

A Zinc(II)-Carboxylate Coordination Polymer Constructed from Zinc Nitrate and 2,6-Naphthalenedicarboxylate

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Crystal engineering and the design of solid-state architectures have recently become areas of increasing interest due to various applications, such as molecular magnets, non-linear optical devices, catalysts, molecular sieves, and sensors.^{1,2} In the past decades, considerable progresses have been achieved in controlling the assembly and orientations of individual molecules in structures with specific network topologies and potentially interesting properties. For example, Yaghi and co-workers have recently reported a series of open frameworks with various cavities or channels in which the rigid spacers such as 1,3,5-benzenetricarboxylic acid and 1,4-benzenedicarboxylic acid were employed as building blocks.^{3,4}

In this work, we chose 2,6-naphthalenedicarboxylic acid (NDCH₂) as a building block because it has two equally spaced carboxylate groups linked to an aromatic ring to make it in a rigid conformation. Because carboxylate groups are expected to bond to the zinc metal as either bidentate or monodentate ligands, the reaction of NDCH₂ with Zn(NO₃)₂ should give a metal-carboxylate coordination polymer. Herein we wish to report the synthesis and characterization of a five-coordinate zinc(II) coordination-polymer prepared through self-assembly processes directed by metal-ligand ligation.

Experimental Section

Glassware was soaked in KOH-saturated 2-propanol for ca. 24 h and washed with distilled water and acetone before use. Glassware was either flame-dried or oven-dried. Zn(NO₃)₂ · 6H₂O and 2,6-naphthalenedicarboxylic acid (NDCH₂) were purchased from Aldrich company.

IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. TGA analyses were conducted on a TA4000/SDT 2960 instrument. Elemental analyses were performed by the Korea Basic Science Center.

Preparation of Zn(NDC) · H₂O (1). A mixture of Zn(NO₃)₂ · 6H₂O (0.137 g, 0.460 mmol), 2,6-naphthalenedicarboxylic acid (NDCH₂) (0.100 g, 0.460 mmol), and H₂O (2 mL) in the mole ratio of 1 : 1 : 240 was heated in a 23-mL capacity Teflon-lined-reaction vessel at 180 °C for three

days and then cooled to room temperature by air-cooling. The yellow product was collected by filtration, washed with H₂O (2 × 5 mL), and air-dried to give Zn(NDC) · H₂O (0.111 g, 0.373 mmol, 81% yield).

Anal. Calcd for C₁₂H₈O₅Zn (*M_r* = 295.55): C, 48.43; H, 2.71. Found: C, 48.72; H, 2.98. IR (KBr, cm⁻¹): 3154 (br), 1686 (s, C=O), 1603 (s, C=O), 1576 (s, C=O), 1548 (s, C=O), 1492 (s), 1401 (s), 1356 (s), 1296 (s), 1192 (s), 929 (s), 786 (s).

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 23 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 Lorentz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with ψ -scan data. All calculations were carried out with use of the SHELX-97 programs.⁵

A yellow crystal of **1**, shaped as a block of approximate dimensions 0.20 × 0.14 × 0.12 mm³, was used for crystal and intensity data collection. The unit-cell parameters and systematic absences, *hkl* (*h* + *k* = 2*n* + 1) and *h0l* (*l* = 2*n* + 1), indicated two possible space groups: *Cc* (non-centrosymmetric) and *C2/c* (centrosymmetric). A statistical analysis of reflection intensities suggested a centrosymmetric space group, and the structure analysis converged only in *C2/c*. The structure was solved by the direct method. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the difference Fourier maps.

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

Results and Discussion

Preparation of Zn(NDC) · H₂O (1). A 3-dimensional Zn(II) coordination polymer with a nonporous and infinite network was prepared from a mixture of Zn(NO₃)₂ · 6H₂O, 2,6-naphthalenedicarboxylic acid (NDCH₂), and H₂O in the

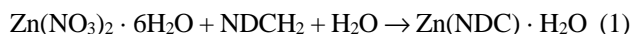
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Table 1. X-ray data collection and structure refinement for **1**

formula	C ₁₂ H ₈ O ₅ Zn
fw	297.55
temperature, K	296(2)
crystal system	monoclinic
space group	C2/c
a, Å	22.6936(17)
b, Å	6.3333(5)
c, Å	7.3027(7)
β, deg	91.748(6)
V, Å ³	1049.1(2)
Z	4
d _{calc} , g cm ⁻³	1.884
μ, mm ⁻¹	2.351
T _{min}	0.3365
T _{max}	0.4250
F(000)	600
2θ range (°)	3.5-50
scan type	ω
scan speed	variable
No. of reflns measured	945
No. of reflns unique	921
No. of reflns with I > 2σ(I)	870
No. of params refined	100
Max., in Δρ (e Å ⁻³)	0.233
Min., in Δρ (e Å ⁻³)	-0.413
GOF on F ²	1.058
R	0.0214
wR ₂ ^a	0.0570

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

mole ratio of 1:1:240 by heating it at 180 °C for three days (eq 1).



The compound **1** is air-stable and is not soluble in common organic solvents. Its FT-IR spectrum shows the expected absorptions corresponding to the asymmetric and symmetric carboxylate stretches for NDC²⁻ (1686, 1603, 1576, and 1548 cm⁻¹) and coordinated water (3154 cm⁻¹).^{6,7} The absence of the carbonyl peak (1694 and 1602 cm⁻¹) corresponding to the free ligand indicates that 2,6-naphthalenedicarboxylic acid (NDCH₂) has been completely coordinated to zinc metals under the reaction conditions, with the concurrent deprotonation of NDCH₂ to NDC²⁻. The formulation

Table 2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å³ × 10³)

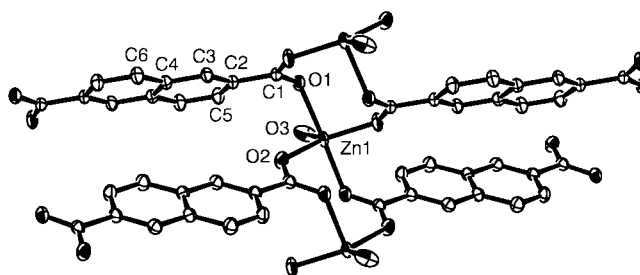
	x	y	z	U (eq) ^a
Zn(1)	5000	1816(1)	7500	20(1)
O(1)	4644(1)	2011(2)	10247(2)	24(1)
O(2)	4238(1)	732(3)	6620(2)	31(1)
O(3)	5000	4934(4)	7500	42(1)
C(1)	4200(1)	981(3)	10753(3)	21(1)
C(2)	3596(1)	1841(3)	10353(3)	22(1)
C(3)	3106(1)	690(3)	10783(3)	22(1)
C(4)	2532(1)	1483(3)	10405(3)	21(1)
C(6)	2017(1)	320(4)	10825(3)	26(1)

^aEquivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

of **1** has been further confirmed by X-ray diffraction and elemental analysis.

Thermogravimetric analysis performed under nitrogen shows that the compound loses 5.33% of its mass between 155.16 and 200.41 °C, corresponding to the loss of one coordinated water molecule (calculated 6.05%). Above 250 °C, the second process occurs with the loss of the NDC²⁻ ligand, ultimately giving a ZnO solid (observed 27.30%, calculated 27.35%).

Structure of 1. Figure 1 shows the local coordination of the zinc center, and Figure 2 shows the packing diagram projected on the ac plane. A single crystal X-ray diffraction study of **1** clearly reveals a 3-D coordination network. Compound **1** crystallizes in the monoclinic space group C2/c, and the Zn1 and O3 atoms lie on the crystallographic C₂ axis. The coordination sphere of zinc can be described as a distorted trigonal bipyramid, with the four oxygen atoms from the four 2,6-naphthalenedicarboxylate ligands [Zn-O =

**Figure 1.** ORTEP drawing of the local coordination of Zn in complex **1**.**Table 3.** Selected bond distances (Å) and bond angles (°) in **1**

Zn1-O2	1.951(1)	Zn1-O3	1.974(2)	Zn1-O1	2.189(1)
O1-C1	1.266(3)	C1-O2 ^c	1.258(3)		
O2-Zn1-O2 ^a	138.77(10)	O2-Zn1-O3	110.62(5)	O2 ^a -Zn1-O3	110.62(5)
O2-Zn1-O1	88.50(6)	O2 ^a -Zn1-O1	93.78(6)	O3-Zn1-O1	86.76(4)
O2-Zn1-O1 ^a	93.78(6)	O2 ^a -Zn1-O1 ^a	88.50(6)	O3-Zn1-O1 ^a	86.76(4)
O1-Zn1-O1 ^a	173.52(7)				

Symmetry transformations used to generate equivalent atoms: a = -x + 1, y, -z + 3/2; b = x, -y, z - 1/2; c = x, -y, z + 1/2; d = -x + 1/2, -y + 1/2, -z + 2

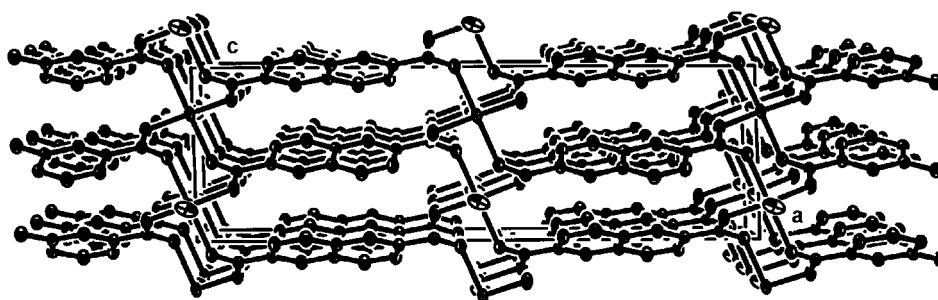


Figure 2. A perspective drawing of the building block unit along the *b* axis.

1.951(1), 2.189(1) Å] and one water oxygen atom [Zn-O = 1.974(2) Å]. These are comparable with those reported for [Zn₂(BTC)(NO₃)(H₂O)(C₂H₅OH)₅] (BTC = 1,3,5-benzenetricarboxylate)⁸ and [Zn₂Co₄(PO₄)₄(H₂O)₅ · 2H₂O].⁹ The zinc metals are bridged by four carboxylate groups to neighboring zinc metals to form an infinite 3-D network.

Each 2,6-naphthalenedicarboxylate ligand acts as a tetrakis(monodentate) unit, linking two pairs of zinc atoms to yield a tightly held framework. The equatorial plane, defined by Zn1, O3, O2, and O2^a, is perfectly planar due to its generation by symmetry.

A unique feature is demonstrated in Figure 2, which shows cross-linking channels parallel to the crystallographic *b* axis. These channels are approximately bisected by the coordinated water molecules. The 2-dimensional layers are formed in the *ab* plane by connecting Zn metal centers through NDC²⁻ ligands. These layers stack on top of each other along the *c*-axis at a distance of (1/2)*c* to complete the 3-dimensional structure. The closest Zn...Zn contact within each pair is 4.316 Å, whereas that involving different pairs are 5.440 and 11.780 Å.

In conclusion, whereas Yaghi's group prepared porous zinc coordination-polymers, we obtained the 3-dimensional Zn polymer with a nonporous and infinite network. The formation of different types of coordination products might be due to the difference in ligand identity (1,4-benzenedicarboxylic acid versus 2,6-naphthalenedicarboxylic acid) and reaction conditions (vapor diffusion versus hydrothermal

reaction).

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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