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Paddle-wheel 유형의 2차 쌓음 단위 $Zn_2(CO_2R)_4$에 기초한 2차원 아연 배위 고분자: [Zn(ATP)(DMF)] (ATP = 2-aminoterephthalate, H_2N-C_6H_3-1,4-$(COO)_2$; DMF = *N*,*N*-dimethylformamide)

민동원 · 이희근 · 이순원*
성균관대학교 화학과

Two-dimensional Zinc Coordination Polymer Based Paddle-Wheel Type Secondary Building Units of $Zn_2(CO_2R)_4$: [Zn(ATP)(DMF)] (ATP = 2-aminoterephthalate, H_2N-C_6H_3-1,4-$(COO)_2$; DMF = *N*,*N*-dimethylformamide)

Dongwon Min, Hee K. Lee and Soon W. Lee*
Department of Chemistry (BK21), Sungkyunkwan University, Suwon 440-746, Korea

요 약

벤젠 존재 하에서, DMF와 에탄올의 혼합 용매에서 zinc(II) nitrate ($Zn(NO_3)_2 \cdot 6H_2O$)와 ATP (2-aminoterephthalate, H_2N-C_6H_3-1,4-$(COO)_2$)의 용매열 반응으로 2차원 배위 고분자 [Zn(ATP)(DMF)] (**1**)이 얻어졌다. X-ray 구조 결정 결과, 2개의 아연 금속과 4개의 ATP 리간드가 paddle-wheel 유형의 2차 쌓음 단위들을 형성하고, 이것들은 ATP 리간드에 의해서 연결되어 2차원 4각 망을 이룬다는 것이 밝혀졌다. 아연 금속을 기준으로 각 4각형의 크기는 약 11.1×11.1 Å이다. 고분자 1을 양질의 결정 상태로 얻기 위해서는 벤젠이 요구되었다.

Abstract

The solvothermal reaction of zinc(II) nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) with ATP (2-aminoterephthalate, H_2N-C_6H_3-1,4-$(COO)_2$) in a mixture of solvents of DMF and ethanol, in the presence of benzene, gave a 2-dimensional zinc polymer [Zn(ATP)(DMF)] (**1**). X-ray structure determination revealed that two zinc metals and four ATP ligands form the paddle-wheel SBUs, which are linked by the ATP ligands to give a 2-D square-grid network. Each square grid has approximate dimensions of 11.1×11.1 Å based on Zn metals. Benzene was required to produce high-quality crystals of polymer **1**.

1. Introduction

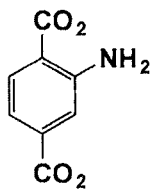
Coordination polymers (or metal-organic frameworks) with various cavities or channels are currently under intensive study due to their useful zeolite-like properties and potential applications as functional materials.[1-6] In the preparation of multi-dimensional coordination polymers, appropriate ligands play a fundamental role in determining the structural outcome of target polymers.

Secondary building units (SBUs) are molecular complexes or clusters, in which ligand-coordination modes and metal-coordination environments are utilized to incorporate these fragments into extended networks through multidentate ligands.[7] The SBUs have long been fundamental concepts in zeolite chemistry,[8-10] and now draw considerable attention as a firm basis of synthetic strategies for construct-

ing high-dimensional coordination polymers. For example, Yaghi and co-workers used the paddle-wheel cluster of the type $[M_2(CO_2R)_4]$ (M = Cu or Zn) as a square-planar SBU to prepare porous polymers with large voids and channels.[7]

We recently prepared several coordination polymers based on dicarboxylates or bipyridyls by hydrothermal or hydro(solvo)thermal reactions.[11-24] In particular, we reported several triply interpenetrating coordination polymers based on paddle-wheel type SBUs of $M_2(CO_2R)_4$: $[Ni_3(2,6\text{-NDC})(bipy)_{1.5}]$,[22] $[Co_3(2,6\text{-NDC})(bipy)_{1.5}]$,[22] and $[Co_3(2,6\text{-NDC})(bipyien)_{1.5}]$[24] (2,6-NDC = 2,6-naphthalenedicarboxylate; bipy = 4,4-bipyridine; bipyien = *trans*-1,2-bis(4-pyridyl)ethylene).

As a continuation of our work, we set out to prepare zinc coordination polymers that also possess paddle-wheel type SBUs of $M_2(CO_2R)_4$ constructed by ATP (2-aminoterephthalate, $H_2N\text{-}C_6H_3\text{-}1,4\text{-}(COO)_2$), which is 1,4-benzenedicaboxylate with an NH_2 side-arm at the C2 position. The appended NH_2 group is expected to help to introduce guest molecules into the cavity formed in the resulting polymer. On the contrary to our expectation, the solvothermal treatments of zinc(II) nitrate ($Zn(NO_3)_2\cdot 6H_2O$), ATP, and benzene, in a mixed solvent of *N,N*-dimethylformamide (DMF, Me_2NCHO) and ethanol gave a 2-dimensional zinc network, in which DMF serves as a monodentate ligand, not the guest molecule. In this paper, we report the synthesis and structure of a novel 2-D zinc coordination polymer, [Zn(ATP)(DMF)] (1), which possesses paddle-wheel type SBUs of $Zn_2(CO_2R)_4$.



ATP

2. Experimental section

Zinc(II) nitrate, ATP, benzene, DMF (*N,N*-dimethylformamide, Me_2NCHO), and ethanol were purchased from Aldrich company. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer. Elemental analyses were performed with EA1110 (CE instrument, Italy) at the Korea Basic Science Institute.

Preparation of [Zn(ATP)(DMF)] (1). A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.202 g, 0.695 mmol), ATP (0.126 g, 0.695 mmol), benzene (0.186 mL, 2.805 mmol), DMF (10 mL), and ethanol (4 mL) was heated in a 23-mL Teflon-lined autoclave at 90°C for 3 days, and then cooled to room temperature. The yellow crystalline product was filtered, washed with H_2O (2 × 5 mL) and ethanol (2 × 5 mL), and air-dried to give crystals of **1** (0.045 g, 0.142 mmol, 70.3% yield). Anal. Calcd for $C_{11}H_{12}N_2O_5Zn$: C, 41.60; H, 3.81; N, 8.82. Found: C, 41.38; H, 3.95; N, 8.95. IR (KBr, cm^{-1}): 1689, 1624, 1582, 1496, 1433, 1379, 1329, 1256, 1151, 1057, 961, 908, 827, 772, 694, 576, 528, 419 cm^{-1}.

Table 1. X-ray data collection and structure refinement

empirical formula	$C_{11}H_{12}N_2O_5Zn$
fw	317.60
temperature, K	293(2)
crystal system	monoclinic
space group	*C*2
a, Å	11.337(7)
b, Å	15.265(10)
c, Å	8.124(5)
β, deg	111.70(2)
V, Å^3	1306(2)
Z	4
d_{cal}, g cm^3	1.615
μ, mm^{-1}	1.897
F(000)	648
T_{min}	0.5573
T_{max}	0.8640
2θ range (°)	3.5~50
scan type	ω
scan speed	variable
No. of reflns measured	1249
No. of reflns unique	1187
No. of reflns with $I > 2\sigma(I)$	1091
No. of params refined	147
Max., in Δρ (e Å^{-3})	0.817
Min., in Δρ (e Å^{-3})	−0.701
GOF on F^2	1.083
R	0.0424
wR_2[a]	0.1089

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

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^4$)

	x	y	z	*U*(eq)
Zn1	1036(1)	2401(2)	4289(1)	27(1)
O1	−169(15)	3294(8)	2743(19)	56(4)
O2	1694(14)	3306(7)	6220(20)	59(4)
O3	−84(14)	1441(8)	2652(19)	58(4)
O4	1719(15)	1419(8)	6228(16)	61(4)
N1	−3005(12)	−130(8)	3050(13)	82(3)
C1	−1140(20)	3562(10)	2660(20)	47(5)
C2	−1895(18)	4240(9)	1340(20)	40(4)
C3	−2736(17)	4883(12)	1620(20)	55(5)
C4	−1660(20)	505(10)	−270(20)	50(5)
C5	−1880(20)	498(11)	1280(30)	46(5)
C6	−2789(18)	−73(9)	1530(20)	45(4)
C7	−1640(17)	4328(11)	−240(30)	47(4)
C8	−1226(13)	1175(10)	2740(18)	41(4)
O5	2454(5)	2269(6)	3384(7)	54(2)
N2	4151(15)	2802(10)	2810(20)	106(4)
C9	4240(20)	2057(15)	1800(30)	145(9)
C10	5030(30)	3540(20)	3270(50)	221(15)
C11	3273(13)	2878(10)	3586(19)	79(3)

X-ray Structure Determination. All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 28 reflections in the range $10.0^\circ < 2\theta < 25.0^\circ$. Intensity data were empirically corrected for absorption with ψ-scan data. All calculations were carried out with the use of SHELXTL programs.[25]

A yellow crystal of **1**, shaped as a plate of approximate dimensions 0.30 × 0.28 × 0.16 mm^3, was used for crystal- and intensity-data collection. The unit-cell parameters and systematic absences indicated three possible space groups: *C*2, *C2/m*, and *Cm*. The structure analysis converged only in *C*2. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically, except for extremely disordered DMF ligands that were refined isotropically. All hydrogen atoms were generated in ideal positions and refined in a riding mode. Details on crystal data and refinement details are given in Table 1. Final atomic coordinates and selected bond lengths and angles for **1** are given in Tables 2 and 3, respectively.

3. Results and Discussion

Preparation. The title compound was prepared by solvothermal reactions. In the presence of benzene, $Zn(NO_3)_2 \cdot 6H_2O$ reacts with ATP in a mixture of solvents of DMF and ethanol at 90°C for 3 days to give a 2-D zinc coordination polymer with an empirical formula of [Zn(ATP)(DMF)] (**1**) (eq. 1). Yellow crystalline polymer **1** is stable in air and insoluble in common organic solvents. The IR spectrum of **1** exhibits peaks at 1689, 1624, 1582, 1496, 1433, 1379, and 1329 cm^{-1} that can be assigned to the asymmetric and symmetric C=O stretches.[26,27]

$$Zn(NO_3)_2 \cdot 6H_2O + ATP + DMF \rightarrow [Zn(ATP)(DMF)] \quad (1)$$

The preparation of polymer **1** deserves some considerations. With an attempt to prepare guest-containing open frameworks, we examined solvothermal reactions of $Zn(NO_3)_2 \cdot 6H_2O$ with ATP under various conditions. However, only solvothermal reactions in the presence of benzene led to the formation of single crystalline products. Although we do not know the exact function of benzene in our reaction system, benzene appears to have promoted the formation of good crystals. A similar approach was previously employed in the preparations of $Cu_3(C_6H_8O_4)_3(H_2O)_2(C_6H_{11}OH)$,[28] $[M_3(2,6\text{-NDC})_3(bipy)_{1.5}]$[22] (Ni or Co), and $[Co_3(2,6\text{-NDC})(bipyien)_{1.5}]$.[24]

Table 3. Selected bond lengths (Å) and bond angles (°)

Zn1-O1	2.01(1)	Zn1-O5	2.01(1)	Zn1-O2	2.02(2)
Zn1-O3	2.07(1)	Zn1-O4	2.10(1)	Zn1-Zn1#1	2.977(2)
O1-Zn1-O2	89.5(7)	O3-Zn1-O4	86.9(7)	O1-Zn1-Zn1#1	77.9(4)
O5-Zn1-Zn1#1	174.1(3)	O2-Zn1-Zn1#1	79.4(4)	O3-Zn1-Zn1#1	82.2(4)
O4-Zn1-Zn1#1	80.5(4)				

Symmetry transformations used to generate equivalent atoms: #1 = $-x$, y, $-z + 1$.

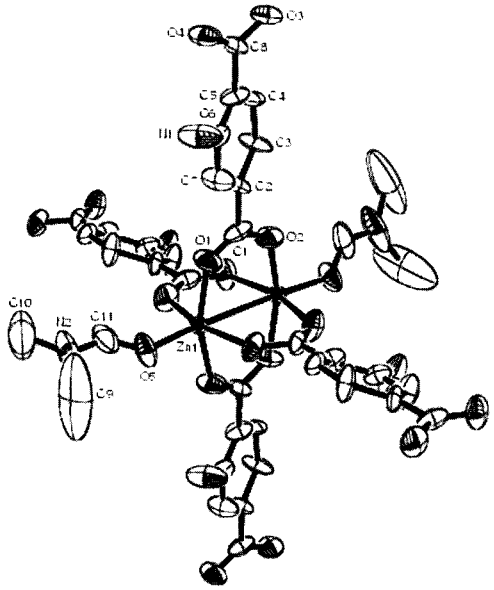


Fig. 1. ORTEP drawing of a paddle-wheel unit of polymer 1.

Structure. Fig. 1 illustrates a paddle-wheel SUB of the type $[Zn_2(OOCR)_4]$ in polymer **1**, which comprises two zinc metals and four di(monodentate) bridging carboxylates. A monomer unit consists of one ATP ligand, one DMF ligand, and a zinc(II) metal. The Zn-O (carboxylate) bond lengths lie in the range of 2.01(1)2.10(1) Å, and the Zn-Zn bond length of 2.977(2) Å indicates a Zn-Zn single bond. Each zinc metal has a pseudo-octahedral geometry, whose equatorial plane consists of four oxygen atoms from four ATP carboxylates. In addition, the axial positions are occupied by one zinc atom and one DMF ligand. The NH_2 hydrogens participate in one intramolecular N-H···O (N1-H1···O1) and one intermolecular N-H···O (N1-H2···O4) hydrogen bond.

Two zinc metals and four ATP ligands form the paddle-wheel SBUs, which are linked by the ATP ligands to give a 2-D network. The packing diagram of polymer **1** (Fig. 2) demonstrates a 2-dimensional square-grid network in the [111] direction. Each square grid has approximate dimensions of 11.1 × 11.1 Å based on Zn metals.

In summary, solvothermal reactions of $Zn(NO_3)_2 \cdot 6H_2O$ and ATP, in the presence of benzene, in a mixture of solvents of DMF and ethanol gave a 2-dimensional zinc coordination polymer, [Zn(ATP)(DMF)] (**1**), which is based on the paddle-wheel SBUs ($[Zn_2(CO_2R)_4]$). Benzene was required to produce high-quality crystals of polymer **1**. These results indicate that a solvent composition can exert a great influence on the structural outcome of the resulting coordination polymer.

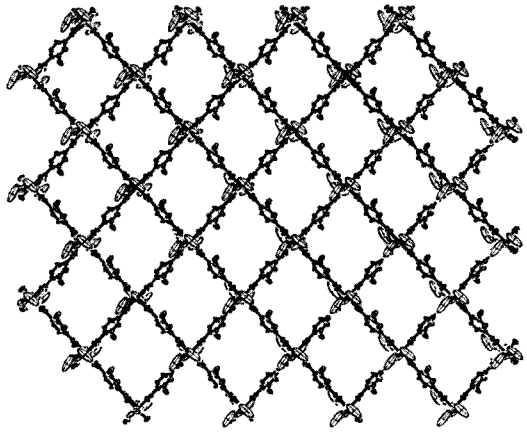


Fig. 2. Packing diagram of polymer 1.

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