

A Two-Dimensional Zinc Coordination Polymer Based on a Pyridyl–Carboxylate Linking Ligand Containing an Intervening Amide Group: $[\text{ZnCl}(\text{L})]_{\infty}$ (HL = 6-(nicotinamido)-2-naphthoic acid)

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Coordination polymers (CPs) and metal–organic frameworks (MOFs) continually gain much attention due to their interesting structures and remarkable applications to a wide range of fields.^{1–9} According to the very recent IUPAC recommendations for the terminology, CPs are coordination compounds with repeating coordination entities extending in 1, 2, or 3 dimensions, and MOFs are coordination networks with organic ligands containing potential voids.¹⁰ IUPAC also recommended the use of the term “coordination networks” to indicate (i) coordination compounds extending, through repeating coordination entities, in 1 dimension, but with cross-links between two or more individual chains, loops, or spiro-links, or (ii) coordination compounds extending through repeating coordination entities in 2 or 3 dimensions. For the successful preparation of such polymeric species, the choice or design of proper linking ligands is essential, and those possessing either pyridyl or carboxylate terminals are typically employed.^{1,2,11–13}

Several *d–f* coordination polymers, which contain both *d*- and *f*-block metals as nodes in their frameworks, were recently constructed from asymmetric linking ligands possessing pyridyl–carboxylate or pyridyl–imidazole terminals.^{14–22} We recently launched a research program that involves the synthesis of novel pyridyl–carboxylate-type linking ligands and their CPs possessing *d*, *f*, or *d–f* metals, and a few linking ligands and their CPs have been prepared.^{23–34}

In particular, we became interested in the pyridyl–carboxylate-type ligands containing an amide (–C(O)–NH–) fragment, which might be utilized further for the so-called post-synthetic modification of CPs and MOFs.^{35–37} In this context, our group recently prepared two ligands of this type (HL and HL' in Chart 1), both of which contain a 3-pyridyl and a carboxylate terminals. The ligand HL³¹ was employed to prepare a 2D copper coordination polymer with a layer framework, $\{[\text{CuL}_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_{\infty}$.²⁸ In addition, the ligand HL' was utilized to construct cadmium and nickel coordination polymers: $\{[\text{Cd}(\text{L}')_2](\text{H}_2\text{O})\}_{\infty}$ (a 2D layer) and $\{[\text{Ni}(\text{L}')_2(\text{H}_2\text{O})_2](\text{H}_2\text{O})\}_{\infty}$ (a 1D double-chain).²⁴ In order to further examine the linking capability of the ligand HL, we attempted to construct new coordination polymers with it. We herein report the preparation, structure, and thermal behavior of a 2D zinc coordination polymer, $[\text{ZnCl}(\text{L})]_{\infty}$.

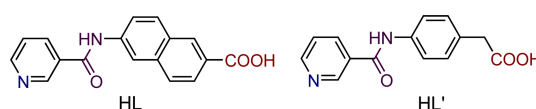


Chart 1. Pyridyl–carboxylate-type linking ligands containing an amide group.

Experimental

All solid chemicals were purified by recrystallization, and all solvents were distilled. Infrared (IR) samples were prepared as KBr pellets, and their spectra were obtained in the range 400–4000 cm^{-1} on a Vertex 70 FTIR spectrophotometer. Elemental analyses were carried out with an Elementar Vario EL cube at the Cooperative Center for Research Facilities (CCRF) in Sungkyunkwan University. Thermogravimetric analysis (TGA) was performed on a TA4000/SDT 2960 instrument (CCRF). The ligand (HL = 6-(nicotinamido)-2-naphthoic acid) was prepared by the literature methods.³¹

Synthesis of $[\text{ZnCl}(\text{L})]_{\infty}$ (1). An aqueous solution containing of anhydrous ZnCl_2 (14 mg, 0.1 mmol), HL (58 mg, 0.1 mmol), H_2O (15 mL), and 1 N NaOH (0.2 mL, 0.1 mmol) was heated in a 23-mL Teflon-lined reaction vessel at 150 °C for 3 days, and then air-cooled slowly to room temperature. The resulting pink crystals were filtered, washed with dimethyl sulfoxide (DMSO, 5 mL \times 5), H_2O (5 mL \times 3), and ethanol (5 mL \times 3), and then vacuum-dried to give the product (12 mg, 0.031 mmol, 31% yield). mp 435–437 °C. IR (KBr, cm^{-1}): 3729 (w), 3335 (w), 2981 (w), 2897 (w), 1690 (s), 1613 (m), 1549 (m), 1475 (m), 1422 (m), 1302 (m), 1262 (m), 1216 (m), 1118 (m), 1058 (w), 910 (w), 835 (w), 755 (w), 628 (w), 462 (w). Anal. Calc. for $\text{C}_{17}\text{H}_{11}\text{ClN}_2\text{O}_3\text{Zn}$: C 52.07; H 2.83; N 7.14; O 12.24. Found: C 53.12; H 2.14; N 7.01; O 12.84.

X-ray Structure Determination. All X-ray data were collected with a Bruker Smart APEX2 diffractometer equipped with a Mo X-ray tube (CCRF). Collected data were corrected for absorption with SADABS based upon the Laue symmetry by using equivalent reflections.³⁸ All calculations were carried out with SHELXTL programs.³⁹

A pink crystal of polymer 1, shaped as a block of approximate dimensions 0.40 \times 0.36 \times 0.12 mm, was used for crystal-

Table 1. X-ray data collection and structure refinement for polymer **1**

Empirical formula	C ₁₇ H ₁₁ ClN ₂ O ₃ Zn
Formula weight	392.10
Temperature, K	296(2)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	10.9510(2)
<i>b</i> , Å	15.3715(2)
<i>c</i> , Å	9.4637(2)
α , (°)	90
β , (°)	107.718(1)
γ , (°)	90
<i>V</i> , Å ³	1517.49(5)
<i>Z</i>	4
<i>d</i> _{calc} , g cm ⁻³	1.716
μ , mm ⁻¹	1.813
<i>F</i> (000)	792
<i>T</i> _{max}	0.8118
<i>T</i> _{min}	0.5309
θ range (°)	2.36–28.35
No. of reflns collected	24057
No. of reflns independent	3742
No. of reflns with <i>I</i> > 2 σ (<i>I</i>)	3049
No. of parameters	217
Max., in $\Delta\rho$ (e Å ⁻³)	0.408
Min., in $\Delta\rho$ (e Å ⁻³)	-0.316
<i>GOF</i> on <i>F</i> ²	1.025
<i>R</i> ^a	0.0292
<i>wR</i> 2 ^b	0.0769

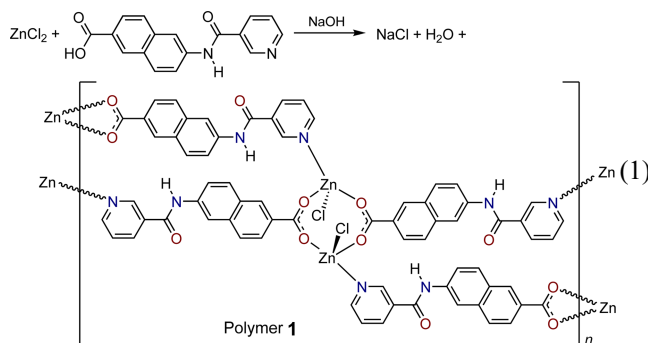
$$^a R = \sum[|F_o| - |F_c|] / \sum|F_o|, \quad ^b wR2 = \sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]^{1/2}$$

and intensity-data collection. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in idealized positions and refined in a riding mode. Details on crystal data, intensity collection, and refinement details are given in Table 1. Selected bond lengths and bond angles are presented in Table 2.

Results and Discussion

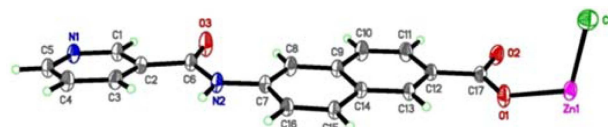
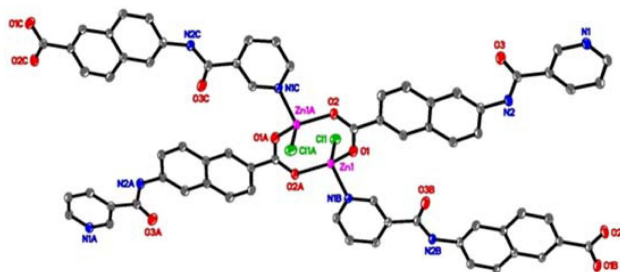
Preparation. Polymer **1** was prepared from anhydrous ZnCl₂, HL, and NaOH in the mole ratio of 1:1:1, under hydrothermal conditions (eq. 1). The base was added to deprotonate the free ligand (HL) to its deprotonated form (L⁻), and the unreacted ligand could be removed with DMSO during the work-up process. The product was characterized by elemental analysis, IR spectroscopy, TGA, and single-

crystal X-ray crystallography.



The IR spectrum of the free ligand displays a characteristic N–H stretching band at 3328 cm⁻¹ and C=O stretching band at 1621 cm⁻¹.³¹ On the other hand, the IR spectrum of the polymer **1** shows the corresponding N–H and C=O stretching bands at 3335 and 1613 cm⁻¹, respectively

Crystal Structure. Figure 1 shows an asymmetric unit that consists of a Zn²⁺ ion, an L⁻ ligand, and a Cl⁻ ligand. All non-hydrogen atoms occupy general positions. The local coordination environment of the Zn²⁺ ion in polymer **1** is given in Figure 2, in which two Zn²⁺ ions are joined by two bridging carboxylate groups. The Zn²⁺ ion is coordinated to one nitrogen and two oxygen atoms from three ligands, in addition to the chloro ligand. The amide group does not coordinate to the metal. The amide N–H bond forms a weak intermolecular hydrogen bond with the Cl⁻ ligand [N2–HN2 = 0.86 Å, N2⋯Cl1 (*x* + 1, *y*, *z* + 1) = 3.555(2) Å, Cl1⋯HN2

**Figure 1.** The asymmetric unit of polymer **1**. Displacement ellipsoids for non-hydrogen atoms exhibit 40% probability level.**Figure 2.** Local coordination environment around the Zn²⁺ ion.**Table 2.** Selected bond lengths (Å) and bond angles (°) in polymer **1**

Zn1–O2#1	1.938(1)	Zn1–O1	1.950(1)	Zn1–N1#2	2.019(1)
Zn1–Cl1	2.2204(7)	O3–C6	1.216(2)	N1–C1	1.340(2)
O1–Zn1–N1#2	97.62(6)	O2#1–Zn1–Cl1	111.23(5)	O1–Zn1–Cl1	112.32(5)
N1#2–Zn1–Cl1	110.16(5)				

Symmetry transformations used to generate equivalent atoms: #1 = -*x* + 1, -*y*, -*z*; #2 = -*x* + 2, *y* + 1/2, -*z* + 3/2; #3 = -*x* + 2, *y* - 1/2, -*z* + 3/2.

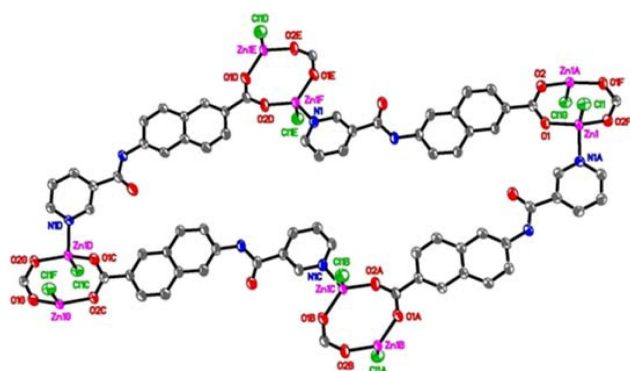


Figure 3. Repeat unit consisting of two subunits.

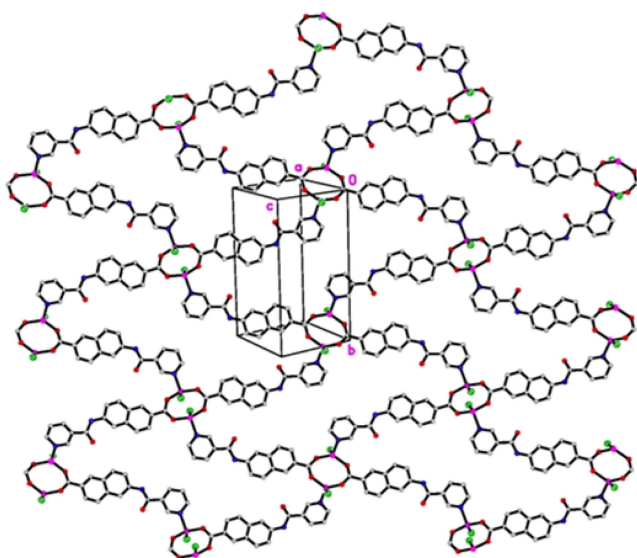


Figure 4. Packing diagram showing a part of a two-dimensional layer.

$= 2.71 \text{ \AA}$, $\text{N2-HN2}\cdots\text{Cl1} = 168^\circ$). As mentioned in Introduction, the ligand HL was previously employed to produce a two-dimensional copper polymer, $[\text{CuL}_2(\text{H}_2\text{O})]\cdot(\text{H}_2\text{O})_2]_\infty$, in which the Cu^{2+} ion has a distorted square-pyramidal coordination sphere.²⁸ On the other hand, the Zn^{2+} ion in polymer **1** has a distorted tetrahedral coordination sphere.

Figure 3 shows a repeat unit in polymer **1**, which consists of two subunits: (1) two Zn^{2+} ions and two carboxylate groups (subunit 1, an 8-membered ring) and (2) four Zn^{2+} ions and four ligands (subunit 2, a 60-membered ring). The $\text{Zn}\cdots\text{Zn}$ separations in subunits 1 and 2 are 3.5735(4) and 16.2769(4) \AA , respectively. These two subunits are linked to form a two-dimensional layer structure in the $[10\bar{1}]$ direction (Figure 4), in which the Cl^- ligands lie nearly perpendicular to this layer.

To the best of our knowledge, only the two ligands in Scheme 1 and 5-(nicotinamido)isophthalic acid (H_2NAIP),^{24,28,40} all of which are basically pyridine-carboxylate ligands and possess an intervening amide group in common, have been employed so far to prepare CPs. For instance, the hydrothermal reactions involving the H_2NAIP ligand, a pyridyl-dicarboxylate ligand, produced 1-D and 3-D polymers:

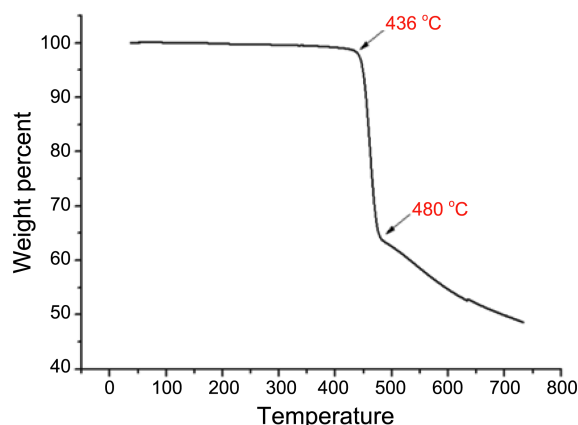
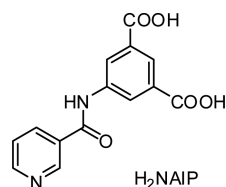


Figure 5. TGA curve for polymer **1**.

$\{[\text{M}(\text{NAIP})(\text{H}_2\text{O})_4]\cdot 2(\text{H}_2\text{O})\}_\infty$ ($\text{M} = \text{Co}, \text{Mn}$), $\{[\text{Zn}(\text{NAIP})]\cdot 0.5(\text{H}_2\text{O})\}_\infty$, and $\{\text{Cd}(\text{NAIP})(\text{H}_2\text{O})_2\}\cdot 1.5(\text{H}_2\text{O})\}_\infty$. Hence, polymer **1** is another example of a coordination polymer constructed from the pyridine-carboxylate-type linking ligand with an intervening amide group.



In order to examine the thermal behavior of polymer **1**, the thermogravimetric analysis was performed. The TGA curve displays a single well-defined weight loss. This polymer is stable up to 436 $^\circ\text{C}$, which clearly demonstrates its high thermal stability (Figure 5). The abrupt weight loss occurs from 436 to 480 $^\circ\text{C}$, above which the gradual decomposition ensues.

In summary, a two-dimensional zinc coordination polymer, $[\text{ZnCl}(\text{L})]_\infty$ (**1**), was prepared from ZnCl_2 , 6-(nicotinamido)-2-naphthoic acid (HL), and NaOH, under hydrothermal conditions. Polymer **1** contains a pyridyl-carboxylate-type linking ligand with an intervening amide group. This polymer is constructed on the basis of a repeat unit consisting of two subunits: an 8-membered ring and a 60-membered ring, and its framework appears to have a very high thermal stability that is retained up to 436 $^\circ\text{C}$.

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Supporting Information. CCDC 985715 contains the supplementary crystallographic data for polymer **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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