellow precipitates were first isolated, and then red plate crystals were obtained after standing for 7 days at 25 °C. Calcd for $CuC_6H_4N_3O_3S$: C, 27.53; H, 1.54; N, 16.05. Found: C, 27.38; H, 1.21; N, 15.94.

Synthesis of $\{[Ag(btd)](ClO_4)\}_\infty$ (4). An acetone solution (10 mL) of silver(I) perchlorate (1.2 mM, 248.8 mg) was added to btd (1.2 mM, 163.4 mg) under an argon atmosphere. The colorless solution was

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transferred in a glass tube, *n*-pentane (10 mL) was added slowly as a diffusion solvent, and the glass tube was sealed under an argon atmosphere. After standing for 7 days at 25 °C in dark room, colorless prism crystals were obtained.

Synthesis of {[Cu$_2$(bpm)$_2$(C$_2$H$_4$)(Me$_2$CO)](ClO$_4$)$_2$}$_\infty$ (5). Copper(II) perchlorate hexahydrate (0.16 mM, 8.2 mg) and copper plates (3 × 3 × 1 mm, five pieces) were stirred in acetone (8 mL) for 0.5 h under an ethylene atmosphere, and btd (0.32 mM, 6.9 mg) was added. The mixture (5 mL) was transferred in a glass tube, *n*-pentane (5 mL) was added slowly as a diffusion solvent, and the glass tube was sealed under an argon atmosphere.. After standing for 3 days at 25 °C, yellow plate crystals were obtained.

X-ray Data Collection, Structure Solution, and Refinement. Four crystals of Cu(I) complexes were coated with paraffin to avoid decomposition in the air. Diffraction data were obtained on a Rigaku AFC-5R four-circle diffractometer at 23 °C. Crystal data and details of measurements for the Cu(I) (**1**–**3**, **5**) and Ag(I) (**4**) complexes are summarized in Table 1. The standard reflections were monitored every 25 measurements, and the decay of their intensities was within 5%. Reflection data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied.

The structures were solved by a direct method[25] and refined anisotropically for non-hydrogen atoms by block-diagonal least-squares calculations. 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.[26] Hydrogen atoms were included as a fixed contribution in the last cycle; their temperature factors were assumed to be isotropic. The calculations were performed on the VAX computer by using the program system TEXAN.[27] The final R and R_w values were 0.051 and 0.060 for **1**, 0.045 and 0.052 for **2**, 0.030 and 0.036 for **3**, 0.045 and 0.048 for **4**, and 0.055 and 0.064 for **5**, respectively. The final parameters for non-hydrogen atoms and selected bond distances and angles for **1**–**5** are given in Tables 2–7, respectively.

Results

Construction of 2D Compounds with Hexanuclear Copper Rings.

(A) {[Cu$_2$(btd)$_3$(ClO$_4$)]ClO$_4$·2thf}$_\infty$ (1). Figure 1A,B depicts the structure and labeling scheme of a segment of the two-dimensional sheets of **1**, which is a huge polynuclear complex composed of a [Cu$_6$(btd)$_6$]$^{6+}$ framework of six-membered rings of coppers interconnected by btd molecules. Such a ring connecting aromatic compounds could be clearly distinguished from the six-membered rings of organic compounds such as benzene and cyclohexane. The Cu(1) atom is coordinated in a tetrahedral geometry to one oxygen atom of perchlorate and three nitrogen atoms of different btd molecules, which act as interconnecting ligands and lie ca. 0.30 Å from the plane defined by N(2), N(3), and N(5) because of the coordination of the oxygen [Cu(1)–O(5) = 2.242(5) Å]. The Cu(2) atom is not coordinated to perchlorate and subsequently is found in a trigonal geometry, the nearest Cu(2)···O(ClO$_4$) distance being 2.501(5) Å. The Cu–N distances of 1.998(5) Å (average) for the three-coordinate Cu(2) are essentially the same as 2.004(5) Å (average) for the four-coordinate Cu(1). The six-membered rings of coppers are slightly distorted because of the different Cu···Cu distances of 6.22 and 6.30 Å. The two-dimensional sheet of **1** is shown in Figure 1C, where only copper centers are presented. The coppers in the sheet approximately lie on the same plane. All btd molecules are at some intermediate angle between parallel and perpendicular angles to the sheet plane as described later.

Table 2. Positional and Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of {[Cu$_2$(btd)$_3$(ClO$_4$)](ClO$_4$)·2thf}$_\infty$[a]

atom	x	y	z	B(eq)[b]
Cu(1)	0.09577(4)	0.04295(7)	0.32192(5)	3.49(3)
Cu(2)	−0.26130(4)	−0.03892(7)	0.29241(5)	3.78(3)
Cl(1)	0.2699(1)	0.0333(2)	0.4852(1)	3.98(6)
Cl(2)	0.7345(1)	0.1215(2)	0.1097(1)	4.97(8)
S(1)	0.1564(1)	−0.2228(1)	0.3253(1)	3.67(6)
S(2)	−0.0889(1)	0.0472(1)	0.2956(1)	3.85(6)
S(3)	0.1837(1)	0.2904(1)	0.3350(1)	3.58(6)
O(1)	0.7548(3)	0.0329(5)	0.1686(3)	6.9(3)
O(2)	0.8009(4)	0.1496(7)	0.0899(4)	10.1(4)
O(3)	0.6783(4)	0.0729(8)	0.0441(4)	12.2(5)
O(4)	0.7012(6)	0.2183(6)	0.1347(6)	13.1(5)
O(5)	0.1912(3)	0.0754(5)	0.4388(3)	5.9(2)
O(6)	0.2827(6)	0.054(1)	0.5671(4)	7.4(5)
O(7)	0.2836(8)	−0.085(1)	0.4725(7)	9.4(6)
O(8)	0.3223(7)	0.108(1)	0.464(1)	14(1)
O(9)	0.4934(5)	0.2575(6)	0.8553(5)	10.5(4)
O(10)	0.4693(5)	0.1187(6)	0.3341(4)	8.6(4)
O(11)	0.304(1)	0.097(2)	0.545(1)	5.2(5)
O(12)	0.320(2)	0.030(3)	0.444(2)	9.4(9)
O(13)	0.256(2)	−0.086(3)	0.497(2)	7.3(8)
N(1)	−0.1416(3)	−0.0319(4)	0.3345(3)	3.2(2)
N(2)	−0.0001(3)	0.0036(4)	0.3512(3)	3.3(2)
N(3)	0.1086(3)	0.2071(4)	0.2853(3)	3.2(2)
N(4)	0.1614(3)	0.4073(4)	0.2798(3)	3.2(2)
N(5)	0.1457(3)	−0.0934(4)	0.2841(3)	3.3(2)
N(6)	0.1953(3)	−0.2941(4)	0.2693(3)	3.2(2)
C(1)	−0.0896(3)	−0.0950(5)	0.3940(3)	3.0(2)
C(2)	−0.0080(3)	−0.0747(5)	0.4031(3)	2.9(2)
C(3)	0.0543(4)	−0.1336(6)	0.4633(4)	3.6(3)
C(4)	0.0318(4)	−0.2083(6)	0.5100(4)	4.3(3)
C(5)	−0.0499(4)	−0.2287(6)	0.5015(4)	4.7(3)
C(6)	−0.1108(4)	−0.1747(6)	0.4445(4)	3.9(3)
C(7)	0.0627(3)	0.2702(5)	0.2235(4)	3.2(2)
C(8)	0.0927(3)	0.3862(5)	0.2203(4)	3.1(2)
C(9)	0.0523(4)	0.4656(6)	0.1594(4)	4.4(3)
C(10)	−0.0164(4)	0.4266(7)	0.1052(4)	5.4(3)
C(11)	−0.0477(4)	0.3106(7)	0.1083(4)	5.3(3)
C(12)	−0.0092(4)	0.2335(6)	0.1652(4)	4.3(3)
C(13)	0.1999(3)	−0.2176(5)	0.2148(4)	3.2(2)
C(14)	0.2294(4)	−0.2420(6)	0.1537(4)	4.6(3)
C(15)	0.2306(5)	−0.1508(8)	0.1049(4)	5.5(4)
C(16)	0.2054(5)	−0.0345(7)	0.1146(5)	5.6(4)
C(17)	0.1756(4)	−0.0068(6)	0.1723(4)	4.4(3)
C(18)	0.1728(3)	−0.1007(5)	0.2234(4)	3.2(2)
C(19)	0.4985(7)	0.272(1)	0.9363(6)	10.5(7)
C(20)	0.5487(7)	0.378(1)	0.9606(8)	13.3(9)
C(21)	0.6043(8)	0.368(1)	0.917(1)	13(1)
C(22)	0.5567(7)	0.321(2)	0.8432(7)	14(1)
C(23)	0.5079(6)	0.014(1)	0.3740(6)	9.3(6)
C(24)	0.4710(7)	−0.085(1)	0.3272(8)	10.1(6)
C(25)	0.3860(7)	−0.043(1)	0.2862(9)	12.3(7)
C(26)	0.3889(6)	0.090(1)	0.2885(6)	8.5(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] B(eq) is the isotropic equivalent of the anisotropic thermal parameter.

(B) [Cu(btd)(HPO$_3$F)]$_\infty$ (2). The Cu(I) complex **2** with btd was synthesized using hexafluorophosphate in the place of perchlorate in order to examine the effect of counteranion on the six-membered structure. The structure and labeling of [Cu(btd)(HPO$_3$F)]$_\infty$ are shown in Figure 2A,B, respectively. An important feature of **2** is that HPO$_3$F$^-$ takes part in the formation of the six-membered ring [Cu$_6$(btd)$_4$(HPO$_3$F)$_4$]$^{2+}$ as a interconnecting ligand as well as btd. Two-dimensional sheets are nevertheless maintained. Each Cu(I) in **2** is coordinated to two nitrogen atoms of different btds and two oxygen atoms of different HPO$_3$F$^-$ ions in a distorted tetrahedral geometry. The Cu–N distances of 1.997(9) Å (average) are essentially the same as those of 2.001(5) Å (average) for **1**. The Cu–O distances of 2.171(4) Å (average) for HPO$_3$F$^-$ bridging are slightly longer than those of 2.117(7) Å (average) for the acetate bridging of [Cu$_2$(CH$_3$COO)$_2$]$_\infty$.[28]

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[25] (a) MITHRIL-an integrated direct methods computer program: Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42. (b) DIRDIF-Direct methods for difference structures-an automatic procedure for phase extension and refinement of difference structure factors: Beurskens, P. T. *Technical Report 1984/1*; Crystallography Laboratory: Toenhooiveld, 6525 Nijimegen, Netherlands.

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[27] TEXRAY Structure Analysis Package: Molecular Structure Corp., 1985.

[28] Mounts, R. D.; Ogura, T.; Fernando, Q. *Inorg. Chem.* **1974**, *13*, 802.

Table 3. Positional and Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of $[\mathrm{Cu(btd)(HPO_3F)}]_\infty$[a]

atom	*x*	*y*	*z*	*B*(eq)[b]
Cu(1)	0.76557(6)	0.01745(8)	0.16254(7)	2.90(4)
Cu(2)	0.76246(5)	–0.24319(7)	–0.33821(7)	2.62(3)
S(1)	0.7269(1)	–0.1153(2)	–0.0922(1)	2.70(7)
S(2)	0.7351(1)	–0.1040(2)	–0.5887(1)	2.64(7)
P(1)	0.5861(1)	0.1240(2)	0.1462(1)	2.20(6)
P(2)	0.9210(1)	0.1405(2)	0.3646(2)	3.08(8)
F(1)	0.5891(3)	0.2479(4)	0.0717(4)	5.2(2)
F(2)	0.9300(3)	0.0260(5)	0.4447(5)	5.5(2)
O(1)	0.6686(2)	0.1135(4)	0.2276(4)	2.5(2)
O(2)	0.5703(3)	0.0236(5)	0.0474(5)	3.8(2)
O(3)	0.5157(3)	0.1386(5)	0.2110(5)	4.2(2)
O(4)	0.8396(3)	0.1582(4)	0.2826(4)	2.6(2)
O(5)	0.9219(4)	0.2527(5)	0.4644(5)	5.3(3)
O(6)	0.9936(3)	0.1683(7)	0.3161(7)	7.8(4)
N(1)	0.7769(3)	–0.0047(5)	–0.0085(4)	2.3(2)
N(2)	0.7634(3)	–0.0975(5)	–0.2163(4)	2.2(2)
N(3)	0.7808(3)	–0.2192(5)	–0.5065(4)	2.0(2)
N(4)	0.7703(3)	–0.1264(5)	–0.7140(4)	2.3(2)
C(1)	0.8168(4)	–0.0005(5)	–0.1975(5)	2.0(2)
C(2)	0.8612(4)	0.0494(7)	–0.2837(6)	2.7(3)
C(3)	0.9108(5)	0.1468(8)	–0.2463(7)	4.1(4)
C(4)	0.9199(5)	0.1994(8)	–0.1266(7)	3.9(4)
C(5)	0.8792(5)	0.1529(7)	–0.0407(6)	3.3(3)
C(6)	0.8250(4)	0.0530(6)	–0.0767(5)	2.2(2)
C(7)	0.8197(4)	–0.2269(5)	–0.6963(5)	1.9(2)
C(8)	0.8620(4)	–0.2815(6)	–0.7830(6)	2.7(3)
C(9)	0.9080(4)	–0.3844(7)	–0.7481(6)	3.0(3)
C(10)	0.9158(4)	–0.4351(6)	–0.6261(6)	2.7(3)
C(11)	0.8770(4)	–0.3852(6)	–0.5407(6)	2.4(3)
C(12)	0.8266(3)	–0.2803(5)	–0.5747(5)	1.8(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] *B*(eq) is the isotropic equivalent of the anisotropic thermal parameter.

Table 4. Positional and Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of $[\mathrm{Cu(btd)(NO_3)}]_\infty$[a]

atom	*x*	*y*	*z*	*B*(eq)[b]
Cu(1)	0.65215(6)	0.12149(6)	0.45611(8)	2.90(3)
Cu(2)	0.14757(6)	0.28372(6)	–0.02548(9)	3.33(3)
S(1)	0.8948(1)	0.2229(1)	0.7005(2)	2.67(5)
S(2)	0.4036(1)	0.1686(1)	0.1821(2)	2.62(5)
O(1)	0.4615(3)	0.1396(3)	0.5853(4)	2.9(1)
O(2)	0.5751(4)	0.1412(4)	0.8435(5)	4.2(2)
O(3)	0.3946(4)	0.0518(3)	0.7468(4)	3.4(2)
O(4)	–0.0441(4)	0.4186(3)	0.0833(4)	3.2(1)
O(5)	0.0787(5)	0.5055(4)	0.3257(5)	5.1(2)
O(6)	–0.1139(4)	0.6167(3)	0.2309(5)	3.8(2)
N(1)	0.4786(4)	0.1106(3)	0.7258(5)	2.5(2)
N(2)	0.3279(4)	0.2886(3)	0.1156(5)	2.4(1)
N(3)	0.5423(4)	0.2199(3)	0.3021(5)	2.2(1)
N(4)	0.8236(4)	0.1005(3)	0.6112(5)	2.2(1)
N(5)	1.0327(4)	0.1640(3)	0.8160(5)	2.3(1)
N(6)	–0.0248(4)	0.5129(4)	0.2146(5)	2.9(2)
C(1)	0.9076(4)	0.0054(4)	0.6687(6)	2.1(2)
C(2)	0.8833(5)	–0.1167(4)	0.6250(6)	2.7(2)
C(3)	0.9798(5)	–0.1979(5)	0.7011(7)	3.1(2)
C(4)	1.1001(5)	–0.1612(4)	0.8185(6)	2.8(2)
C(5)	1.1286(5)	–0.0439(4)	0.8614(6)	2.5(2)
C(6)	1.0285(4)	0.0425(4)	0.7872(5)	1.9(2)
C(7)	0.4117(5)	0.3746(4)	0.1813(5)	2.1(2)
C(8)	0.5363(4)	0.3346(4)	0.2883(5)	1.9(2)
C(9)	0.6380(5)	0.4122(4)	0.3679(6)	2.6(2)
C(10)	0.6104(6)	0.5250(5)	0.3375(6)	3.1(2)
C(11)	0.4850(6)	0.5638(4)	0.2305(7)	3.2(2)
C(12)	0.3849(5)	0.4926(4)	0.1530(6)	2.8(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] *B*(eq) is the isotropic equivalent of the anisotropic thermal parameter.

Table 5. Positional and Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of $[\mathrm{Ag(btd)}](\mathrm{ClO})_\infty$[a]

atom	*x*	*y*	*z*	*B*(eq)[b]
Ag(1)	1.0000	0.15693(5)	$^3/_4$	3.73(5)
Ag(2)	1.5000	0.19300(5)	$^3/_4$	3.79(5)
Cl(1)	1.0000	0.1459(2)	$^1/_4$	4.2(2)
Cl(2)	1.0000	0.3213(2)	$^3/_4$	4.8(2)
S(1)	1.2454(2)	0.2016(1)	0.7526(4)	3.6(1)
O(1)	0.989(2)	0.3754(9)	0.869(3)	9(1)
O(2)	1.043(3)	0.275(1)	0.890(3)	13(2)
O(3)	0.9137(9)	0.1845(5)	0.215(2)	10.5(7)
O(4)	0.9960(7)	0.1032(4)	0.401(1)	7.6(5)
O(5)	0.926(4)	0.340(2)	0.845(5)	12(3)
O(6)	1.092(2)	0.302(2)	0.801(6)	11(2)
N(1)	1.3394(5)	0.1582(4)	0.705(1)	3.2(3)
N(2)	1.1645(5)	0.1441(3)	0.747(1)	3.1(3)
C(1)	1.2081(6)	0.0864(4)	0.709(1)	3.0(4)
C(2)	1.1658(7)	0.0245(5)	0.698(1)	3.8(4)
C(3)	1.2250(9)	–0.0273(5)	0.662(1)	4.6(5)
C(4)	1.3251(8)	–0.0176(5)	0.635(1)	4.1(5)
C(5)	1.3670(6)	0.0426(5)	0.642(1)	3.7(4)
C(6)	1.3093(6)	0.0956(4)	0.682(1)	2.8(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] *B*(eq) is the isotropic equivalent of the anisotropic thermal parameter.

Table 6. Positional and Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of $\{[\mathrm{Cu_2(bpm)_2(C_2H_4)(Me_2CO)}](\mathrm{ClO_4})_2\}_\infty$[a]

atom	*x*	*y*	*z*	*B*(eq)[b]
Cu(1)	1.0000	0.20632(6)	$^1/_4$	4.35(5)
Cu(2)	$^1/_2$	0.13811(5)	$^1/_4$	3.74(4)
Cl(1)	0.7235(1)	0.12242(6)	0.5419(1)	4.17(5)
O(1)	0.6315(6)	0.1593(4)	0.4701(6)	11.4(4)
O(2)	0.8119(6)	0.1059(5)	0.4853(6)	13.1(5)
O(3)	0.6789(8)	0.0597(4)	0.5680(8)	14.5(6)
O(4)	0.781(1)	0.1585(4)	0.6324(6)	14.2(5)
O(5)	1.0000	0.0967(3)	$^1/_4$	9.5(4)
N(1)	0.8258(3)	0.2309(2)	0.2061(3)	3.3(1)
N(2)	0.6189(3)	0.2044(2)	0.2049(3)	3.2(1)
C(1)	0.7420(4)	0.1940(2)	0.2358(4)	3.3(2)
C(2)	0.5790(4)	0.2578(2)	0.1373(4)	3.4(2)
C(3)	0.6616(4)	0.3015(2)	0.1004(4)	3.2(2)
C(4)	0.6223(5)	0.3585(3)	0.0290(5)	4.7(2)
C(5)	0.7095(6)	0.4016(3)	0.0026(5)	4.9(2)
C(6)	0.8367(5)	0.3864(3)	0.0401(4)	4.6(2)
C(7)	0.8764(4)	0.3312(3)	0.1068(4)	4.2(2)
C(8)	0.7884(4)	0.2875(2)	0.1383(4)	3.2(2)
C(9)	1.0000	0.0341(4)	$^1/_4$	4.9(3)
C(10)	1.0667(7)	–0.0071(4)	0.1843(6)	7.6(4)
C(11)	0.5520(5)	0.0379(3)	0.2347(6)	5.5(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] *B*(eq) is the isotropic equivalent of the anisotropic thermal parameter.

The six-membered rings of coppers interconnected by HPO_3F^- and btd possess an extremely distorted hexagonal geometry, the Cu···Cu distances being 3.30 and 6.17 Å, respectively (Figure 2C). In spite of the distorted rings of coppers, the two-dimensional sheets composed of the coppers are only 0.44 Å in thickness. Each btd molecule is not parallel to the sheet plane but is inclined. It is well-known that hexafluorophosphonic acid is hydrolyzed to eventually give phosphoric acid.[29]

$$HPF_6 \xrightarrow{-HF} PF_5 \xrightarrow{H_2O} PF_3O \xrightarrow{H_2O} HPF_2O_2 \xrightarrow{H_2O}$$
$$H_2PFO_3 \xrightarrow{H_2O} H_3PO_4$$

The results of elemental analysis and single-crystal X-ray analysis of this compound indicate that the hydrolysis of PF_6^- takes place in the diffusion process of acetone solutions of $[Cu(CH_3CN)_4](PF_6)$ and btd into *n*-pentane containing water as an impurity and stops in the state of HPO_3F^- before reaching the final product H_3PO_4.

Construction of a Layered Structure Stacking the 2D Sheets: $[\mathbf{Cu(btd)(NO_3)}]_\infty$ (3). Nitrate can be expected to change the

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(29) Ishikawa, N.; Kobayashi, Y. *Fluorine Chemistry*; Kodansya: Tokyo, 1989; p 50.

Table 7. Selected Bond Distances (Å) and Angles (deg) for **1**–**5**

	Distance for **1**		
Cu(1)–O(5)	2.242(5)	Cu(1)–N(2)	2.007(5)
Cu(1)–N(3)	1.998(5)	Cu(1)–N(5)	2.008(5)
Cu(2)–N(1)	2.001(5)	Cu(2)–N(4)	1.978(5)
Cu(2)–N(6)	2.014(5)		
	Distances for **2**		
Cu(1)–O(1)	2.146(4)	Cu(1)–O(4)	2.211(4)
Cu(2)–O(1)	2.145(4)	Cu(2)–O(4)	2.181(4)
Cu(1)–N(1)	1.942(5)	Cu(1)–N(4)	2.045(5)
Cu(2)–N(2)	2.056(5)	Cu(2)–N(3)	1.952(5)
	Distances for **3**		
Cu(1)–O(1)	2.238(3)	Cu(1)–O(3)	2.203(3)
Cu(2)–O(4)	2.212(4)	Cu(2)–O(6)	2.269(4)
Cu(1)–N(3)	1.961(3)	Cu(1)–N(4)	1.904(3)
Cu(2)–N(2)	1.907(3)	Cu(2)–N(5)	1.963(3)
	Distances for **4**		
Ag(1)–N(2)	2.236(6)	Ag(2)–N(1)	2.254(7)
	Distances for **5**		
Cu(1)–O(5)	2.095(6)	Cu(1)–N(1)	1.935(3)
Cu(2)–N(2)	2.007(4)	Cu(2)–C(11)	2.022(6)
C(11)–C(11′)	1.30(1)		
	Angles for **1**		
O(5)–Cu(1)–N(2)	102.6(2)	O(5)–Cu(1)–N(3)	91.6(2)
O(5)–Cu(1)–N(5)	99.7(2)	N(2)–Cu(1)–N(3)	119.9(2)
N(2)–Cu(1)–N(5)	116.3(2)	N(3)–Cu(1)–N(5)	118.2(2)
N(1)–Cu(2)–N(4)	128.4(2)	N(1)–Cu(2)–N(6)	113.4(2)
N(4)–Cu(2)–N(6)	118.0(2)		
	Angles for **2**		
O(1)–Cu(1)–O(4)	80.7(2)	O(1)–Cu(1)–N(1)	127.1(2)
O(1)–Cu(1)–N(4)	94.2(2)	O(4)–Cu(1)–N(1)	121.0(2)
O(4)–Cu(1)–N(4)	99.9(2)	N(1)–Cu(1)–N(4)	123.6(2)
	Angles for **3**		
O(1)–Cu(1)–O(3)	90.1(1)	O(1)–Cu(1)–N(3)	93.2(1)
O(1)–Cu(1)–N(4)	110.9(1)	O(3)–Cu(1)–N(3)	89.9(1)
O(3)–Cu(1)–N(4)	115.6(1)	N(3)–Cu(1)–N(4)	143.9(1)
	Angles for **4**		
N(2)–Ag(1)–N(2′)	166.6(4)	N(1)–Ag(2)–N(1′)	143.3(4)
	Angles for **5**		
O(5)–Cu(1)–N(1)	104.1(1)	N(1)–Cu(1)–N(1′)	151.9(2)
N(2)–Cu(1)–N(2′)	101.8(2)	N(2)–Cu(2)–C(11)	110.4(2)
C(11)–Cu(2)–C(11′)	37.6(3)		

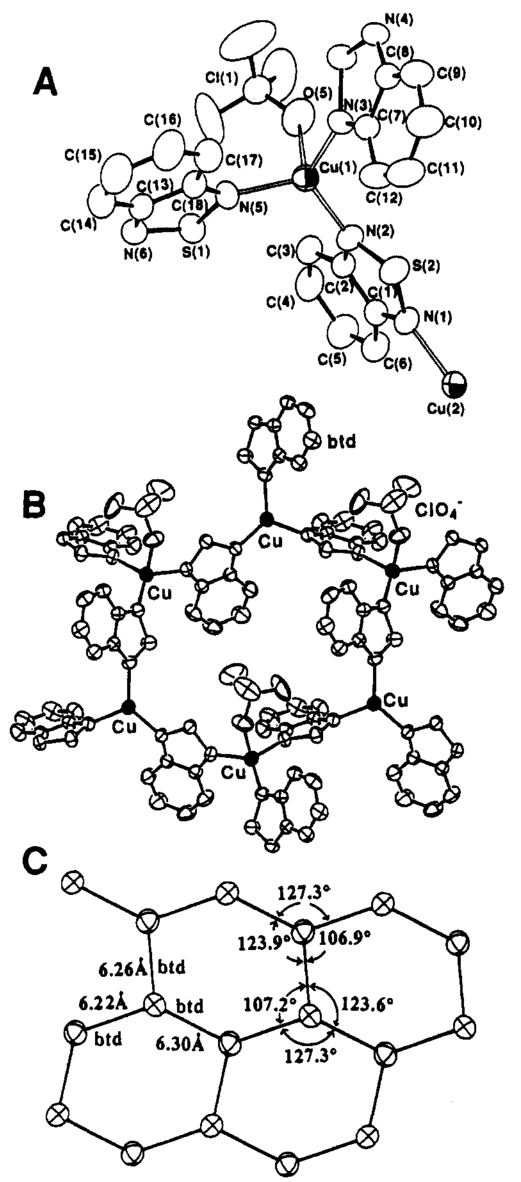

Figure 1. Molecular structures of **1** (A), the six-membered ring of coppers (B), and the 2D sheet consisting of the rings (C) in **1**, where only the copper centers are presented.

framework of the six-membered rings of coppers, since it often functions as a bridging ligand. Figure 3A,B shows the structure and labeling scheme of a segment of two-dimensional sheets of **3**. Each copper is coordinated to two nitrogen atoms of different btd ligands and two oxygen atoms of different nitrates in a distorted tetrahedral geometry. The Cu–N distances of 1.934(4) Å (average) are shorter than those for **2**, whereas the Cu–O distances of 2.231(3) Å (average) are longer than those for **2**. The most remarkable feature of the structure is that the six-membered rings of coppers interconnected by btd and NO_3^-, $[Cu_6(btd)_4(NO_3)_4]^{2+}$, are in a chair form, where two oxygen atoms of NO_3^- connect the top and bottom coppers in the chair form (Figure 4). The coppers of the two-dimensional sheet arranged in the chair form do not lie in the same plane but have a layer of thickness 2.1–2.4 Å. This structure make it possible to stack btd molecules within the sheet. Figure 5 schematically shows the stackings within the sheet along the *ab* and *ac* planes. The btd molecules are overlapped in the benzene moiety. This is similar to [2.2]-paracyclophane.[30] There are the interplanar spacing distances of two kinds, 3.29 and 3.30 Å, indicative of the existence of π–π interactions between two btd molecules within the sheets. One more remarkable feature of the structure is π–π stacking of the btd molecules between the sheets, the interplanar spacing distances being 3.25 and 3.42 Å. Figure 6 clearly shows the stackings within and between the two-dimensional sheets with the six-membered rings of coppers. The stackings resemble those between the two-dimensional sheets with six-membered rings of carbons in graphite and are particularly noteworthy in connection with construction of a layered structure.

Construction of Metal Complex Polymers with Infinite Chains. (A) $\{[Ag(btd)](ClO_4)\}_\infty$ (4). It is interesting to see if the framework of a six-membered ring of silvers is formed in the Ag(I)–btd system. The structure and labeling scheme of **4** is shown in Figure 7A. Silvers do not give the six-membered rings but an infinite chain, although each silver atom is coordinated to two nitrogen atoms of bridging btd molecules. The Ag–N distances of 2.245(7) Å (average) are longer than those (2.073(5)–2.195(15) Å) reported for two-coordinate Ag(I) complexes.[31-33] The N(2)–Ag(1)–N(2′) angle of 166° and N(1)–Ag(2)–N(1′) angle of 144° are bent from a linear angle. The extent of bending does not correspond to the Ag···O interaction:[34] The Ag(2)–O(3) distance

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[30] Nakazaki, M.; Yamamoto, K.; Kametani, H. *J. Org. Chem.* **1977**, *42*, 287.

[31] Munakata, M.; Maekawa, M.; Kitagawa, S.; Adachi, M. *Inorg. Chim. Acta* **1990**, *167*, 181.

[32] Perron, J.; Beuchamp, A. L. *Inorg. Chem.* **1984**, *23*, 2853.

[33] Gagnon, C.; Hubert, J.; Rivest, R.; Beuchamp, A. L. *Inorg. Chem.* **1977**, *16*, 2469.

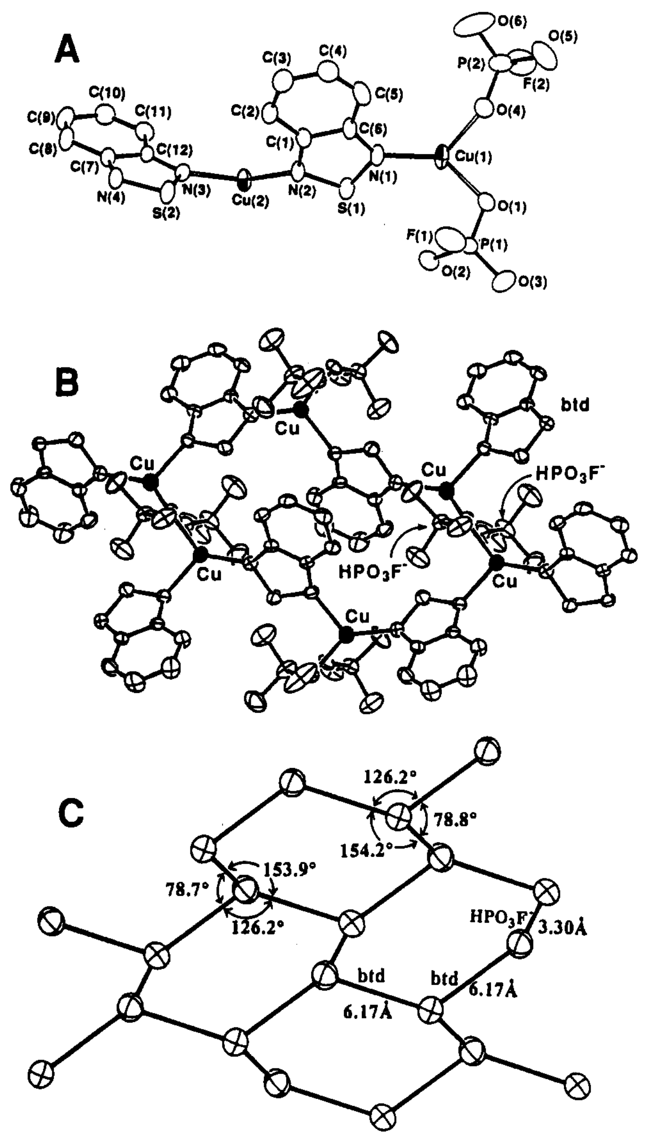

Figure 2. Molecular structures of **2** (A), the six-membered ring of coppers (B), and the 2D sheet consisting of the rings (C) in **2**, where only the copper centers are presented.

of 2.65(2) Å indicates weak interaction between Ag(2) and O(3), whereas interaction between Ag(1) and O(2) may be neglected because of the long Ag(1)–O(2) distance of 2.75(1) Å. The btd molecules of the same chain are oriented in the same direction, i.e. a *cis*-configuration, and the dihedral angle is 17.0° between the neighboring btd molecules. Figure 7B shows that the btd molecules partially overlap between the infinite chains along the *c*-axis at the shortest interplanar spacing distance of 3.35 Å.

(B) $\{[Cu_2(bpm)_2(C_2H_4)(Me_2CO)](ClO_4)_2\}_\infty$ (5). The copper(I) complex with bpm (5,6-benzopyrimidine) was synthesized to compare the role of the pyrimidine frame in the polynuclear complex formation with that of the thiadiazole frame. The molecular structure and labeling scheme of **5** are shown in Figure 8A. Bpm also does not give the six-membered ring of coppers but gives an infinite chain. Both Cu(1) and Cu(2) atoms are coordinated to two nitrogen atoms of interconnecting bpm molecules. Furthermore Cu(1) and Cu(2) are coordinated by acetone and ethylene in a distorted trigonal geometry, respectively. The Cu(1)–N(1) distance of 1.935(3) Å is shorter than the Cu(2)–N(2) distance of 2.007(4) Å because the N(1)–Cu(1)–N(1′) angle of 151.9(2)° is larger than the N(2)–Cu(2)–N(2′) angle of 101.8(2)°. The C=C distance of 1.30(1) Å for the coordinating ethylene is shorter than those (1.33–1.36 Å) reported for the Cu(I) ethylene complexes.[35,36] The coordination of acetone to Cu(I) is rare, and the Cu–O distance of 2.095 Å is short compared with 2.235 Å for $[Cu_2(C_9H_{10}N_2O)_2(Me_2CO)_2]^{2+}$.[37] The dihedral angle between the bpm molecules bound to Cu(1) and Cu(2) is ca. 72°. Figure 8B shows an overview of this compound, which is arranged in a Y-shaped pillar pattern along the *a* axis.

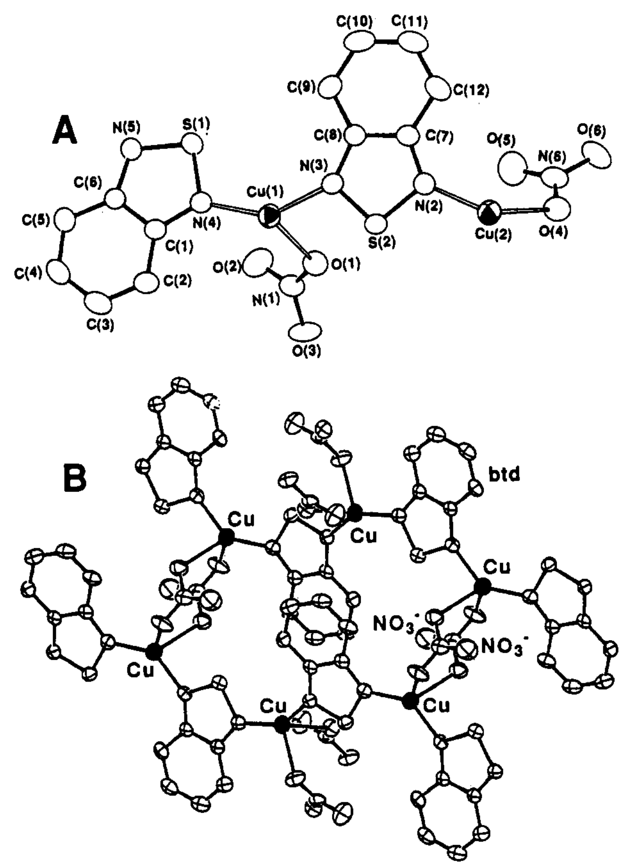

Figure 3. Molecular structures of **3** (A) and the six-membered ring of coppers (B) in **3**.

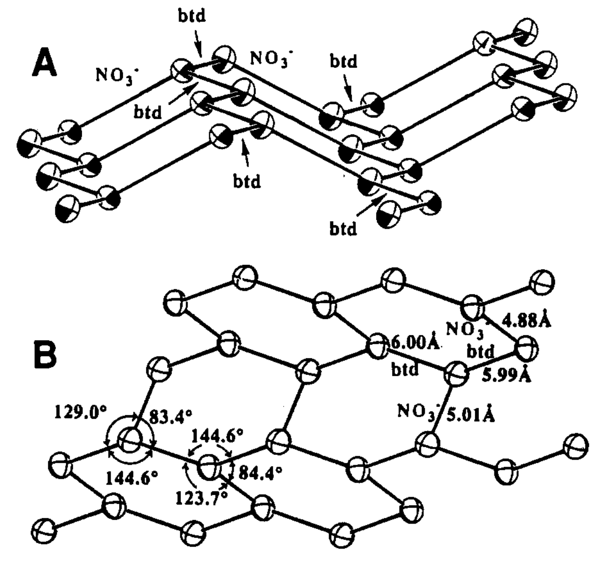

Figure 4. 2D sheet consisting of six-membered rings of coppers in **3** in the *ac* (A) and *ab* planes (B). Only the copper centers are presented.

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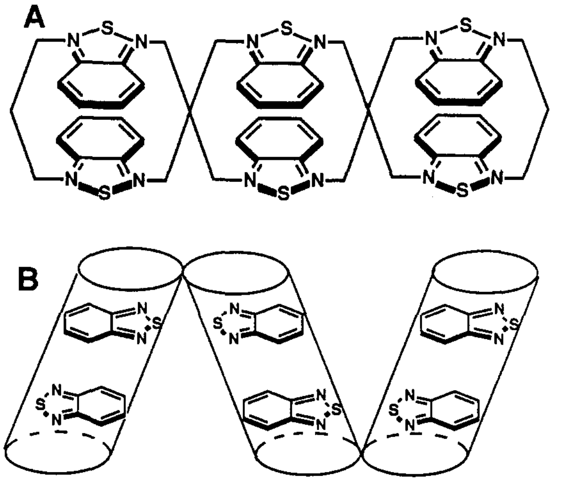

Figure 5. Schematic overlapping of btd molecules within the 2D sheet of 3 in the *ac* (A) and *ab* planes (B).

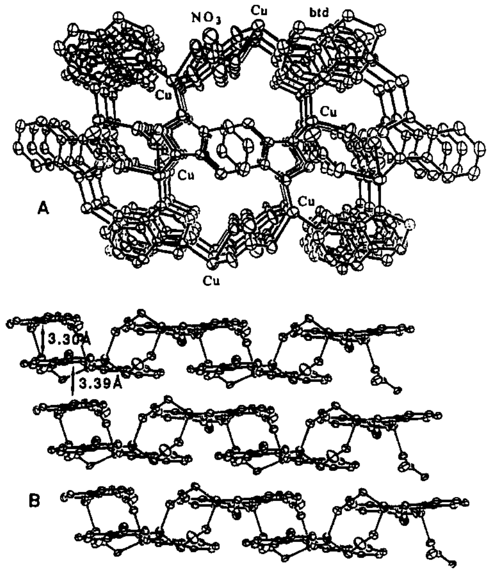

Figure 6. Perspective (A) and side views (B) of the packing arrangement of 3.

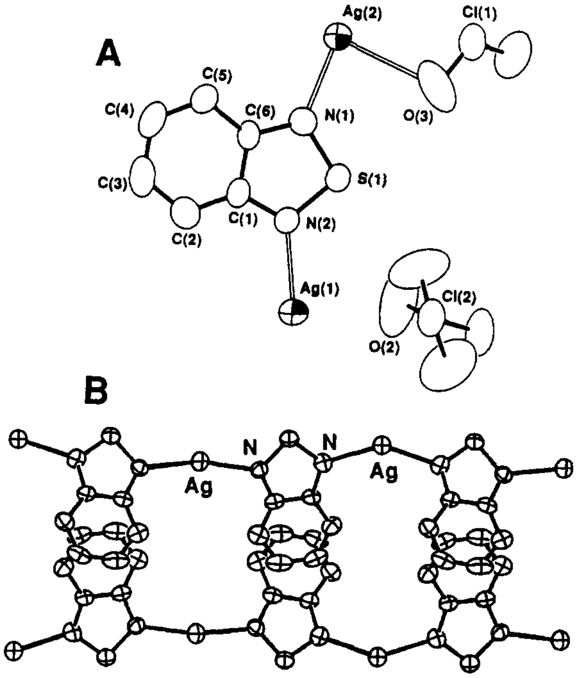

Figure 7. Molecular structures of 4 (A) and the overlapping of btd molecules between the infinite chains of 4 along the *c* axis (B).

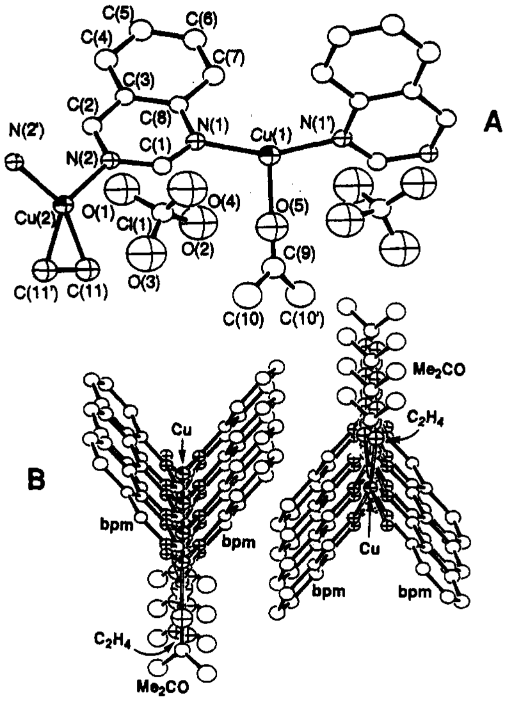

Figure 8. Molecular structures of 5 (A) and a perspective view (B) of the infinite chains of 5.

Electronic Spectra of 2D Polynuclear Complexes. The electronic spectra of complexes **1**–**3** were measured in the solid state (KBr disk), and exhibit new bonds at about 400 and 500 nm which may be assigned to Cu(I) to ligand charge-transfer bands.

Discussion

Perchlorate ions do not act as interconnecting ligands in **1**, and the six-membered rings of coppers interconnected by only btd molecules, $[Cu_6(btd)_6]$, are found in a slightly distorted hexagonal geometry. Coppers in the two-dimensional sheet are arranged in a staggered conformation with a maximum 0.50 Å thickness in the *bc* plane (Figure 9A) and in a slight zigzag pattern in the *ac* plane (Figure 9D). The interconnecting btd molecules stand out of the upper and lower sides of the copper ring plane. The btd planes are neither coplanar nor perpendicular to the ring plane but rather are at some intermediate angle (Figure 10A). The coordinating and noncoordinating perchlorate ions lie on the opposite sides of the copper ring plane, respectively. The largest condensed ring compound has been reported to be part of a 61-member ring system $(C_{150}H_{30})$.[38] Organic compounds having six-membered rings of aromatic compounds, spheland[20] and sexipyridine,[21] have been synthesized by Cram and Newkome, respectively, although they are monomers. A single crystal of **1** has tens and hundreds of thousands of six-membered rings of coppers interconnected by six btd molecules, $[Cu_6(btd)_6]^{6+}$, although the ring numbers depend on the single-crystal size.

Monofluorophosphate in **2** acts as a interconnecting ligand to give remarkably short Cu–Cu distances bridged by HPO_3F^- molecules compared with those by btd molecules . The six-membered ring of coppers, $[Cu_6(btd)_4(HPO_3F)_4]^{2+}$, has therefore an extremely distorted hexagonal geometry. The coppers in the two-dimensional sheet are arranged in a ladder pattern with a 0.44 Å thickness in *ac* plane (Figure 9B) and in a shallow roof pattern in the *ab* plane (Figure 9E) . This arrangement is apparently different from that of **1**. Two interconnecting btd molecules of **2** stand out on the upper side of the copper ring plane, and other two btd molecules are on the lower side (Figure

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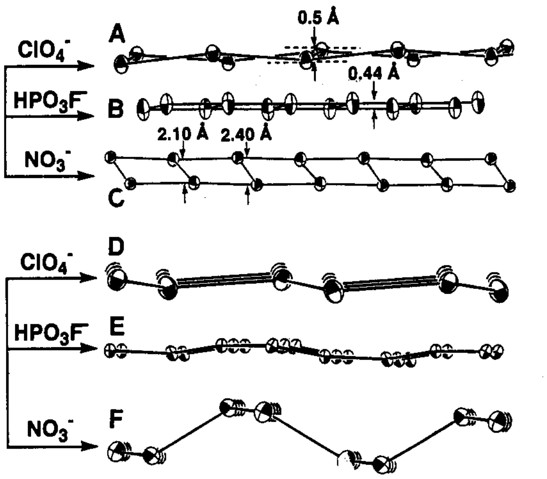

Figure 9. Anion effects on the copper frameworks of 2D sheets of **1** (in the *bc* (A) and *ac* planes (D)), **2** (in the *ac* (B) and *ab* planes (E)), and **3** (in the *ac* (C) and *ab* planes (F)).

10B). The btd molecules are still at some intermediate angle in the extremely distorted six-membered ring. Similarly, four interconnecting HPO_3F^- ions lie on the upper and lower sides of the copper ring plane.

Nitrates of **3** take part in the formation of the six-membered rings of coppers in a chair form as interconnecting ligands together with btd molecules to give the two-dimensional sheet. Coppers in the two-dimensional sheet are arranged in a ladder pattern of thickness 2.1–2.4 Å along the *c*-axis (Figure 9C) and in a roof pattern along the *b*-axis (Figure 9F). Nitrates connect the top and bottom coppers of the chair form (Figure 4A). On the other hand, btd molecules connect the top or bottom coppers and are oriented approximately parallel to the sheet plane. The parallel orientation of btd molecules make it possible for the btd molecules not only to overlap between top and bottom sides within the sheet but to overlap between the sheets (Figures 6 and 10C). The shortest interplanar spacing distance of btds within and between the sheets are 3.30 Å (average) and 3.39 Å (average), respectively, and indicate π–π interactions. The interaction is noted to be similar to that between layers composed of six-membered rings of carbons in graphite. The electric conductivity σ of powder **3** was $10^{-6.3}$ S cm^{-1}.

Benzopyrimidines of **4** do not form six-membered rings of coppers but interconnect a one-dimensional polymer of coppers. This may be mainly attributable to the difference in the bond angles between N–S–N of the 1,2,5-thiadiazole frame and N–C–N of the pyrimidine frame, that is, the direction of N-electrons. Similarly, silver ions of **5** do not give the six-membered rings but an infinite chain of Ag atoms interconnected by btd molecules, because Ag(I) ion prefers a two-coordinate linear geometry rather than three- and four-coordinate geometries.

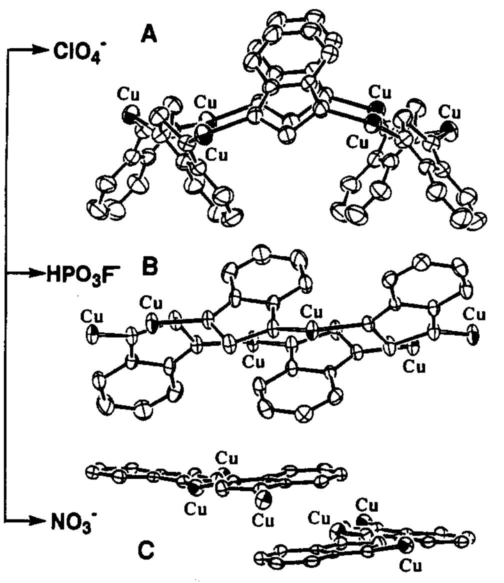

Figure 10. Anion effects on the btd molecule orientations in the six-membered rings of coppers in **1** (A), **2** (B), and **3** (C), where the counteranions are omitted.

In conclusion, a combination of three- or four-coordinate metal ions and ligands having 1,2,5-thiadiazole and pyrazole frames is highly preferred for construction of a two-dimensional sheet composed of six-membered rings of metal ions interconnected by aromatic ligands. The coordination of a suitable counteranion to the metal ion make it possible to deform the frame of the ring which governs the orientation of the aromatic ligand and to stack the aromatic ligand within and between the sheets.

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Supplementary Material Available: Tables S1–S20, giving positional parameters including H atoms, bond angles, bond distances, and anisotropic thermal parameters (29 pages). Ordering information is given on any current masthead page.