Preparation and Structure of a Two-Dimensional Nickel-(Pyridine-2,5-dicarboxylate) Coordination Polymer and [Ni(Pyridine-4-carboxylic acid)$_2$(H$_2$O)$_4$]

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The current interest in the design of crystalline materials, the crystal engineering, of polymeric coordination networks stems from their potential applications as zeolite-like materials for molecular selection, ion exchange, and catalysis, as well as in the variety of architectures and topologies.[1-10] One of the basic strategies for crystal engineering employs the hydrothermal method, which is well known for its effectiveness in promoting crystal growth. When superheated, water behaves very differently from what is observed under ambient conditions. For example, the substantially lowered viscosity increases the solubility as well as the diffusion rate of solid reagents, therefore promoting the crystal growth. In preparing coordination polymers, benzene carboxylates and pyridine carboxylates have been frequently employed, including benzene-1,3,5-tricarboxylic acid, benzene-1,4-dicarboxylic acid, 4-cyanopyridine, pyridine-2,6-dicarboxylic acid (2,6-PDCH$_2$), pyridine-2,5-dicarboxylic acid (2,5-PDCH$_2$), and pyridine-3,5-dicarboxylic acid (3,5-PDCH$_2$).[11-22]

We recently prepared a three-dimensional Zn(II) coordination polymer from Zn(NO$_3$)$_2$·6H$_2$O and naphthalene-2,6-dicarboxylic acid[23] and also reported a three-dimensional Co(II)(2,5-PDC) coordination polymer,[24] by employing hydrothermal reactions. In an attempt to expand the scope of this methodology, we set out to prepare nickel coordination polymers with 2,5-PDCH$_2$ and isonicotinic acid (INTH or pyridine-4-carboxylic acid). Recently, Plater and co-workers reported [M(2,5-PDC)(H$_2$O)$_2$] · (H$_2$O) (M = Co or Ni), which have been prepared from M(OAc)$_2$ · 4H$_2$O and 2,5-PDCH$_2$ in water, together only with the structure of the cobalt compound.[18] We report herein the hydrothermal preparation and crystal structures of two compounds, [Ni(2,5-PDC)(H$_2$O)$_2$] · (H$_2$O) and Ni(INT)$_2$(H$_2$O)$_4$.

Experimental Section

Glassware was soaked in KOH-saturated 2-propanol for about 24 h and washed with distilled water and acetone before use. Glassware was either flame- or oven-dried. Ni(NO$_3$)$_2$ · 6H$_2$O (**1**), pyridine-2,5-dicarboxylic acid, and isonicotinic acid were purchased from Aldrich company.

IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Elemental analyses were performed with EA1110 (CE instrument, Italy) by the Korea Basic Science Center. TGA analysis was conducted on a TA4000/SDT 2960 instrument.

Preparation of [Ni(2,5-PDC)(H$_2$O)$_2$](H$_2$O) (2 · H$_2$O). A mixture of **1** (0.150 g, 0.898 mmol), 2,5-PDCH$_2$ (0.100 g, 0.599 mmol), NaOAc · 3H$_2$O (0.163 g, 1.198 mmol), and H$_2$O (3.0 mL, 0.167 mol) in the mole ratio of 1 : 0.667 : 1.33 : 185 was heated in a 23-mL capacity Teflon-lined reaction vessel at 180 °C for 1 day and then cooled to room temperature by air-cooling. The blue product was collected by filtration, washed with H$_2$O (2 × 5 mL), and air-dried to give compound **2** · H$_2$O (0.131 g, 0.473 mmol, 79% yield).

Anal. Calcd for C$_7$H$_9$O$_7$NNi (M_r = 277.86): C, 30.27; H, 3.27; N, 5.04. Found: C, 30.20; H, 3.31; N, 4.95. IR (KBr): 3262, 1662 (C=O), 1603 (C=O), 1581 (C=O), 1548 (C=O), 1479 (C=O), 1418, 1394, 1361, 771, 694 cm^{-1}.

Preparation of of Ni(isonicotinate)$_2$(H$_2$O)$_4$ (3). A mixture of **1** (0.236 g, 0.813 mmol), isonicotinic acid (0.100 g, 0.813 mmol), NaOAc · 3H$_2$O (0.221 g, 1.63 mmol), and H$_2$O (5.0 mL, 0.278 mol) in the mole ratio of 1.00 : 1.00 : 2.00 : 316 was heated in the Teflon-lined reaction vessel at 180 °C for 1 day and then cooled to room temperature by air-cooling. The blue product was collected by filtration, washed with H$_2$O (2 × 5 mL), and air-dried to give compound **3** (0.134 g, 0.357 mmol, 88% yield).

Anal. Calcd for C$_{12}$H$_{18}$O$_8$N$_2$Ni (M_r = 376.98): C, 38.23; H, 4.81; N, 7.43. Found: C, 38.73; H, 4.72; N, 7.56. IR (KBr): 3384, 3289, 1595 (C=O), 1550 (C=O), 1421 (C=O), 1384 (C=O), 777, 708, 691 cm^{-1}.

X-ray Structure Determination. All X-ray data were collected with use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite-crystal monochromator. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 28 (for **2** · H$_2$O) or 24 (for **3**) reflections in the range 10.0° < 2θ < 25.0°. Three check-reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorenz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected for absorption with ψ-scan data. All calculations were carried out with use of the SHELX-97 programs.[25]

A green crystal of **2** · H$_2$O, shaped as a block of approximate dimensions 0.28 × 0.26 × 0.24 mm^3, was used for crystal and intensity-data collection. The unit-cell parameters and

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systematic absences, $h00$ ($h = 2n + 1$) and $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$), unambiguously indicated $P2_12_12_1$ as a space group. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. Water hydrogen atoms were located in the difference Fourier maps. The phenyl ring hydrogen atoms were generated and refined in a riding model.

A blue crystal of **3**, shaped as a plate of approximate dimensions 0.56 × 0.40 × 0.16 mm^3, was used. The unit-cell parameters indicated two possible space groups: $P1$ (noncentrosymmetric) and $P\overline{1}$ (centrosymmetric). A statistical analysis of intensities suggested a noncentrosymmetric space group, and the structure analysis converged only in $P1$. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The water hydrogen atoms were located and refined isotropically. The phenyl hydrogen atoms were generated in ideal positions and refined in a riding mode.

Details on crystal data and intensity data are given in Table 1. The selected bond distances and bond angles are shown in Tables 2 and 3.

Table 1. X-ray data collection and structure refinement

	2 · H_2O	**3**
formula	$C_7H_9NO_7Ni$	$C_{12}H_{16}N_2O_8Ni$
fw	277.86	374.98
temperature, K	296(2)	296(2)
crystal system	orthorhombic	triclinic
space group	$P2_12_12_1$	$P1$
a, A	7.2944(7)	6.2988(10)
b, A	9.3054(5)	6.9126(7)
c, A	14.0767(8)	9.2561(9)
α, deg		96.447(7)
β, deg		105.140(9)
γ, deg		113.381(8)
V, A^3	955.5(1)	346.32(7)
Z	4	1
d_{cal}, g cm^{-3}	1.932	1.798
μ, mm^{-1}	2.053	1.449
T_{min}	0.2262	0.6447
T_{max}	0.2494	0.8961
$F(000)$	568	194
2θ range (°)	3.5-50	3.5-50
scan type	ω	ω
scan speed	variable	variable
No. of reflns measured	992	1323
No. of reflns unique	992	1323
No. of reflns with $I > 2\sigma(I)$	979	1321
No. of params refined	164	227
Max.. in Δρ (e A^{-3})	0.224	0.239
Min.. in Δρ (e A^{-3})	−0.229	−0.186
GOF on F^2	1.066	1.047
R	0.0203	0.0185
wR_2^{a}	0.0526	0.0488

$^a wR_2$ $\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

Table 2. Selected bond distances (Å) and bond angles (°) in **2** · H_2O

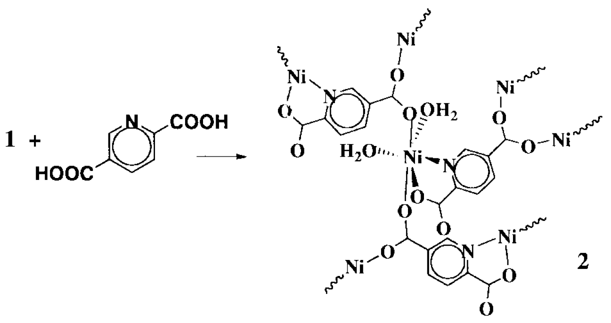
Ni1-O1	2.033(3)	Ni1-O2	2.034(2)	Ni1-O5	2.036(2)
Ni1-N1	2.081(3)	Ni1-O3	2.108(2)	Ni1-O4	2.114(2)
O1-Ni1-O2	97.3(1)	O1-Ni1-O5	88.2(1)	O2-Ni1-O5	173.2(1)
O1-Ni1-N1	166.8(1)	O2-Ni1-N1	94.8(1)	O5-Ni1-N1	79.4(1)
O1-Ni1-O3	89.4(1)	O2-Ni1-O3	86.8(1)	O5-Ni1-O3	89.2(1)
N1-Ni1-O3	85.9(1)	O1-Ni1-O4	92.4(1)	O2-Ni1-O4	86.7(1)
O5-Ni1-O4	97.2(1)	N1-Ni1-O4	93.7(1)	O3-Ni1-O4	173.4(1)

Table 3. Selected bond distances (Å) and bond angles (°) in **3**

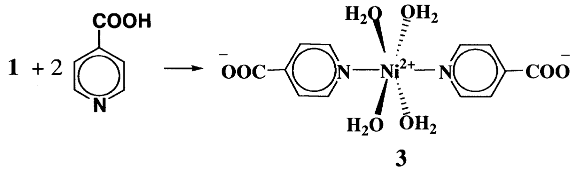
Ni1-O6	2.035(5)	Ni1-N1	2.057(7)	Ni1-O5	2.098(5)
Ni1-O7	2.096(5)	Ni1-O8	2.106(5)	Ni1-N2	2.120(5)
O1-C6	1.28(1)	O2-C6	1.24(1)	O3-C12	1.23(1)
O4-C12	1.26(1)				
O6-Ni1-N1	88.4(2)	O6-Ni1-O5	179.2(3)	N1-Ni1-O5	92.2(2)
O6-Ni1-O8	87.4(2)	N1-Ni1-O8	90.4(2)	O5-Ni1-O8	93.2(2)
O7-Ni1-O8	178.3(3)	O6-Ni1-N2	91.8(2)	N1-Ni1-N2	179.3(3)
O2-C6-O1	124.5(8)	O2-C6-C3	121.4(8)	O1-C6-C3	114.1(8)
O3-C12-O4	127.4(8)	O3-C12-C9	117.8(8)	O4-C12-C9	114.8(7)

Results and Discussion

Preparation. Compounds have been prepared by hydrothermal reactions. Nickel(II) nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) reacts with 2,5-$PDCH_2$ at 180 °C in the presence of $NaOAc \cdot 3H_2O$ (pH ≈ 5) to give bisaqua(2,5-pyridinedicarboxylato)nickel (II) (**2**), a two-dimensional polymer (eq 1). We added the base ($NaOAc \cdot 3H_2O$) to accelerate the reaction by the deprotonation of 2,5-$PDCH_2$. Nickel(II) nitrate also reacts with isonicotinic acid in the presence of $NaOAc \cdot 3H_2O$ (pH ≈ 5) to give tetraaquabis(isonicotinato)nickel(II) (**3**), a mononuclear octahedral Ni(II) compound (eq 2). The crystalline products have been characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis, and X-ray diffraction.



(1)



3

(2)

Compounds **2** · H_2O and **3** have been obtained as crystals in relatively high isolation yields (79% for **2** · H_2O and 88% for **3**). The IR spectrum of **2** · H_2O exhibits peaks at 1662, 1603, 1581, 1548, and 1479 cm^{-1} that can be assign to the asymmetric and symmetric C=O stretches.[26,27] The IR spectrum of **3** also shows strong peaks characteristic of carboxylate groups at 1595, 1550, 1421, and 1384 cm^{-1}.

Thermal analysis (TGA) was performed between room temperature and 1000 °C under nitrogen. The TGA analysis shows that compound **2** · H_2O loses 20.2% of its mass between 186 and 251 °C, corresponding to the loss of two aqua ligands and one uncoordinated water molecule (calculated 19.4%). Above 355 °C, the second process occurs with the loss of the pyridine-2,5-dicarboxylate ligand. On the other hand, compound **3** starts to release the aqua ligands at 119 °C, and the process is completed by 166 °C with the residual weight of 8.94%.

Structure. The monomeric unit of **2** · H_2O with the atom-numbering scheme is shown in Figure 1. This unit consists of one Ni metal, one 2,5-pyridinedicarboxylato ligand, and two aqua ligands, together with one free water molecule. The coordination sphere of Ni can be described as a distorted octahedron. The formal oxidation state of the nickel metal is +2. The equatorial plane, defined by O1, O2, O5, and N1 atoms, is roughly planar with an average atomic displacement of 0.0115 Å. The nickel atom lies above the equatorial plane by 0.079(1) Å.

Compound **2** · H_2O forms a two-dimensional polymer in the *ab*-direction through the carboxylate group in the 5-position of the PDC^{2-} ligand. All Ni–O and Ni–N bond distances are normal Ni–O and Ni–N single bonds. The nitrogen atom of the PDC^{2-} ligand is bonded to the nickel, and the two carboxylate groups act in different manners. One carboxylate group (in the 2-position) acts simply as a monodentate ligand, and the other carboxylate group (in the 5-position) acts as a bidentate ligand, linking two neighboring nickel centers through the Ni–O–C–O–Ni bridge. All six hydrogen atoms (HO1A, HO1B, HO2A, HO2B, HO7A, and HO7B) in the aqua ligands and the free water molecule are involved in hydrogen bonding of the type O–H···O. The six hydrogen bonds consist of one intramolecular hydrogen bond (O1–H···O7) and five intermolecular ones.

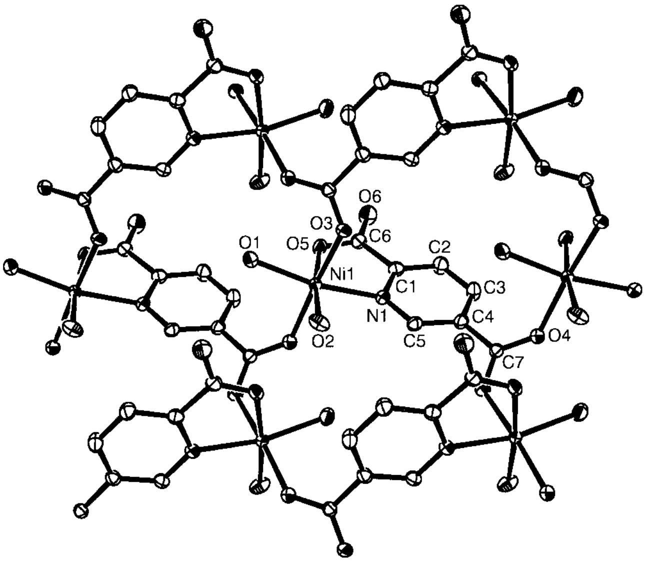


Figure 1. ORTEP drawing of compound **2**, showing 50% probability thermal ellipsoids.

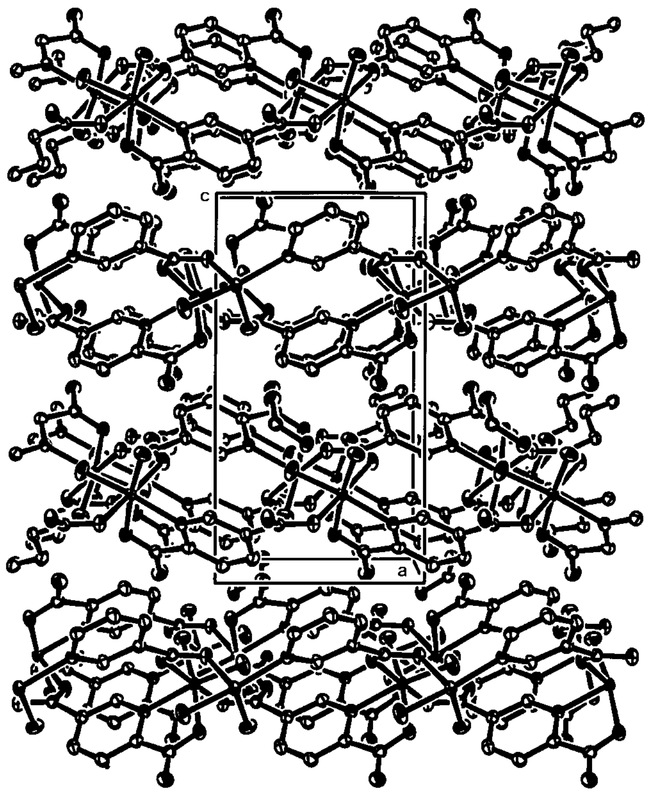


Figure 2. A perspective view of compound **2** along the *b*-axis.

Figure 2 shows a two-dimensional polymeric structure of **2** · H_2O. Each 2,5-PDC^{2-} ligand links three Ni(II) centers by the coordination of four out of five potential donor atoms (one nitrogen and four oxygen atoms). Each Ni metal is coordinated by two aqua ligands as well as three PDC^{2-} ligands. The adjacent infinite 2-D polymeric chains are separated from each other by about a half of the *c*-axis length (7.03 Å). As stated above, one carboxylate oxygen atom does not coordinate to the metal but participates in the intermolecular hydrogen bonding.

Plater and his co-workers recently reported compound **2** · H_2O and its cobalt analogue $[Co(PDC)(H_2O)_2](H_2O)$ (**4**), which have been prepared from $M(OAc)_2 \cdot 4H_2O$ (M = Co or Ni) and 2,5-$PDCH_2$ in water, together only with the structure of compound **4**.[18] The structures of compounds **2** · H_2O and **4** are isostructural. For example, the bite angles of O5-Ni1-N1 are 79.44(9)° for **2**·H_2O and 77.4(1)° for **4**. However, there is a significant difference in the orientation of the carboxylate group with respect the pyridine ring. Whereas the dihedral angle of the plane of C4, C7, O3, and O4 with respect to the pyridine ring is 75.5(7)° in compound **2** · H_2O, the corresponding dihedral angle in compound **4** is 32.5°. Recently, we reported a one-dimensional coordination

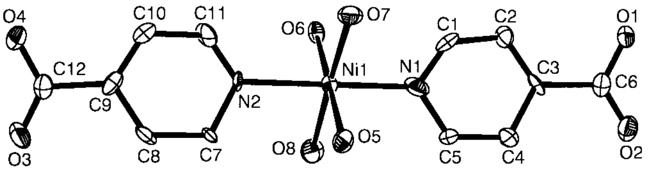


Figure 3. ORTEP drawing of compound **3**.

polymer with the empirical formula of Cu(2.5-PDC)(H_2O) from the reaction $Cu(NO_3)_2 \cdot 2.5H_2O$ with pyridine-2,5-dicarboxylic acid (2,5-$PDCH_2$). The resulting polymer exhibits strong antiferromagnetic coupling between the paramagnetic Cu(II) metals in the adjacent layers even in the absence of intervening groups.[28]

The molecular structure of **3** with the atom-numbering scheme is shown in Figure 3. Compound **3** has four aqua ligands and two isonicotato ligands. The coordination sphere of Ni can be described as an octahedron in which the isonicotato ligands are mutually *trans*. The equatorial plane, defined by Ni1, O5, O6, O7, and O8 atoms, is nearly planar with the average atomic displacement of 0.0176 Å. The two aryl planes in the isonicotato ligands are nearly perpendicular to the equatorial plane, with dihedral angles of 83.5(2)° and 84.7(2)°. These two aryl rings are almost parallel to each other, with a dihedral angle of 1.3(2)°.

The isonicotinato ligands are bonded to the metal through their nitrogen atoms. All bonds distances and bond angles are normal. All hydrogen atoms in aqua ligands are involved in hydrogen bonds of the type O–H···O (intermolecular) or O–H···N (intramolecular).

In summary, the hydrothermal reactions of $Ni(NO_3)_2 \cdot 6H_2O$ with 2,5-$PDCH_2$ and isonicotinic acid, in the presence of sodium acetate, gave a 2-D coordination polymer with the empirical formula of $[Ni(2,5\text{-}PDC)(H_2O)_2] \cdot H_2O$ and a monomeric Ni(II) compound $Ni(INT)_2(H_2O)_4$, respectively. In both compounds, the coordination sphere of Ni is octahedral.

Supplementary material. Tables of full bond distances and bond angles, anisotropic thermal parameters, and atomic coordinates of hydrogen atoms are available from the author Soon W. Lee.

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