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Formation of Two, One, and Zero-Dimensional Coordination Assemblies from Cd(II) Ion and 4,4′-Bipyridine

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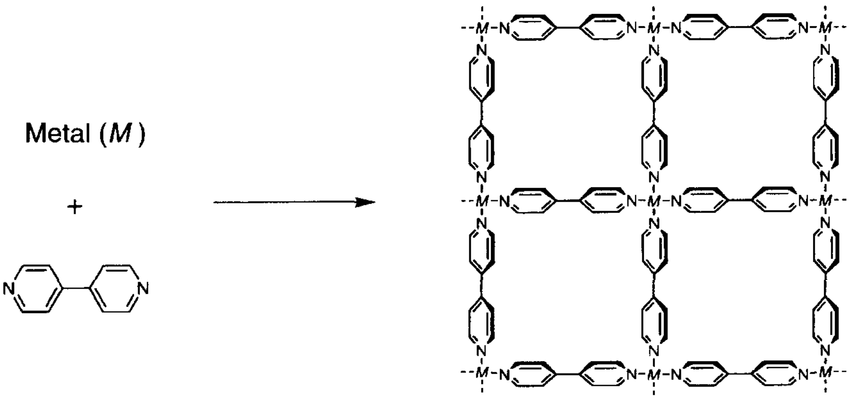
Complexation of $Cd(NO_3)_2$ with 4,4′-bipyridine (4,4′-bpy) gave, depending on the L/M ratios and concentrations, two-dimensional, one-dimensional or zero-dimensional coordination assemblies, which were characterized by X-ray crystallography. The two dimensional structure was shown to be a non-interpenetrated square grid network in which the square cavities were occupied by water and nitrate ions. The one-dimensional polymer also formed a two-dimensional network with the assistance of O–H···N hydrogen bonds. The zero-dimensional structure was composed of two Cd^{2+} centers, four unidentate 4,4′-bpy, and a bridging bidentate 4,4′-bpy. The networks and the packing of these structures were analyzed in terms of coordination and hydrogen bonds.

The coordination polymeric networks of a transition metal-(4,4′-bipyridine) have been studied intensively during the last decade.[1] Reports show that the 4,4′-bipyridine (4,4′-bpy) ligand forms various topological networks with/without altering L/M ratios because of its linear and exobidentate nature. Possible 4,4′-bpy networks include 1D chain,[2—4] ladder,[5] square and hexagonal grid,[6,7] bilayer,[8] and diamondoid[9] structures. These networks have large cavities in their framework and the structures possess the potential to act as microporous solid materials (including molecular absorption,[8] heterogeneous catalyst). Among all the networks, a square grid **I** is the prototypical infinite framework (Scheme 1).[6] The grid **I** could be regarded as a polymer version of a molecular square[10] and was first observed in an interpenetrated complex prepared from $Zn(PF_6)_2$ and 4,4′-bpy.[6a] On the other hand, complexation of $Cd(NO_3)_2$ with 4,4′-bpy in the presence of an organic guest provided the first example of a non-interpenetrated grid sheet **I** which accommodates the guest in the square grid cavity.[6b] Although the crystal structure of the clathrate complex, $[Cd(4,4'\text{-bpy})_2](NO_3)_2\cdot2\textit{o}\text{-}C_6H_4Br_2$, has been solved, the question arises of whether Cd(II)(4,4′-bpy) complex forms a similar non-interpenetrated framework even in the absence of a guest molecule? In order to address this question, we further examined the synthesis and the crystal structures of metal complexes assembled from $Cd(NO_3)_2$ and 4,4′-bpy at various L/M ratios.

Results and Discussion

Reaction of $Cd(NO_3)_2\cdot4H_2O$ and 4,4′-bpy. The crystallization experiments have been carried out by increasing the L/M ratio from 1.0 to 4.0 in increments of 0.5 and decreasing the concentration from 200 to 20 mM in decrements



Scheme 1. Formation of a square grid from metal ions and 4,4′-bpy.

[#] CREST, Japan Science and Technology Corporation (JST).

of 30 mM (1 M = 1 mol dm^{-3}). The reactions were done by adding aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ (8 cm^3) to EtOH solution of 4,4′-bpy (2 cm^3). The products obtained were characterized by X-ray crystallography and elemental analyses. Interestingly, the variation of L/M ratios and concentrations led to the formation of three types of structures (Table 1):

$\{[Cd(4,4'\text{-bpy})_2(H_2O)_2](NO_3)_2 \cdot 4H_2O\}_n$ (**1**),
$\{[Cd(4,4'\text{-bpy})_3(H_2O)_2](NO_3)_2 \cdot 2(4,4'\text{-bpy}) \cdot 4.5H_2O\}_n$ (**2**), and
$[Cd_2(4,4'\text{-bpy})_5(H_2O)_4(NO_3)_2](NO_3)_2 \cdot 4H_2O$ (**3**).

In all three complexes, the cadmium atom has an octahedral coordination, but with different coordination environments. In **1** and **2**, each cadmium atom coordinates to four 4,4′-bpy ligands and two water molecules, while in **3**, it coordinates to three 4,4′-bpy ligands, one nitrate and two water molecules. The network features and crystal packing will be discussed in the following sections.

Table 1. Selected Reaction Conditions and Products

[M]	L/M ratio 1.0	2.0	2.5	3.0	4.0
200 mM	**1**	**1**	**1**	**1**+**2**	**1**+**2**
110 mM	**1**	**1**	**1**	**1**+**2**	**1**+**2**
80 mM	**1**	**1**	**1**	**1**+**2**	**1**+**2**
50 mM	—	—	**1**	**1**+**2**	**3**
20 mM	—	—	—	—	—

Structure of $\{[Cd(4,4'\text{-bpy})_2(H_2O)_2](NO_3)_2 \cdot 4H_2O\}_n$ (1): Two-Dimensional. The structure of **1** is a two-dimensional layer with no interpenetration and no enclathration of organic guest molecules (Fig. 1a). It has two 4,4′-bpy moieties: one of them sits on the inversion center (labeled as **A**) while the other sits on the glide plane (labeled as **B**). **A** is planar with a 0° interplanar angle between the two pyridine rings, whereas **B** is non-planar with a 40° interplanar angle between two pyridine rings. Each square cavity of dimension 8×8 Å is occupied by two cyclic tetramers that are formed via hydrogen bonding interactions between two nitrates and two solvated water molecules (Fig. 1b, O···O: 2.772(2), 2.774(2), 2.804(2), 2.862(2) Å). Two of these tetramers further interact with ligated water molecules to form a wheel like hydrogen bonding network around 4,4′-bpy ligand (O···O: 2.678(2) Å). As a result, a rotaxane structure via hydrogen bonds is formed (Fig. 1c). Interestingly, the ligated water molecules do not accept any protons, whereas solvated water molecules accept one proton. The 2D layers stack in zigzag (Fig. 1d) and slipped (Fig. 1e) fashion along the 4,4′-bpy rings **A** and **B**, respectively. Noticeably, the interlayer separation (4.79 Å) is remarkably smaller than in its clathrate complex (6.30

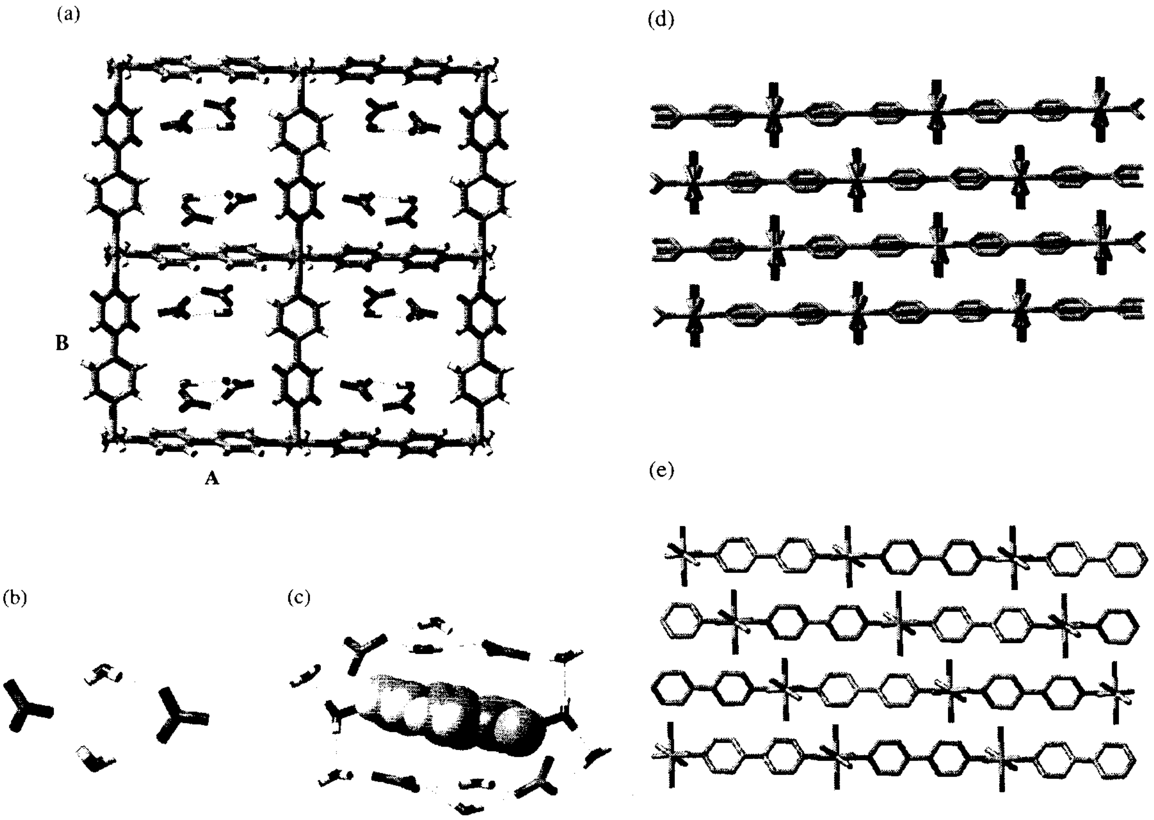


Fig. 1. Illustrations for the crystal structure **1**: (a) Representation of the two-dimensional grid sheet. Notice the nitrate ions and the water molecules in the square cavities. (b) The hydrogen-bonded tetramers of nitrates and water molecules. (c) Representation of the molecular rotaxane via hydrogen bonds. The threading 4,4′-bpy molecule and Cd ions are represented in space filling mode. (d) Stacking of grid sheets in zigzag fashion. A view along 4,4′-bpy **B**. (e) Stacking of grid sheets in slipped fashion. A view along 4,4′-bpy **A**.

Å).[6b] The stacking of the grids results in channels that are occupied by the above-described nitrate and water tetramers.

Structure of $\{[Cd(4,4'\text{-}bpy)_3(H_2O)_2](NO_3)_2\cdot 2(4,4'\text{-}bpy)\cdot 4.5H_2O\}_n$ (2): One-Dimensional. The structure **2** has three coordinated and two enclathrated 4,4′-bpy molecules per metal atom. One of the coordinated 4,4′-bpy ligands serves as a bifunctional ligand to form a one-dimensional coordination network, while the other two form side arms for the one-dimensional chain by acting as mono-functional ligands (Fig. 2a). This structure could be termed as a molecular antenna, a prototypical structure of the railroad polymer.[2c] The antennas join together via O–H···N hydrogen bonds which are formed between ligated H_2O molecules and uncoordinated N-atoms of 4,4′-bpy (Fig. 2b, O···N: 2.787(7), 2.828(6) Å). The rocurrence of the cyclic ···H_2O–Cd–(4,4′-bpy)···H_2O–Cd–(4,4′-bpy)··· pattern suggests that it can be used as a supramolecular synthon in crystal engineering.[11] As a result of the hydrogen bonding, a two-dimensional layer was formed with the cavities (8×9 Å) that are occupied by guest 4,4′-bpy molecules (Fig. 2b). These layers stack along the *a*-axis in a zigzag fashion with an interlayer separation of 8.79 Å. The second guest 4,4′-bpy molecule lies in between the layers via a plethora of aromatic interactions.

Structure of $[Cd_2(4,4'\text{-}bpy)_5(H_2O)_4(NO_3)_2](NO_3)_2\cdot 4H_2O$ (3): Zero-Dimensional. The structure **3** is a dinuclear complex. The two coordinated water molecules have the cis geometry around the Cd-atom (Fig. 3a). The asymmetric unit contains two Cd-atoms, five 4,4′-bpy ligands, coordinated and non-coordinated nitrate ions, and four water molecules. The Cd–O and Cd–N bond lengths vary from 2.291(3) to 2.384(3) Å and from 2.323(3) to 2.365(3) Å, respectively.

The bond distances on Cd1 and Cd2 differ only in the second decimal point. The crystal structure lacks, however, an inversion center because of the complexity of the three-dimensional hydrogen-bonded network. Interestingly, the network contains a one-dimensional chain that is formed by O–H···N hydrogen bonds (O···N: 2.732(3), 2.757(4) Å) between the ligated water molecules and the terminal N-atom of 4,4′-bpy (Fig. 3b). The 4,4′-bpy ligands also interact via π···π interactions. These one-dimensional hydrogen-bonded chains form a three-dimensional network by joining each other via tetramers of two water molecules and two nitrates (Fig. 3c, O···O: 2.804(4), 2.800(6), 2.824(4), 2.801(5) Å). This cyclic tetramer composed of 10-atoms, unlike the tetramer in **1** (9-atoms, Fig. 1b).

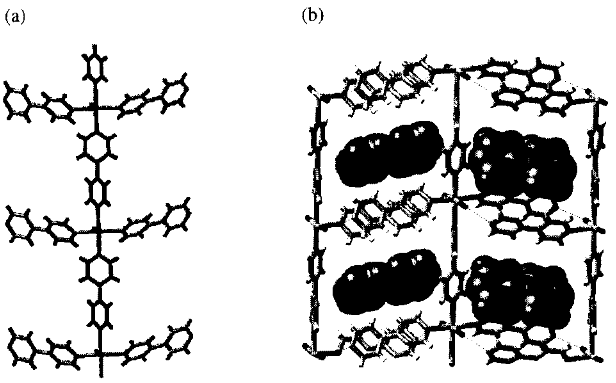


Fig. 2. Illustrations for the crystal structure **2**: (a) Representation of the one-dimensional chain. (b) Representation of the two-dimensional hydrogen bonded network. The guest 4,4′-bpy molecules are represented in space filling mode.

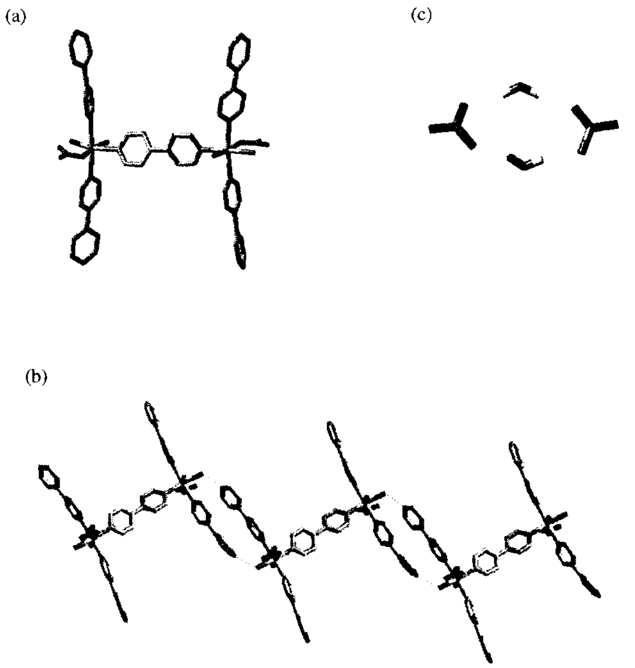


Fig. 3. Illustrations for the crystal structure **3**: (a) Representation of the zero-dimensional species. Notice the cis geometry of the coordinated water molecules. (b) One-dimensional hydrogen-bonded network based on the cyclic ···H_2O–Cd–(4,4′-bpy)···H_2O–Cd–(4,4′-bpy)··· dimers—part of the three-dimensional hydrogen-bonded network. (c) Representation of the hydrogen bonded tetramer formed by water and nitrates. Compare with Fig. 1b.

Conclusion

L/M ratio and concentration dependence of the formation of three types of coordination assemblies are related to coordination aggregates in the solution. In lower L/M ratio, the square aggregate consistsing of four cadmium and four 4,4′-bpy tends to generate at almost all conditions. The aggregate associates and crystallizes to form 2D network **1**. In the ratio of $L/M \geq 3$, however, formation of a 1D-chain aggregate which is caused by excess of ligand competes with formation of the square aggregate. Then, the two types of aggregates associate and crystallize as **1** and **2**, fractionally. On the other hand, in a high L/M ratio and low concentration, a dinuclear complex, which is the lowest degree of aggregation among **1**—**3**, is favored in the solution, and crystallizes to form the product **3**.

Three types of complexes **1**, **2**, and **3** are formed from Cd(II) ion and 4,4′-bpy. The network in **1** was shown to exist as a non-interpenetrated grid structure even in the absence of aromatic guest molecules. Instead of organic guest, water molecules and nitrate ions located in the cavity and formed a

Table 2. Crystallographic Details for Complexes **1**, **2**, and **3**

	1	**2**	**3**
Formula	$C_{20}H_{28}CdN_6O_{12}$	$C_{50}H_{103}N_{12}CdO_{12.5}$	$C_{25}H_{28}CdN_7O_{10}$
F.W./g mol^{-1}	656.89	1184.84	698.95
T/K	167	193	173
Crystal size/mm	0.20 × 0.20 × 0.15	0.25 × 0.20 × 0.20	0.25 × 0.25 × 0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2$	Pc
a/Å	18.9015(11)	17.5815(16)	12.4725(18)
b/Å	11.7948(7)	11.7413(11)	15.195(2)
c/Å	12.1547(7)	24.836(2)	15.390(2)
β/°	97.4380(10)	94.3215(18)	96.625(3)
V/Å^3	2687.0(3)	5112.3(8)	2897.2(7)
Z	4	4	4
d_{calc}/g cm^{-3}	1.624	1.539	1.602
F(000)	1336	2540	1420
μ(Mo $K\alpha$)/mm^{-1}	1.009	0.506	0.821
$2\theta_{max}$/°	55.86	50	56.22
No. collected reflns	8362	13740	18522
No. unique reflns	3105	8232	10014
	(R_{int} = 0.0138)	(R_{int} = 0.0237)	(R_{int} = 0.0173)
Parameters	185	553	791
R_1, wR_2 [$I > 2\sigma(I)$]	0.0176, 0.0499	0.0518, 0.1347	0.0221, 0.0541
R_1, wR_2 [all data]	0.0184, 0.0503	0.636, 0.1400	0.0251, 0.0553
$S^{c)}$	1.009	1.088	0.953
Max peak in final ΔF/e Å^{-3}	0.445	0.791	0.707

hydrogen bond network. It is important to note that the L/M ratios and concentration of the solutions resulted in three different crystals with different dimensionality of the network. In **2** and **3**, the hydrogen bonding interactions played an important role in forming three-dimensional networks. The motifs observed here could serve as metal-coordinated or hydrogen-bonded synthons in crystal engineering experiments.

Experimental

General: 4,4′-Bpy and $Cd(NO_3)_2 \cdot 4H_2O$ were obtained commercially and used as received. Melting points were determined on a Yanaco MP-500V. FTIR spectra were recorded on a Shimadzu FTIR-8300 spectrometer. Microanalysis were performed by Research Center for Molecular Materials in Institute for Molecular Science.

Preparation of 1, 2 and 3: Complexes **1**, **2**, and **3** were also prepared under the following conditions.

$\{[Cd(4,4'\text{-}bpy)_2(H_2O)_2](NO_3)_2 \cdot 4H_2O\}_n$ (1): An aqueous solution (8 cm^3) of $Cd(NO_3)_2 \cdot 4H_2O$ (308 mg, 1 mmol) was combined with an ethanol (2 cm^3) solution of 4,4′-bpy (312 mg, 2 mmol). The initially formed fine precipitate (very small amount) was filtered and the clear filtrate was allowed to stand at room temperature for 3 d to give single crystals of **1** in 70% yield. Mp > 300 °C. IR (KBr), 3394, 1603, 1533, 1491, 1385, 1221, 1074, 1007, 806, 631 cm^{-1}. Found: C, 36.69; H, 4.09; N, 12.86%. Calcd for $[Cd(4,4'\text{-}bpy)_2(H_2O)_2](NO_3)_2 \cdot 4H_2O$: C, 36.57; H, 4.30; N, 12.79%.

$\{[Cd(4,4'\text{-}bpy)_3(H_2O)_2](NO_3)_2 \cdot 2(4,4'\text{-}bpy) \cdot 4.5H_2O\}_n$ (2): An aqueous solution (1.6 cm^3) of $Cd(NO_3)_2 \cdot 4H_2O$ (86 mg, 0.28 mmol) was combined with an ethanol (0.4 cm^3) solution of 4,4′-bpy (175 mg, 1.12 mmol). The initially formed fine precipitate (small amount) was filtered and the clear filtrate was allowed to stand at room temperature for 3 d to give mixture of single crystals of **1** and **2** in 24 and 34% yields, respectively. Mp > 300 °C. IR (KBr) 3385, 1600, 1533, 1491, 1384, 1221, 1074, 995, 810, 629, 617, 507 cm^{-1}. Found: C, 52.72; H, 4.43; N, 14.76%. Calcd for $[Cd(4,4'\text{-}bpy)_3(H_2O)_2](NO_3)_2 \cdot 2(4,4'\text{-}bpy) \cdot 4.5H_2O$: C, 52.94; H, 4.71; N, 14.82%.

$[Cd_2(4,4'\text{-}bpy)_5(H_2O)_4(NO_3)_2](NO_3)_2 \cdot 4H_2O$ (3): An aqueous solution (12 cm^3) of $Cd(NO_3)_2 \cdot 4H_2O$ (154 mg, 0.5 mmol) was combined with an ethanol (3 cm^3) solution of 4,4′-bpy (234 mg, 1.5 mmol). The initially formed fine precipitate (very small amount) was filtered and the clear filtrate was allowed to stand at room temperature for 3 d to give single crystals of **3** in 71% yield. Mp > 300 °C. IR (KBr) 3150, 1600, 1530, 1480, 1400, 1380, 1220, 1070, 1000, 820, 625 cm^{-1}. Found: C, 45.43; H, 3.72; N, 14.67%. Calcd for $[Cd(4,4'\text{-}bpy)_{2.5}(H_2O)](NO_3)_2$: C, 45.30; H, 3.65; N, 14.79%. Because of the loss of water molecules, the formula obtained by elemental analysis does not correspond to the formula based on X-ray crystallography.

X-Ray Crystal Structure Determinations: Single crystal X-ray diffraction data for all the complexes were collected on a Siemens SMART/CCD diffractometer equipped with a low temperature device. Diffracted data were corrected for absorption using the SADABS[12] program. SHELXTL[13] was used for the structure solution and refinement was based on F^2. All non-hydrogen atoms were refined anisotropically. The H-atoms of the C–H groups were fixed in calculated positions and refined isotropically with thermal parameters based upon the corresponding C-atoms [U(H) = 1.2 U_{eq} (C)]. The H-atoms of water molecules in **1** and **3** were located and refined isotropically. In **2**, pyridine rings in the bifunctional ligand and the guest 4,4′-bpy were fixed as regular hexagons, nitrate anions and guest water molecules have a disorder which is unresolved and all these disordered positional atoms were refined isotropically by treating them as carbon atoms. PLATON[14] program was used for detecting inversion centers in complexes **2** and **3**. For **2**, no inversion center was found, whereas for **3**, an approximate inversion center was found but the water molecules did not lie on it. Pertinent crystallographic data are given in Table 2. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on requests, free of charge, by quoting the publication citation and the deposition number of 143095-143097. The complete data are deposited as Document No. 73034 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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