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Interpenetrating Coordination Polymers from Cu^I or Ag^I and Flexible Ligands: 2D Polyrotaxanes and Interpenetrating Grids

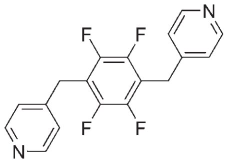
Kayoko Kasai* and Mariko Sato[a]

Abstract: The reaction of $[Cu(CH_3CN)_4]NO_3$ or $AgNO_3$ with flexible ligands 1,4-bis(4-pyridylmethyl)-2,3,5,6-tetrafluorobenzene (bpf) or 4,4′-bis(4-pyridylmethyl)-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (bpfb) afforded two types of interpenetrating coordination polymers. The structures of $[Cu_2(bpf)_3(NO_3)_2]_n$ and $[Ag_2(bpf)_3(NO_3)_2]_n$ are 2D polyrotaxane networks in which 1D polymeric chains are aligned in a grid. The structure of $\{[Cu(bpfb)_2]NO_3\}_n$ is a 2D grid polymer with two-fold parallel interpenetration.

Keywords: coordination polymers · copper · interpenetration · N ligands · silver

Introduction

The construction of coordination polymers with metal ions and bridging ligands is a highly topical area owing to their potential application as new functional materials.[1,2] Various successful syntheses and structural characterizations have been reported. The use of well-designed bridging ligands and metal ions of various geometries has led to a number of coordination polymers with interesting topologies. In particular, bridging ligands connected by flexible linkages such as methylene groups have attracted much attention due to their wide diversity of structures and topologies.[3] We have reported the preparation of a series of clathrate coordination polymers with flexible ligands whose network structures differ significantly depending on the guest organic molecules.[4] It was demonstrated that the diversity of structures and topologies among these compounds is caused by conformational freedom around the methylene groups bridging the pyridine and fluorinated aromatic rings in ligands such as 1,4-bis(4-pyridylmethyl)-2,3,5,6-tetrafluorobenzene (bpf) or 4,4′-bis(4-pyridylmethyl)-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (bpfb). The reaction of the flexible fluorinated ligands with $Cd(NO_3)_2$ in the presence of aromatic compounds afforded 1D cyclic chains, 2D grids, and 3D diamond networks.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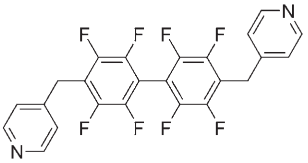
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In this series of compounds, we represented clathration and interpenetration[1a,5] of coordination polymers as “hetero-recognition” and “self-recognition”, respectively. Interpenetration is regarded as a kind of clathration as the space surrounded by individual coordination polymers is filled with the polymers themselves. In other words, polymers that incorporate guest aromatic compounds recognize “nonself” molecules, whereas those involved in interpenetration recognize each other as “selves”. Herein we report the preparation of two different types of interpenetrating 2D polyrotaxane coordination polymers $[Cu_2(bpf)_3(NO_3)_2]_n$ (**1**) and $[Ag_2(bpf)_3(NO_3)_2]_n$ (**2**) and a 2D grid with twofold parallel interpenetration $\{[Cu(bpfb)_2]NO_3\}_n$ (**3**), both of which favor “self-recognition” over “hetero-recognition”, by using metal ions with lower coordination numbers.

Results and Discussion

The reaction of $[Cu(CH_3CN)_4]NO_3$ or $AgNO_3$ with bpf affords 2D polyrotaxane polymers **1** or **2**, while the reaction of $[Cu(CH_3CN)_4]NO_3$ with bpfb affords 2D grid polymer **3** with two-fold parallel interpenetration. Crystals of **1** and **3** are air-stable. Single-crystal X-ray crystallographic analysis

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[a] Dr. K. Kasai, M. Sato
Department of Science Education
Miyagi University of Education
149 Aramaki, Aoba-ku, Sendai 980-0845 (Japan)
Fax: (+81) 22-214-3429
E-mail: kasai@staff.miyakyo-u.ac.jp

of **1**–**3** (Table 1) confirms that these are interpenetrating polymeric structures based on tetrahedrally coordinated metal centers.

Table 1. Crystallographic data for **1**, **2**, and **3**.

	1	**2**	**3**
Formula	$C_{27}H_{18}CuF_6N_4O_3$	$C_{27}H_{18}AgF_6N_4O_3$	$C_{52}H_{32}CuF_{16}N_7O_4$
M_r	623.99	668.32	1186.39
Size [mm^3]	0.20×0.20×0.25	0.35×0.40×0.50	0.20×0.20×0.25
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	*Pnna*
a [Å]	13.2426(8)	13.1867(9)	23.7569(14)
b [Å]	13.3936(8)	13.2605(9)	34.3409(19)
c [Å]	14.6684(9)	15.1625(10)	6.0656(4)
β [°]	100.6640(10)	99.3640(10)	90
V [Å^3]	2556.7(3)	2616.0(3)	4948.5(5)
Z	4	4	4
T [K]	173	173	173
ρ_{calcd} [g cm^{-3}]	1.621	1.697	1.592
μ (Mo$_{K\alpha}$) [mm^{-1}]	0.937	0.851	0.557
Max/min transmission	0.87/0.68	0.7783/0.6942	0.9205/0.7294
$F(000)$	1260	1332	2392
Unique reflections	6052	6040	5912
Parameters	370	370	375
Goodness-of-fit	1.011	1.035	1.030
Final R_1 ($I>2\sigma(I)$)	0.0360	0.0263	0.0452
wR_2 (all data)	0.0958	0.0705	0.1269
Reflections collected (R_{int})	23962, 0.0309	16263, 0.0150	30427, 0.0526
Reflections collected ($I>2$ s(I))	4160	5114	3898
Largest diff. peak/hole [eÅ^{-3}]	0.338/−0.370	0.535/−0.442	0.588/−0.369

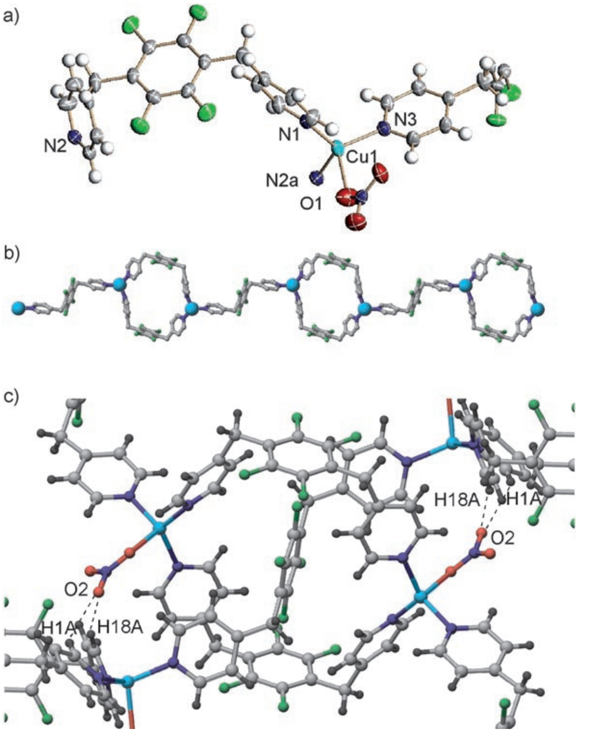

Figure 1. Views of the polyrotaxane polymer **1**. a) ORTEP view around the metal center. Thermal ellipsoids are shown with 50 % probability. b) Top view of the 1D chain. Hydrogen atoms and nitrate anions are omitted for clarity. c) View of the rotaxane association of **1**, with atomic labeling showing hydrogen bonding between nitrogen anions and pyridine rings. Selected bond lengths [Å] and angles [°]: Cu1−N1 1.9945(17), Cu1−N2a 2.0276(17), Cu1−N3 2.0122(18), Cu1−O1 2.3019(18), N1−Cu1−N3 120.22(7), N1−Cu1−N2a 119.09(7), N3−Cu1−N2a 112.00(7), N1−Cu1−O1 101.70(7), N3−Cu1−O1 107.33(8), N2a−Cu1−O1 90.07(7).

The coordination geometry of **1** is shown in Figure 1 a. The Cu^I centers are all equivalent and in a trigonal pyramidal N_3O coordination environment consisting of three bpf pyridine rings and a monodentate nitrate anion. The N−Cu−N angles vary from 112.00(7)° to 120.22(7)° and the Cu−N bond lengths from 1.9945(17) Å to 2.0276(17) Å. One oxygen atom of a nitrate anion coordinates to the Cu^I center with a bond length of 2.3019(18) Å at the apical position. An individual infinite 1D chain structure, in which the Cu^I ions correspond to the 3-connected nodes, is shown in Figure 1 b. The infinite chain has two sections: one is a macrocyclic [Cu$_2$(bpf)$_2$] ring with bpf in a *cis* conformation (Cu···Cu: 11.205 Å); the other is a rod composed of a linear ligand, with bpf in a *trans* conformation, that connects the rings (Cu···Cu: 16.464 Å). These 1D chains are aligned in a grid in which the rods penetrate the macrocyclic rings at the intersections. Each chain is entangled through rotaxane interactions with an infinite number of other chains to generate a 2D polyrotaxane sheet (Figure 2 a). A detailed view of the rod-to-ring rotaxane interactions is shown in Figure 1 c. Although there are no π–π interactions between the aromatic rings of "host" ring and "guest" rod, hydrogen bonding occurs between one oxygen atom of a nitrate anion and the hydrogen atoms of the pyridine rings corresponding to the [Cu$_2$(bpf)$_2$] ring (O2···H1A: 2.470 Å, O2···H18A: 2.550 Å).

In the Ag^I polyrotaxane polymer **2**, which is isostructural with **1**, the N−Ag−N angles vary from 104.17(6)° to 123.93(6)° and the Ag−N bond lengths from 2.2546(16) Å to 2.3148(16) Å. Whereas the Ag···Ag distances of the macrocyclic ring and rod (11.353 and 16.985 Å, respectively) are longer than the corresponding Cu···Cu distances of **1**, the hy-

Abstract in Japanese:

柔軟な配位子1, 4–ビス(4–ピリジルメチル)–2, 3, 5, 6–テトラフルオロベンゼン（bpf）あるいは4, 4’–ビス(4–ピリジルメチル)–2, 2’, 3, 3’, 5, 5’, 6, 6’–オクタフルオロビフェニル（bpfb）と、テトラキス（アセトニトリル）銅（I）硝酸塩（[Cu(CH$_3$CN)$_4$]NO$_3$）あるいは硝酸銀（AgNO$_3$）との反応より、二種類の相互貫通型配位高分子が得られた。[Cu$_2$(bpf)$_3$(NO$_3$)$_2$]$_n$（1）と[Ag$_2$(bpf)$_3$(NO$_3$)$_2$]$_n$（2）の構造は、一次元高分子鎖が格子状に配列した二次元ポリロタキサンネットワークである。{[Cu(bpfb)$_2$]NO$_3$}$_n$（3）は、2枚の二次元格子状ネットワークが平行に相互貫通する構造である。

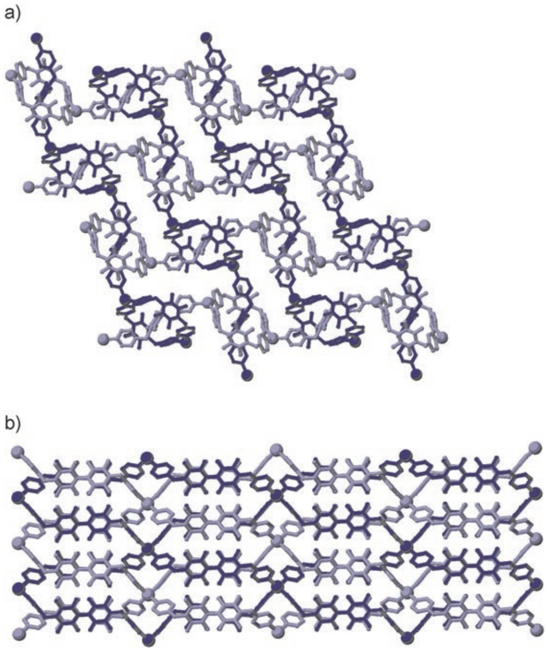

Figure 2. a) Top view of the 2D polyrotaxane sheet structure of **1**. b) View of the two-fold parallel interpenetration of **3**. Hydrogen atoms and nitrate anions are omitted for clarity.

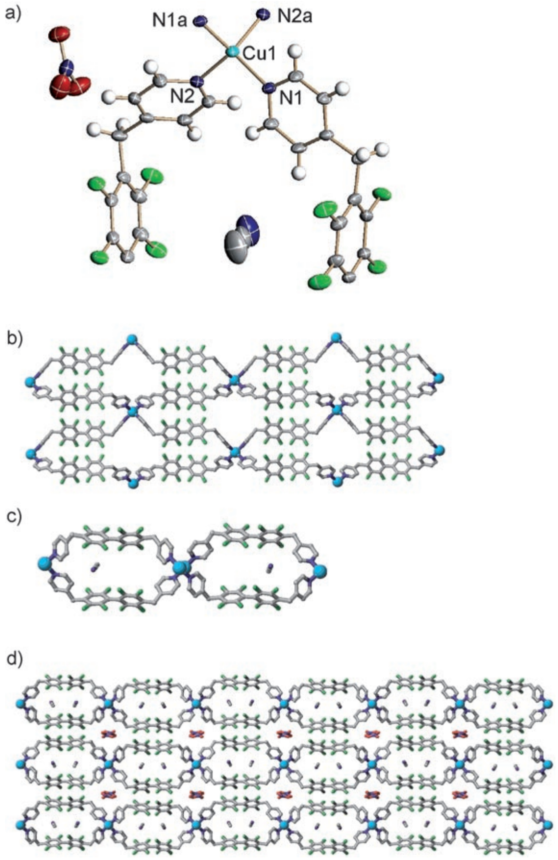

Figure 3. Views of the 2D sheet structure of **3**. a) ORTEP view around the metal center. Thermal ellipsoids are shown with 50 % probability. b) Top view of the 2D sheet. c) Side view of extremely twisted cavity incorporating two acetonitrile molecules. d) Side view of stacking sheets. Hydrogen atoms and nitrate anions are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1−N1 2.0408(19), Cu1−N1a 2.0408(19), Cu1−N2a 2.064(2), Cu1−N2 2.064(2), N1−Cu1−N1a 117.54(11), N1−Cu1−N2a 106.80(8), N1a−Cu1−N2a 107.38(8), N1−Cu1−N2 107.38(8), N1a−Cu1−N2 106.79(8), N2a−Cu1−N2 110.95(11).

drogen bonds connecting the ring and rod are shorter (2.355 and 2.491 Å). The structures of **1** and **2** are very similar to $[Ag_2(bix)_3(NO_3)_2]$ (bix = 1,4-bis(imidazol-1-ylmethyl)benzene),[6] except for the coordination of the nitrate anions.

Polymer **3** adopts an entirely different network structure from that of **1** and **2**. The Cu^I centers are in a distorted tetrahedral N_4 coordination environment consisting of the four pyridine rings of bpfb (Figure 3a). The N−Cu−N angles vary from 106.79(8)° to 117.54(11)° and the Cu−N bond lengths from 2.0408(19) Å to 2.064(2) Å. The extended structure is a 2D grid with [4,4] topology in the *bc* plane (Figure 3b). Each cavity, surrounded by four metal ions and four ligands with *trans* conformation, is extremely twisted to form two small, half-isolated cavities in which solvent acetonitrile molecules are incorporated (Figure 3c). The diagonal-to-diagonal Cu···Cu distances are 34.34 and 12.13 Å. These two independent sheets interpenetrate in parallel (Figure 2b). The mode of interpenetration is topologically the same as those of the previously reported complexes $[Re_4(CO)_{12}(OH)_4]\cdot(4,4'\text{-bipy})_2\cdot(MeOH)_2$,[7] $[Ag(3,3'\text{-dcpa})_2]X$ (3,3′-dcpa = 3,3′-dicyanodiphenylacetylene, $X^- = PF_6^-$, AsF_6^-, or SbF_6^-),[8] and Zn(3-{[4-(4-pyridylethenyl)phenyl]ethenyl}-benzoate)$_2$,[9] represented as a “doubly interwoven carpet-like structure” by Zaworotko and co-workers.[7] Interestingly, the twisted twofold interpenetrating grid has chirality derived from its twisted structure, as shown clearly in Figure 2b; the frameworks of the two interpenetrating sheets are twisted in the same direction, whereas those of adjacent sheets are in the opposite. These enantiomeric sheets are stacked alternately with an interplane distance of 11.7 Å (Figure 3d). In spite of the parallel interpenetration, microchannels remain along the *c* axis, incorporating acetonitrile molecules. The disordered nitrogen anions are packed between the layers to fill the vacancies.

The magnetic susceptibility of polymers **1** and **3** was measured at 300 and 10 K with a SQUID magnetometer MPMS 5S (Quantum Design) at 1 T. It was confirmed that these complexes are diamagnetic at both temperatures, and this result reveals that **1** and **3** include Cu^I centers.

The ability of these interpenetrating polymers to incorporate aromatic compounds was examined. Reaction mixtures of $[Cu(CH_3CN)_4]NO_3$ and bpf in the presence of phenyl acetate, methyl benzoate, or *o*-, *m*-, or *p*-xylene all afforded the 2D polyrotaxane polymer **1**. Reaction mixtures of $[Cu(CH_3CN)_4]NO_3$ and bpfb in the presence of *m*- or *p*-xylene afforded the interpenetrating 2D grid **3**, but other aromatic compounds formed no product. The interpenetrating polymers were unable to incorporate aromatic compounds. In contrast, polymers constructed from Cd^{II}, which favors an octahedral geometry, and bpf/bpfb in the presence of aromatic compounds have shown a remarkable ability to incorporate guest aromatic compounds.[4] Cu^I and Ag^I have some propensity to form interpenetrating frameworks rather than clathrate ones. For Cu^I and Ag^I, the bond angles around the metal ions appear too great to allow clathration of aromatic compounds, but are suitable for interpenetration.

Conclusions

We have synthesized and characterized two types of interpenetrating coordination polymers: 2D polyrotaxane polymers and interwoven 2D grids with two-fold parallel interpenetration. The use of Cu^I and Ag^I, both of which adopt a tetrahedral geometry, led to "self-recognition" (interpenetration) rather than "hetero-recognition" (clathration).

Experimental Section

Preparations

Coordination polymers containing Cu^I were prepared under nitrogen atmosphere with degassed solvents. $Cu(NO_3)_2 \cdot 3H_2O$ and *N*-methylaniline were purchased from Kanto Chemical Co. Ltd. $AgNO_3$ was purchased from Nacalaitesque Co. Ltd. Ligands bpf and bpfb were prepared in a similar manner to that described in the literature.[4] Acetonitrile was degassed by bubbling with dry nitrogen gas. Aromatic compounds were purchased from Tokyo Chemical Industry Co., Ltd.

1: Copper powder (2.9 mg, 0.045 mmol) was added to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (7.2 mg, 0.03 mmol) in acetonitrile (2 mL), and the mixture was warmed to 60 °C and stirred for 30 min. *N*-methylaniline (0.1 mL) as an antioxidant and bpf (30 mg, 0.09 mmol) in acetonitrile (2 mL) were then added dropwise. The mixture was allowed to stand for 24 h at room temperature to give **1** as yellow crystals (15 mg, 40 %). Elemental analysis: calcd (%) for $C_{27}H_{18}O_3N_4CuF_6$ ($[Cu_2(bpf)_3(NO_3)_2]$): C 51.97, H 2.91, N 8.98; found: C 51.98, H 3.01, N 8.90.

2: A solution of bpf (15 mg, 0.045 mmol) in methanol (8.3 mL) was added to a solution of $AgNO_3$ (5.1 mg, 0.03 mmol) in aqueous methanol (1 mL of H_2O, 7.3 mL of CH_3OH) with stirring. The mixture was allowed to stand for 24 h at room temperature to give **2** as colorless crystals (12 mg, 60 %). Elemental analysis: calcd (%) for $C_{27}H_{18}O_3N_4AgF_6$ ($[Ag_2(bpf)_3(NO_3)_2]$): C 48.52, H 2.71, N 8.38; found: C 48.49, H 2.83, N 8.41.

3: Copper powder (2.9 mg, 0.045 mmol) was added to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (7.2 mg, 0.03 mmol) in acetonitrile (2 mL), and the mixture was warmed to 60 °C and stirred for 30 min. *N*-methylaniline (0.1 mL) and bpfb (58 mg, 0.12 mmol) in acetonitrile (7 mL) were then added dropwise. The mixture was allowed to stand for 4 days at room temperature to give **3** as yellow crystals (19 mg, 27 %). Elemental analysis: calcd (%) for $C_{48}H_{26}O_4N_5CuF_{16}$ ($[Cu(bpfb)_2]NO_3 \cdot H_2O$): C 52.21, H 2.37, N 6.34; found: C 52.31, H 2.23, N 6.43.

Examination of 1 and 3 for Clathration of Aromatic Compounds

The reaction of $[Cu(CH_3CN)_4]NO_3$, bpf, and phenyl acetate (0.48 mL, 3.8 mmol) was carried out by the same procedure as that for **1** and **3**. After the mixture was left to stand for 24 h at room temperature, **1** was obtained as yellow crystals. The structure was identified by preliminary single-crystal X-ray diffraction for the determination of unit-cell parameters and space group. The same reaction in the presence of methyl benzoate or *o*-, *m*-, or *p*-xylene also gave **1**, and its structure was identified by preliminary single-crystal X-ray diffraction. When bpfb was used with *m*- or *p*-xylene, the reaction mixture gave **3** as yellow crystals after 4 days of standing at room temperature, and its structure was identified by preliminary single-crystal X-ray diffraction for the determination of unit-cell parameters and space group. No products were formed when phenyl acetate, methyl benzoate, or *o*-xylene was used with bpfb.

X-ray Crystallography

Crystal data for all the structures were collected with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 173 K on a Bruker SMART/CCD diffractometer with ω scans using steps of 0.3° ($1.90 \leq 2\theta \leq 28.02°$ for **1**, $2.05 \leq 2\theta \leq 27.98°$ for **2**, and $1.19 \leq 2\theta \leq 28.03°$ for **3**). An empirical absorption correction was applied by using the SADABS program. The structures were solved by direct methods (SIR 97 for **1** and SHELXS 97 for **2** and **3**) and refined by full-matrix least-squares against F^2 of all data with the SHELXL 97 package. The positions of the hydrogen atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective parent atoms before the final cycle of least-squares refinements. Crystal data and experimental details are listed in Table 1.

CCDC-256316–256318 (for **1**–**3**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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