A Novel Bi-Metal $Ni^{II}Cd^{II}$ Supramolecular Structure with 4-Hydroxypyridine Ligands, $[\{Cd^{II}(4\text{-OHpy})_2\}\{Ni^{II}(CN)_4\}]$, and Deprotonated 3-Hydroxypyridine Ligands, $[\{Cd^{II}_3(3\text{-}O^-py)_2(mea)_2\}\{Ni^{II}(CN)_4\}_2]$

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Synthesis and crystal structures of new bimetallic polynuclear complexes in 2-dimensional (2D) architectures, $[\{Cd^{II}(4\text{-OHpy})_2\}\{Ni^{II}(CN)_4\}]$ (4-OHpy = 4-hydroxypyridine) (**1**) and $[\{Cd^{II}_3(3\text{-}O^-py)_2(mea)_2\}\{Ni^{II}(CN)_4\}_2]$ (3-O^-py = pyridin-3-onato anion, mea = monoethanolamine) (**2**) are described. These compounds are prepared by the same method. However, hydroxypyridine ligands are different, thus these structures differ.

In recent years, metal–organic frameworks (MOFs), also known as coordination polymers, are a rapidly evolving area of research that has implications for coordination chemistry and functional materials sciences.[1] The increasing interest in this field is justified by the intellectual challenge in controlling and manipulating the self-assembly process. This endeavor starts with activities aimed at studying intermolecular interactions to elucidate the underlying processes of self-assembly and is a prerequisite for progress in crystal engineering.[2] In particular, Hofmann-like structures (shown in S1, Supporting Information) have interested the scientific community from a fundamental point of view, but they have also been of interest because of their possible applications.[3] Against this background, we have developed a synthetic route to prepare several bimetallic CN-bridged coordination polymers with pyridine derivatives, as we previously reported,[4] demonstrating Hofmann-like crystal structure and spin transition. In our continuing efforts to further understand synthesis of Hofmann-like compounds by building a crystal engineering "toolbox," we now report a simple synthetic method to create the complexes and X-ray crystal structures of a unusually coordination-type of Hofmann-like structure, $[\{Cd^{II}(4\text{-OHpy})_2\}\{Ni^{II}(CN)_4\}]$ (**1**) (4-OHpy = 4-hydroxypyridine) and quite different unique

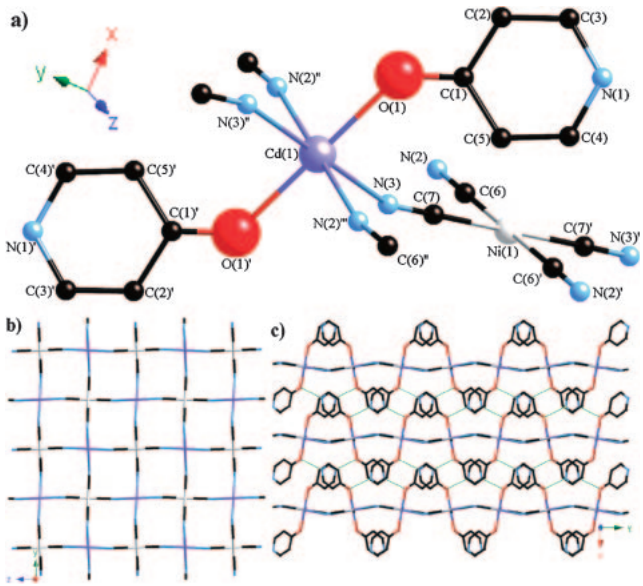

Figure 1. Coordination structure of the Cd and Ni ions in **1** (a). The cylinder drawing, 2D structure of **1**. In this picture, 4-hydroxypyridine omitted for clarity (b). Stacking of three consecutive layers of **1** with intermolecular hydrogen bond (green dotted line). Atom code: Cd (purple), Ni (white), N (blue), C (black), and O (red) (c). In these pictures, hydrogen atoms are omitted for clarity.

structure $[\{Cd^{II}_3(3\text{-}O^-py)_2(mea)_2\}\{Ni^{II}(CN)_4\}_2]$ (**2**) (3-O^-py = pyridin-3-onato anion, mea = monoethanolamine).

The crystal structures of **1** and **2** were analyzed by single-crystal X-ray diffraction at 293 K. The asymmetric unit of **1** consists of the bimetallic $Cd^{II}Ni^{II}$ unit of $[\{Cd^{II}(4\text{-OHpy})_2\}\{Ni^{II}(CN)_4\}]$ (Figure 1a). The complex exhibits a 2D coordination square shape mesh network array (Figures 1b and 1c) which is a Hofmann-like structure. The Cd(1)–N(3)–C(7) and Cd(1)–N(2)‴–C(6)″ angles are 167.4(3) and 161.3(2)°, respectively. Therefore, the $[Cd^{II}Ni^{II}(CN)_4]_2$ 2D-network edges are bent. This complex has one type of Cd^{II} ion which lies on an inversion center with a octahedral coordination environment by four nitrogen atoms in the equatorial plane and two oxygen atoms in the axial positions and the $[Ni^{II}(CN)_4]$ moieties are also located on inversion centers. All Ni^{II} ions have square-planar coordination geometries with bidentate cyano substituents binding to the adjacent Cd^{II} ion centers (Ni–C (av.) = 1.862 Å, Cd–N (av.) = 2.309 Å, this is common for Cd–$[Ni^{II}(CN)_4]$ complexes[5]) to form extended coordination networks. In the axial positions, 4-OHpy are monodentated ligands and the O(1)–Cd(1)–O(1)′ angle is perfectly linear. In the above coordination model, bond angle (C(1)–O(1)–Cd(1): 133.03(13)°) is in conformity with Cd–O coordination in its neutral form. The Cd···Cd distances in the Cd(1)–N(2)–C(6)–Ni(1)–C(6)′–N(2)′–Cd(1) and Cd(1)–N(3)–C(7)–Ni(1)–C(7)′–N(3)′–Cd(1) one-dimensional zigzag-chain edges are 10.561 and 10.495 Å, respectively. The nearest Cd···Cd interlayer distance is about 7.899 Å. The closest approach between Cd(1) and Cd(1)′ is 7.445 Å. By the intermolecular hydrogen bond O(1)···N(1) (2.818 Å), **1** produces a 3D network (Figure 1c).

The asymmetric unit of **2** consists of the mixed-metal $Cd^{II}Ni^{II}$ unit of $[\{Cd^{II}_3(3\text{-}O^-py)_2(mea)_2\}\{Ni^{II}(CN)_4\}_2]$

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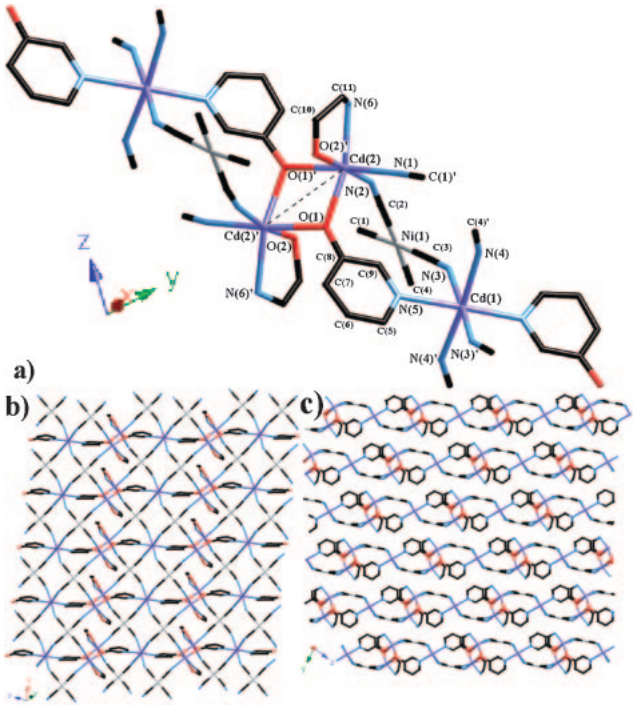

Figure 2. Coordination structure of the Cd and Ni ions in **2** with Cd(2)···Cd(2)′ interaction (dotted line) (a). The cylinder drawing, 2D structure of **2** (b). Stacking of six consecutive layers of **2**. Atom code: Cd (purple), Ni (white), N (blue), C (black), and O (red) (c). In these pictures, hydrogen atoms are omitted for clarity.

Table 1. Crystal Data

Crystal data	**1**	**2**
Empirical formula	$C_{14}H_{10}Cd_1Ni_1N_6O_2$	$C_{22}H_{22}Cd_3Ni_2N_{12}O_4$
FW	465.39	973.14
Temperature/K	293	293
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	7.8987(12)	7.7066(8)
b/Å	10.4951(16)	8.9430(10)
c/Å	10.5613(16)	12.4915(13)
α/°		76.671(2)
β/°	101.744(10)	84.180(2)
γ/°		69.409(2)
V/Å^3	857.2(2)	784.01(14)
Z	2	1
d(calcd)/Mg m^{-3}	1.803	2.061
Absorption coefficient/mm^{-1}	2.357	3.229
F(000)	456	470
Crystal size/mm^3	0.35 × 0.35 × 0.35	0.35 × 0.35 × 0.35
Reflections collected	6042	3142
Independent reflections	2101 [R(int) = 0.0286]	2276 [R(int) = 0.0244]
GOF on F^2	1.201	0.826
$R1$[a], $wR2$[b]	0.0552, 0.1303	0.0329, 0.0670
Largest diff. peak and hole/e Å^{-3}	0.677 and −4.584	0.652 and −0.611

a) $R1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. b) $wR2 = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$.

(Figure 2a). The structure comprises a 2D array (Figures 2b and 2c). Cd^{II} ions in $[\{Cd^{II}_3(3\text{-}O^-py)_2(mea)_2\}\{Ni^{II}(CN)_4\}_2]$ are two types of crystallographically distinct octahedrally coordination units. $Cd^{II}(1)$ and $Cd^{II}(2)$ are coordinated by CdN_6 and CdN_3O_3 respectively. Ni^{II} ions have square-planar coordination geometries with the cyano substituents (Ni–C (av.) = 1.860 Å) binding to the Cd^{II} ions. This is common for $[Ni^{II}(CN)_4]^{2-}$ complexes with square-planar coordination geometry. Mea is a bidentate ligand, and chelates with Cd(2) (Cd(2)–N(6) = 2.346(4) Å, Cd(2)–O(2) = 2.467(4) Å). Cd(2) ions are bound by two deprotonated exocyclic O atoms of different 3-O^-py bridging ligands, forming a basic binuclear Cd_2O_2 core (Figure 2c). In the above coordination model, bond distances and angles are in agreement with other reported Cd^{II} coordination polymers.[5] The closest approach of Cd(1)···Cd(2) and Cd(2)···Cd(2)′ distances are 7.562 and 3.560 Å. Comparing with previous compounds which have a four-membered Cd_2O_2 core,[6] the Cd(2)···Cd(2)′ distance in the core is on the short side.

In the current study, we successfully isolated analytically pure complexes of bimetallic $Cd^{II}Ni^{II}$ and succeeded in growing single crystals. X-ray crystal structure analysis revealed that the complexes **1** and **2** are coordination polymers. It is notable that 4-hydroxypyridine is neutral and 3-hydroxypyridine is deprotonated to pyridin-3-onato anion although both compounds are synthesized by the same method. One of the most interesting features in compound **1** is the N ligation site at the 4-OHpy remains free and the O ligation site at the 4-OHpy coordinats to metal centers as a monodentate ligand. This coordination environment is the only example in Hofmann-like 2D networks. While in compound **2**, the N ligation site and O ligation site at the pyridin-3-onato anion act as peripheral linkers in connecting Cd(1) and Cd(2) centers to yield extended coordination 2D networks. The exploitation of simple synthetic method for the preparation of such Cd^{II} coordination polymers could be important as crystalline model compounds for studying spin-crossover in analogous Fe^{II} compounds and for new functional luminescent materials in the solid state.[7]

Experimental

Structure Determination. Crystal structures of the two complexes were determined using a BRUKER APEX SMART CCD area detector diffractometer with monochromated Mo Kα radiation (λ = 0.71073 Å). The diffraction data were treated using SMART and SAINT, and absorption correction was performed using SADABS.[8a] The structures were solved by using direct methods with SHELXTL.[8b] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically except for –NH and –OH.

Pertinent crystallographic parameters are displayed in Table 1 and selected metric parameters for the complexes are presented in S2 and S3 (see Supporting Information). Crystallographic dates have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-683295 for compound No. **1** and CCDC-682122 for compound No. **2**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis. The complexes were prepared and crystallized by reaction of an aqueous mixture. One containing a mixture $CdCl_2 \cdot 2.5H_2O$ (0.4 mmol) and $K_2[Ni(CN)_4]$ (0.4 mmol), citric acid (0.2 mmol) were dissolved in 15 mL of water, after the pH was adjusted at ca. 11.0 with mea, the solution was filtered through a membrane (Millipore 4 μm), the other contained 3-hydroxypyridine or 4-hydroxypyridine (1.0 mmol) in 15 mL of water at room temperature. The two solutions were combined. A few days later, yellow crystals suitable for X-ray diffraction were obtained from the mixture by crystallization in a glass tube. Elemental analysis confirmed the organic content (**1**: Elemental Analysis: Found: C, 36.48; H, 2.17; N, 18.06%. Calculated for $C_{14}H_{10}Cd_1Ni_1N_6O_2$: C, 36.13; H, 2.17; N, 18.06%. IR (nujol method, cm^{-1}): 2152 (ν(C≡N)). **2**: Elemental Analysis: Found: C, 26.84; H, 2.39; N, 17.08%. Calculated for $C_{22}H_{22}Cd_3Ni_2N_{12}O_4$: C, 27.15; H, 2.28; N, 17.27%; IR (nujol method, cm^{-1}): 2151 (ν(C≡N)). The solid-state IR spectra of **1** and **2** had C≡N bands at 2152 cm^{-1} for **1** and 2151 cm^{-1} for **2**, which are both at higher wavenumbers than that of free $[Ni(CN)_4]^{2-}$ (2121 cm^{-1}), at room temperature. This suggests that both of the CN groups of $[Ni(CN)_4]^{2-}$ act as tetradentate bridging ligands.

Supporting Information

S1 is a figure of the Hofmann-like 2D sheet. S2 and S3 are tables of selected bond lengths and angles for **1** and **2**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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