Korean J. Crystallography
Vol. 13, No. 1, pp.17~20, 2002

Crystal Structure of Two-Dimensional Bis(isonicotinato)tetraaquazinc(II) Complex Linked by Hydrogen-Bonds

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水素 結合에 의한 二次元의 Bis(isonicotinato)tetraaquazinc(II) 錯物의 結晶構造

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Abstract

The complex $[Zn(L)_2(H_2O)_4]$ (**1**) (L = isonicotinate) has been prepared and characterized by X-ray crystallography. Compound **1** crystallizes in the triclinic space group $P\bar{1}$, with a = 6.9062(4) Å, b = 9.2618(7) Å, c = 6.3313(3) Å, α = 104.986(6)°, β = 112.865(4)°, γ = 96.213(6)°, V = 350.41(4) Å^3, Z = 1, $R_1(wR_2)$ for 1225 observed reflections of $[I > 2\sigma(I)]$ was 0.0209 (0.0591). The coordination environment of the zinc atom can be described as an octahedron in which the isonicotinato ligands are mutually *trans*. Compound **1** is also connected into a two-dimensional chain via hydrogen-bonds.

要 約

$[Zn(L)_2(H_2O)_4]$ (**1**) (L = isonicotinate) 錯物을 合成하고 構造를 糾明하였다. 이 錯物은 三斜晶系, 空間群 $P\bar{1}$, a = 6.9062(4) Å, b = 9.2618(7) Å, c = 6.3313(3) Å, α = 104.986(6)°, β = 112.865(4)°, γ = 96.213(6)°, V = 350.41(4) Å^3, Z = 1로 決定化 되었다. 이 錯物의 構造는 最小自乘法으로 精密化하였으며, 最終 信賴度 $R_1(wR_2)$ 값은 1225個의 回折班點에 對하여 0.0209 및 0.0591이었다. Zn 原子의 配位環境은 isonicotinate 리간드가 서로 *trans*에 位置한 八面體 構造를 갖는다. 또한 化合物 **1**은 水素結合에 의한 二次元의 사슬 構造로 連結되어 있다.

1. Introduction

The ambidentate isonicotinate is known to coordinate to nitrogen or to oxygen in metal complexes. Recently, various copper(II) complexes $CuL_2 \cdot nH_2O$ (L = nicotinate, isonicotinate, 2-methylthionicotinate, or 2-chloronicotinate; n = 0-4) have been synthesized and characterized.[1-5] Among these complexes, Cu(nicotinate)$_2$,[4] Cu(nicotinate)$_2 \cdot 4H_2O$,[5] Cu(isonicotinate)$_2 \cdot 4H_2O$[5], and Cu(2-chloronicotinate)$_2 \cdot H_2O$[2] reveal the monomeric, dimeric or polymeric chain structures. In order to better understand some aspects of interaction between zinc(II) and isonicotinate, we have became interested in the synthesis of the complex $[Zn(L)_2(H_2O)_4]$ (**1**), which is connected into a two-dimensional chain via hydrogen-bonds.

2. Experimental

Materials and Physical Measurements. All

Table 1. Crystal Data and Structure Refinement for 1

Empirical formula	$C_{12}H_{16}N_2O_8Zn$
Formula weight	381.64
Temperature	293(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 6.9062(4) Å, α = 104.986(6)°
	b = 9.2618(7) Å, β = 112.865(4)°
	c = 6.3313(3) Å, γ = 96.213(6)°
Volume	350.41(4) Å^3
Z	1
Density (calculated)	1.809 Mg/m^3
Absorption coefficient	1.800 mm^{-1}
Diffractometer	Enraf-Nonius CAD4
Radiation/wavelength	Mo Kα (graphite monochrom.)/0.71073 Å
F(000)	196
Crystal size	0.30 × 0.20 × 0.15 mm^3
θ range for data collection	2.34 to 24.97°
Index ranges	$-8 \le h \le 7$, $-11 \le k \le 10$, $0 \le l \le 7$
Reflection collected/unique	1361/1237 (R_{int} = 0.0116)
Absorption correction (φ-scan)	T_{max} = 0.7150 and T_{min} = 0.6518
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1237/0/110
Goodness-of-fit on F^2	1.150
Final R indices [$I > 2\sigma(I)$]	R_1[a] = 0.0209, wR_2[b] = 0.0591
R indices (all data)	R_1[a] = 0.0213, wR_2[b] = 0.0594
Largest diff. peak and hole	0.361 and −0.398 eÅ^{-3}

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$.

chemicals and solvents used in the synthesis were of reagent-grade and were used without further purification. Infrared spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240C analyzer. FAB mass spectra were obtained using a Jeol JMS-HA 100A/100A spectrometer.

Synthesis of $[Zn(L)_2(H_2O)_4]$ (1). An ethanol solution (20 m*l*) of $ZnCl_2$ (134 mg, 1 mmol) and sodium isonicotinate (145 mg, 1 mmol) was refluxed for 1 h and then cooled to room temperature. The solution was filtered and allowed to stand for a few days until colorless crystals formed. The product was filtered and recrystallized from water/ethanol (1:1, 10 m*l*) mixture. Found: C, 37.84; H, 4.32; N, 7.41. Calc. for $C_{12}H_{16}N_2O_8Zn$: C, 37.77; H, 4.23; N, 7.34%. IR (KBr, cm^{-1}): 3369, 3249, 2915, 1598 (C=O), 1553 (C=O), 1421 (C=O), 1385 (C=O), 1059, 1024, 775, 709, 691. FAB mass (m/z): 380 (M^+).

X-ray Crystallography. Analysis on a colorless crystal of **1** was carried out with an Enraf-Nonius CAD4 diffractometer equipped with a graphite-monochroamated Mo Kα radiation. A summary of the data collection and details of the structure

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (×10^3) for 1

	x	y	z	U(eq)[a]
Zn	5000	5000	5000	25(1)
O(1)	7839(3)	12986(2)	10928(3)	38(1)
O(2)	9206(2)	12316(2)	14246(3)	37(1)
N	6386(2)	7302(2)	7433(3)	25(1)
C(1)	8318(3)	12024(2)	11997(3)	27(1)
C(2)	7715(3)	10362(2)	10408(3)	23(1)
C(3)	7770(3)	9176(2)	11371(3)	28(1)
C(4)	7086(3)	7677(2)	9837(3)	29(1)
C(5)	6413(3)	8455(2)	6526(3)	26(1)
C(6)	7060(3)	9981(2)	7937(3)	26(1)
Ow(1)	7597(2)	4191(2)	7258(3)	36(1)
Ow(2)	6953(2)	5424(2)	3283(2)	29(1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ii} tensor.

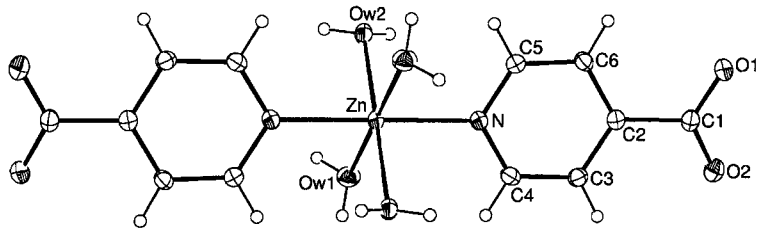

Fig. 1. An ORTEP plot showing the molecular structure of $[Zn(L)_2(H_2O)_4]$ (1) (50% probability ellipsoids).

refinement are listed in Table 1. Accurate cell parameters and orientation matrix were determined from the least-squares fit of 25 reflections. An asymmetric unit of intensity data were collected in the $\omega/2\theta$ scan mode. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on φ-scan was applied. The structure was solved by direct methods[6] and the least-squares refinements of the structure were performed by the program SHELXL97.[7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the aryl group were located at their calculated positions with U_{iso} to be 1.2 times the equivalent isotropic displacement of the parent atoms. The four hydrogen atoms of two water molecules were found from the difference Fourier map and their position were fixed and refined isotropically. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

3. Results and Discussion

An ORTEP drawing of $[Zn(L)_2(H_2O)_4]$ (**1**) with the atomic numbering scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 3. The title compound has two isonicotinato ligands and four aqua ligands. The coordination environment of the zinc atom can be described as an octahedron in which the isonicotinato ligands are mutually *trans*. The equatorial plane, defined by Zn, Ow(1), Ow(2), Ow(1)', and Ow(2)' atoms, is perfectly planar. The isonicotinato ligands are bonded to the metal through their nitrogen atoms. All bond

Table 3. Selected bond distances (Å) and angles (°) for 1

Zn-N	2.133(2)	Zn-Ow(1)	2.162(1)
Zn-Ow(2)	2.098(1)	C(1)-O(1)	1.250(2)
C(1)-O(2)	1.250(2)	C(1)-C(2)	1.513(3)
N-C(4)	1.337(2)	N-C(5)	1.339(2)
N-Zn-Ow(1)	91.4(1)	N-Zn-Ow(1)^i	88.6(1)
N-Zn-Ow(2)	88.2(1)	N-Zn-Ow(2)^i	91.8(1)
Ow(1)-Zn-Ow(2)	86.8(1)	Ow(1)-Zn-Ow(2)^i	93.2(1)
Zn-N-C(4)	123.3(1)	Zn-N-C(5)	119.1(1)
O(1)-C(1)-O(2)	125.7(2)	O(1)-C(1)-C(2)	116.5(2)
N-C(4)-C(3)	123.0(2)	N-C(5)-C(6)	123.1(2)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

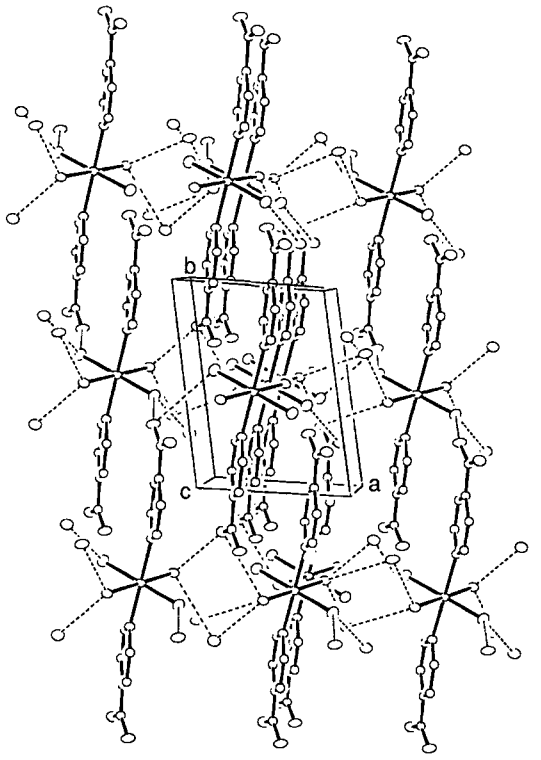

Fig. 2. A packing diagram of 1. The hydrogen bonds are indicated by dotted lines.

Table 4. Hydrogen bonding parameters (Å, °) for 1

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
Ow(1)-H(1B)O(1)^{ii}	0.802(1)	1.985(1)	2.785(2)	174.9(1)
Ow(1)-H(1A)O(2)^{iii}	0.861(1)	2.012(1)	2.870(2)	175.2(1)
Ow(2)-H(2A)O(1)^{iii}	0.875(1)	1.770(1)	2.639(2)	172.5(1)
Ow(2)-H(2B)O(2)^{iv}	0.856(1)	1.946(2)	2.783(2)	165.2(1)

Symmetry codes: (ii) $x, y-1, z$; (iii) $x, y-1, z-1$; (iv) $-x+2, -y+2, -z+2$.

distances and bond angles are normal. The two aryl planes in the isonicotinate ligands are nearly perpendicular to the equatorial plane, with dihedral angle of 84.3(1)°. Moreover, the dihedral angle between the plane of the carboxylate group and aryl plane is 12.4(1)°. Interestingly, the water molecule Ow(1) forms hydrogen-bonds with oxygen atoms of the isonicotinato ligand (Ow(1)O(1)^{ii} 2.785(2) Å, 174.9(1)°; Ow(1) O(2)^{iii} 2.870(2) Å, 175.2(1)$_o$; symmetry codes (ii): x, $y-1$, z (iii): x, $y-1$, $z-1$). The other water molecule Ow(2) also forms hydrogen-bonds with carboxylate oxygens of the isonicotinate (Ow(2)O(1)^{iii} 2.639(2) Å, 172.5(1)°; Ow(2)O(2)^{iv} 2.783(2) Å, 165.2(1)°; symmetry code (iv): $-x+2, -y+2, -z+2$). This interaction, as shown in Fig. 2 and Table 4, gives rise to a two-dimensional hydrogen-bonded network.

4. Supplementary Material

Atomic coordinates, bond lengths and angles, and thermal parameters are available from author K.-Y. Choi on request.

Acknowledgment

This work was supported by the Korea Science & Engineering Foundation, the Material Bank Program grant to MBCP.

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