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# Synthesis, Structure, and Clathration Ability of Two-Dimensional Coordination Networks with Inclined Interpenetration

\*KASAI Kayoko, \*NARA Shizuka and \*YAMADA Satoshi

## Abstract

Two-dimensional (2D) grid coordination networks with inclined interpenetration were prepared by Cd(NO<sub>3</sub>)<sub>2</sub> with 2,7-bis(4-pyridylmethyl)-1,3,4,5,6,8-hexafluoronaphthalene (2,7-bpfn) or 2,6-bis(4-pyridylmethyl)-1,3,4,5,7,8-hexafluoronaphthalene (2,6-bpfn) in the presence of aromatic compounds. Crystal structures of {[Cd(2,7-bpfn)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] · (methyl benzoate)<sub>1.5</sub> · (EtOH)<sub>0.5</sub>}<sub>n</sub> (**1**) and {[Cd(2,6-bpfn)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] · (toluene)<sub>2.5</sub>}<sub>n</sub> (**2**) were determined. Methyl benzoate and toluene molecules were clathrated in cyclic cavities of the grid networks through arene-perfluoroarene interactions.

**Key words** : Coordination Networks (ネットワーク錯体)

Crystal Structure (結晶構造)

Interpenetration (相互貫通)

Clathration (包接)

Arene-perfluoroarene interactions (アレーン-ペルフルオロアレーン相互作用)

## 1. Introduction

The synthesis and structure of metal-organic coordination networks have received significant attention due to their potential applications in separation, gas storage, sensing, and catalysis [1-4]. A deliberate combination of appropriate metal ions and well-designed organic ligands under various reaction conditions can be used to achieve structural and topological diversity of coordination networks and their functional properties. 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. We have reported the preparation of a series of coordination networks with metal ions and fluorinated flexible ligands Py-CH<sub>2</sub>-X-CH<sub>2</sub>-Py (Py=4-pyridyl; X=C<sub>6</sub>F<sub>4</sub>, C<sub>6</sub>F<sub>4</sub>C<sub>6</sub>F<sub>4</sub> or

C<sub>10</sub>F<sub>6</sub>) [5-9]. Most of the networks have remarkable clathration ability for guest aromatic compounds whose structures and topologies differ significantly depending on the size, shape, and number of guest molecules to afford one-dimensional (1D) cyclic chains, two-dimensional (2D) grids, or three-dimensional (3D) diamond networks. Fluorine atoms contained in the flexible ligands are mainly responsible for the clathration ability through C-H...F and/or arene-perfluoroarene interactions [7, 9].

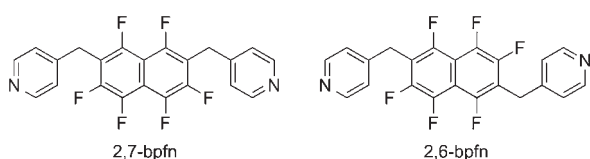
In this series of compounds, we designate clathration and interpenetration [5, 7] of coordination networks as "hetero-recognition" and "self-recognition", respectively. Interpenetration is regarded as a kind of clathration since the space surrounded by individual coordination networks is filled with the networks themselves. In other words, networks that incorporate guest aromatic

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compounds recognize "nonself" molecules, whereas those involved in interpenetration recognize each other as "selves". Clathration is compatible with interpenetration in a considerable number of the coordination networks.

Herein, We report the structures and characterizations of clathrate two-dimensional (2D) grid coordination networks with inclined interpenetration,  $\{[\text{Cd}(2,7\text{-bpf})_2(\text{NO}_3)_2] \cdot (\text{methyl benzoate})_{1.5} \cdot (\text{EtOH})_{0.5}\}_n$  (**1**) and  $\{[\text{Cd}(2,6\text{-bpf})_2(\text{NO}_3)_2] \cdot (\text{toluene})_{2.5}\}_n$  (**2**).



## 2. Experimental

### 2.1. Materials and methods

Ligands 2,7-bpfn and 2,6-bpfn were prepared in a similar manner as described in the literature [8]. Coordination networks were prepared in air.  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was purchased from Nacalai Tesque, Inc. Methyl benzoate and toluene were purchased from Kanto Chemical Co., Ltd. Elemental analysis was performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University (Japan).

### 2.2. Syntheses

#### 2.2.1. Synthesis of $\{[\text{Cd}(2,7\text{-bpf})_2(\text{NO}_3)_2] \cdot (\text{methyl benzoate})_{1.5} \cdot (\text{EtOH})_{0.5}\}_n$ (**1**).

A solution of 2,7-bpfn (25 mg, 0.06 mmol) in ethanol (0.5 mL) was added to a solution of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (9.3 mg, 0.03 mmol) in  $\text{H}_2\text{O}$  (0.125 mL) with stirring. After filtration, methyl benzoate (0.12 mL, 0.9 mmol) was added slowly. The mixture was allowed to stand for 7 d at 15 °C to give colorless block shaped crystals (yield: 25.1 mg, 64%). Anal. Calcd for  $\text{C}_{57}\text{H}_{39}\text{O}_{9.5}\text{N}_6\text{CdF}_{12}$   $\{[\text{Cd}(2,7\text{-bpf})_2(\text{NO}_3)_2] \cdot (\text{methyl benzoate})_{1.5} \cdot (\text{EtOH})_{0.5}\}$ : C, 52.65; H, 3.02; N, 6.46. Found: C, 52.97; H, 3.37; N,

5.98%.

#### 2.2.2. Synthesis of $\{[\text{Cd}(2,6\text{-bpf})_2(\text{NO}_3)_2] \cdot (\text{toluene})_{2.5}\}_n$ (**2**).

A solution of 2,6-bpfn (20 mg, 0.06 mmol) in ethanol (1 mL) was added to a solution of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (9.3 mg, 0.03 mmol) in  $\text{H}_2\text{O}$  (0.25 mL) with stirring. After filtration, toluene (0.21 mL, 1.9 mmol) was added slowly. The mixture was allowed to stand for 4 d at 5 °C to give colorless pillar shaped crystals (yield: 10.6 mg, 27%). Anal. Calcd for  $\text{C}_{61.5}\text{H}_{44}\text{O}_6\text{N}_6\text{CdF}_{12}$   $\{[\text{Cd}(2,6\text{-bpf})_2(\text{NO}_3)_2] \cdot (\text{toluene})_{2.5}\}$ : C, 56.67; H, 3.40; N, 6.45. Found: C, 56.52; H, 3.42; N, 6.30%.

### 2.3. Crystallographic Data Collection and Refinement

Single crystals of the complexes **1** and **2** with appropriate dimensions were mounted on a glass fiber and used for data collection. Crystal data for all the structures were collected with a Bruker-AXS SMART-APEXII CCD diffractometer ( $\text{MoK}_\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) by the  $\varphi$  and  $\omega$  scans ( $1.29 \leq 2\theta \leq 27.68^\circ$  for **1**;  $1.37 \leq 2\theta \leq 27.34^\circ$  for **2**). Multi-scan absorption corrections were applied using the SADABS program. The structures were solved by the direct method and refined by full-matrix least-squares against  $F^2$  of all data using the SHELXS 97 and SHELXL 97 programs [10]. 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. Crystallographic data for the four structures are listed in Table 1.

## 3. Results and discussion

### 3.1. Structure of $\{[\text{Cd}(2,7\text{-bpf})_2(\text{NO}_3)_2] \cdot (\text{methyl benzoate})_{1.5} \cdot (\text{EtOH})_{0.5}\}_n$ (**1**).

Complex **1** crystallizes in the orthorhombic space group  $P2_12_12$ . The asymmetric unit

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

	<b>1</b>	<b>2</b>
Formula	C <sub>57</sub> H <sub>39</sub> O <sub>9.5</sub> N <sub>6</sub> CdF <sub>12</sub>	C <sub>61.5</sub> H <sub>44</sub> O <sub>6</sub> N <sub>6</sub> CdF <sub>12</sub>
Mr	1300.36	1303.45
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2	<i>I</i> ba2
<i>a</i> [Å]	26.6616(16)	29.7962(17)
<i>b</i> [Å]	13.5134(8)	12.8337(7)
<i>c</i> [Å]	15.8179(10)	16.1314(9)
<i>V</i> [Å <sup>3</sup> ]	5699.0(6)	6168.6(6)
<i>Z</i>	4	4
<i>T</i> [K]	130	130
$\rho_{\text{calcd}}$ [Mg m <sup>-3</sup> ]	1.516	1.403
$\mu(\text{MoK}_\alpha)$ [mm <sup>-1</sup> ]	0.485	0.444
Max/min transmission	0.8680 / 0.8110	0.9160 / 0.8420
<i>F</i> (000)	2620	2636
Unique reflections	12028	6179
Parameters	766	411
Goodness-of-fit	1.105	1.064
Final <i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0580	0.0949
<i>wR</i> <sub>2</sub> (all data)	0.1737	0.2878
Reflections collected ( <i>R</i> <sub>int</sub> )	29684, 0.0229	15439, 0.0198
Reflections collected ( <i>I</i> > 2σ( <i>I</i> ))	10259	4598
Largest diff. peak/hole [eÅ <sup>-3</sup> ]	1.157 / -1.115	1.478 / -1.093

of **1**, as illustrated in Fig. 1a, contains two crystallographically independent Cd ions, two 2,7-bpfn molecules with *trans* conformation, one and a half methyl benzoate molecules, and one half of an EtOH solvent molecule. Half-occupancy was assigned to those half molecules. The cadmium

ion adopts an octahedral geometry with four pyridine rings at the equatorial positions and two monodentate NO<sub>3</sub><sup>-</sup> anions at the axial positions. Some selected bond lengths and angles around the Cd center are listed in Table 2. The extended structure forms a 2D rhombus grid (Fig 1b). There are two types of cavities with slightly different sizes that are alternately linked to each other. The cavities are not accurately described as a rhombus but a quadrangle in which two pairs of the distances of adjacent sides are the same (17.63 and 16.29 Å). The distances between diagonal Cd atoms are 29.89 × 16.24 Å. One of the two crystallographically independent guest methyl benzoate molecules has an effective arene-perfluoroarene interaction between the perfluoronaphthalene ring of ligand 2,7-bpfn and the phenyl group of methyl benzoate with a centroid-centroid distance of 3.487 Å. The other guest molecule with half-occupancy is too far away and inclined for face-to-face interaction. The Cd ions within a sheet are all coplanar to form a relatively flat sheet (Fig. 1c). These sheets are stacked in parallel with an interplane distance of 12.1 Å. Each sheet window contains the metal node of one interpenetrating sheet at the center, resulting in diagonal/diagonal inclined interpenetration [11, 12]. There are two inclined sets of interpenetrating sheets at an angle of 53.9° to each other (Fig. 1d). Although the interpenetration severely reduces the porosity, the intersection of grids is still capable of creating large channels along the *b*-axis filled by guest molecules (Fig. 1e). Inclined interpenetration of 2D grid networks occurs to increase the dimension to 3D (Fig. 2).

### 3.2. Structure of {[Cd(2,6-bpfn)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] • (toluene)<sub>2.5</sub>]<sub>n</sub> (**2**).

Complex **2** crystallizes in the orthorhombic space group *I*ba2. The asymmetric unit of **2**, as illustrated by the labeled unprimed atoms of Fig. 2a, contains one half Cd ion, one 2,6-bpfn molecule

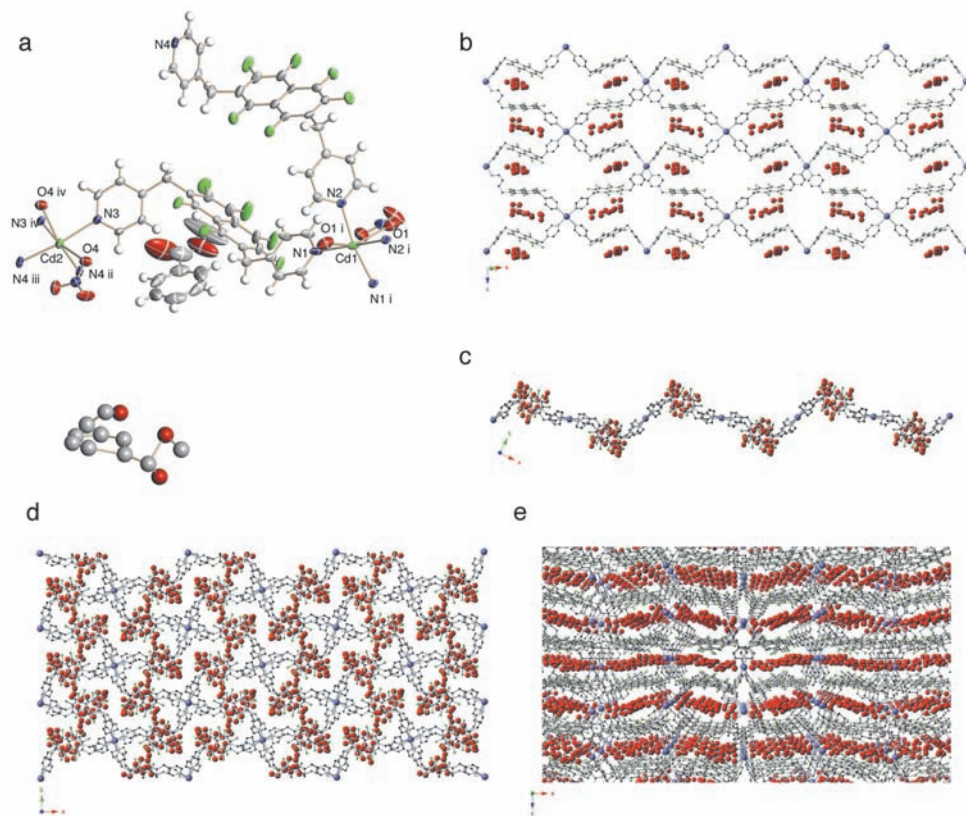


Fig. 1 (a) Coordination environment in **1**. Thermal ellipsoids are shown at 30% probability. Symmetry codes: (i)  $1-x, 1-y, z$ ; (ii)  $x, y, -1+z$ ; (iii)  $-x, -y, -1+z$ ; (iv)  $-x, -y, z$ . (b) Top view of the 2D sheet structure. The methyl benzoate molecules are highlighted in red. Hydrogen atoms, solvent EtOH molecules, and nitrate anions are omitted for clarity. (c) Side view of the 2D sheet structure. (d) Side view of the 2D sheet structures with inclined interpenetration. (e) Top view of the 2D sheet structures with inclined interpenetration. Methyl benzoate molecules are clathrated in microchannels along the  $b$ -axis.

Table 2. Selected bond lengths (Å) and angles (°) of **1**.

Cd1–N1	2.345(2)	N1 <sup>(i)</sup> –Cd1–O1	84.89(7)
Cd1–N2	2.3574(17)	N2–Cd1–O1	82.24(6)
Cd1–O1	2.653(2)	N2 <sup>(i)</sup> –Cd1–O1	73.73(6)
Cd2–N3	2.3877(17)	N4 <sup>(iii)</sup> –Cd2–N4 <sup>(iii)</sup>	93.47(8)
Cd2–N4	2.3662(17)	N4 <sup>(iii)</sup> –Cd2–N3	86.41(6)
Cd2–O4	2.4826(17)	N4 <sup>(iii)</sup> –Cd2–N3 <sup>(iv)</sup>	169.06(6)
N1–Cd1–N1 <sup>(i)</sup>	98.69(9)	N3–Cd2–N3 <sup>(iv)</sup>	95.77(8)
N1–Cd1–N2	86.50(6)	N4 <sup>(iii)</sup> –Cd2–O4	115.92(6)
N1–Cd1–N2 <sup>(i)</sup>	167.08(7)	N4 <sup>(iii)</sup> –Cd2–O4 <sup>(iv)</sup>	86.85(6)
N2–Cd1–N2 <sup>(i)</sup>	90.97(8)	N3–Cd2–O4	83.38(6)
N1–Cd1–O1	118.35(7)	N3–Cd2–O4 <sup>(iv)</sup>	75.00(6)

Symmetry codes: (i)  $1-x, 1-y, z$ ; (ii)  $x, y, -1+z$ ; (iii)  $-x, -y, -1+z$ ; (iv)  $-x, -y, z$ .

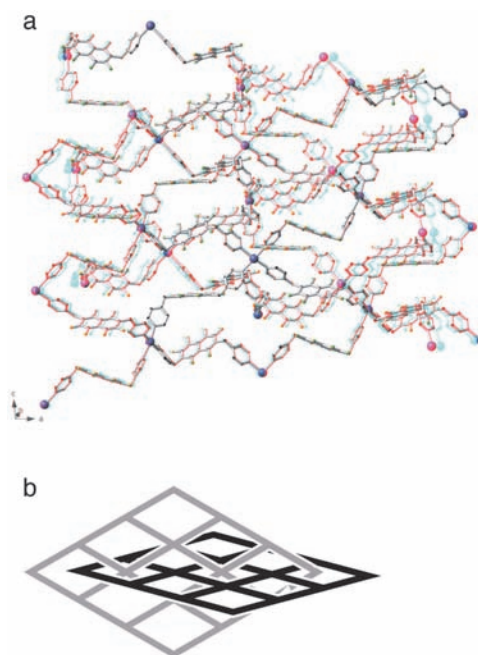


Fig. 2 (a) Stereo view for red/blue 3D glasses of two inclined 2D grid networks. (b) Schematic view of diagonal/diagonal inclined interpenetration of 2D grid networks.

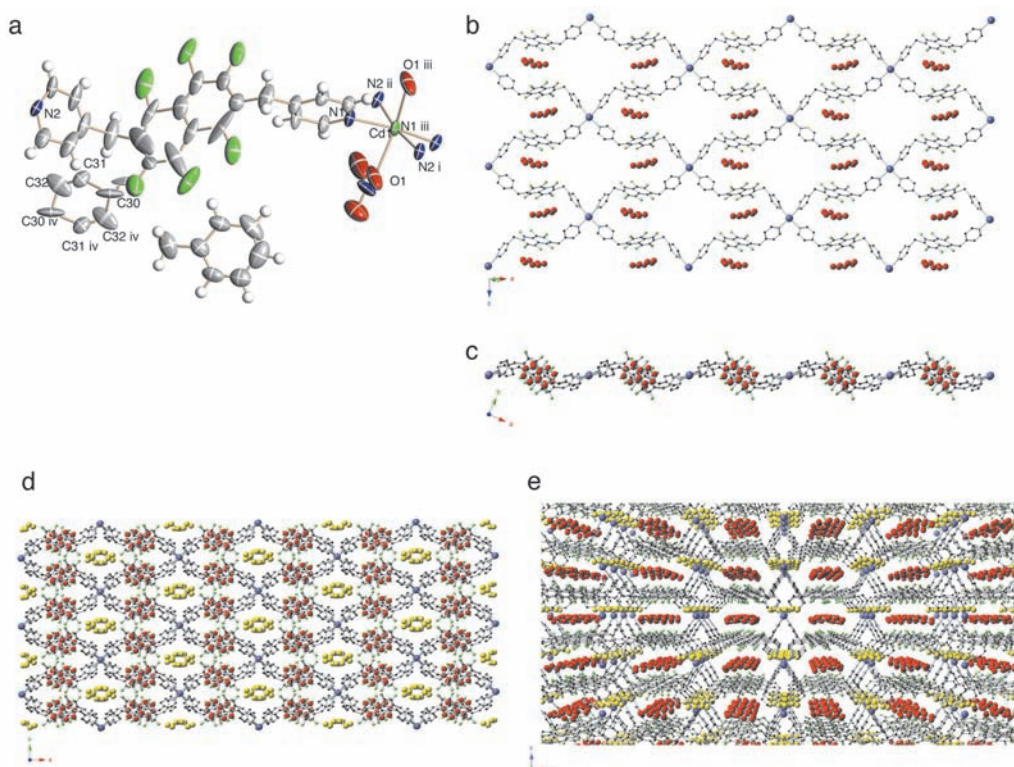
with *trans* conformation, and one and a quarter toluene molecules. The coordination environment of Cd and the network topology in **2** is similar to that of **1** (Fig. 3a). Some selected bond lengths and angles around the Cd center are listed in Table 3. The cavity is an accurate rhombus with diagonal-to-diagonal distances of  $32.44 \times 16.13$  Å, and the grid dimensions are 18.12 Å (Fig. 3b). One of the two crystallographically independent guest methyl benzoate molecules has an effective arene-perfluoroarene interaction between the perfluoronaphthalene ring of ligand 2,6-bpfn and the phenyl group of methyl benzoate with a centroid-centroid distance of 3.770 Å. The other guest molecule with half-occupancy is too far away and inclined for face-to-face interaction. The Cd ions within a sheet are all coplanar to form a relatively flat sheet (Fig. 3c). These sheets are

stacked in parallel with an interplane distance of ca. 12 Å. A side view of the stacking of **2** is in Fig. 3d. The grid layers are puckered, and interpenetrate at an angle of  $46.6^\circ$  to one another. Although the interpenetration severely reduces the porosity, the intersection of grids is still capable of creating large channels along the *b*-axis filled by guest molecules (Fig. 3e).

**Table 3.** Selected bond lengths (Å) and angles ( $^\circ$ ) of **2**.

Cd1–N1	2.353(7)	N1–Cd1–N1 <sup>(iii)</sup>	96.8(4)
Cd1–N2	2.316(7)	N2 <sup>(i)</sup> –Cd1–O1	90.8(3)
Cd1–O1	2.653(2)	N2 <sup>(i)</sup> –Cd1–O1 <sup>(iii)</sup>	109.6(3)
N2 <sup>(i)</sup> –Cd1–N2 <sup>(ii)</sup>	89.3(4)	N1–Cd1–O1	78.9(3)
N2 <sup>(i)</sup> –Cd1–N1	87.6(2)	N1–Cd1–O1 <sup>(iii)</sup>	82.3(3)
N2 <sup>(i)</sup> –Cd1–N1	170.9(2)	O1–Cd1–O1 <sup>(iii)</sup>	151.6(5)

Symmetry codes: (i)  $-1/2+x, 1/2+y, -1/2+z$ ; (ii)  $1/2-x, 1/2-y, -1/2+z$ ; (iii)  $-x, 1-y, z$ .



**Fig. 3** (a) Coordination environment in **2**. Thermal ellipsoids are shown at 30% probability. Symmetry codes: (i)  $-1/2+x, 1/2+y, -1/2+z$ ; (ii)  $1/2-x, 1/2-y, -1/2+z$ ; (iii)  $-x, 1-y, z$ ; (iv)  $1-x, 1-y, z$ . (b) Top view of the 2D sheet structure. The toluene molecules are highlighted in red. Hydrogen atoms, solvent EtOH molecules, and nitrate anions are omitted for clarity. (c) Side view of the 2D sheet structure. (d) Side view of the 2D sheet structures with inclined interpenetration. The half-occupied toluene molecules are highlighted in yellow. (e) Top view of the 2D sheet structures with inclined interpenetration.

## 4. Conclusions

Assembly of Cd(II) with flexible fluorinated ligand 2,7-bpfn or 2,6-bpfn in the presence of aromatic compounds affords 2D grid coordination networks. The guest molecules are clathrated in cyclic cavities of the grid networks. The guest aromatic rings are held in the cavity by arene-perfluoroarene interactions.

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