Crystal Structure of Zinc(II) Complex of a Pyridine Containing Self-Assembling System

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The self-assembling system ligand LH_2 , $[\text{pyda}\cdot\text{H}_2]^{2+}[\text{pydc}]^{2-}$, (pyda = 2,6-pyridinediamine; $\text{pydc}\cdot\text{H}_2$ = 2,6-pyridinedicarboxylic acid), that has been recently synthesized in our laboratory is a novel self-assembling system which arises from both ion pairing and hydrogen bonding simultaneously.¹ The anionic form of $\text{pydc}\cdot\text{H}_2$ is a rigid tridentate ligand, which is capable of forming many stable complexes with divalent transition metals.²⁻⁴ The $[\text{Ag}(\text{pydc})(\text{pydc}\cdot\text{H}_2)]\cdot\text{H}_2\text{O}$,² $[\text{Ni}(\text{pydc}\cdot\text{H}_2)_2]\cdot 3\text{H}_2\text{O}$,³ and $[\text{Cu}(\text{pydc}\cdot\text{H}_2)_2]\cdot 3\text{H}_2\text{O}$,⁴ complexes are some examples in this regard. Using the thermal analysis and high temperature reflectance spectroscopy, Ascenzo *et al.* found out that the reaction between ZnCO_3 and $\text{pydc}\cdot\text{H}_2$ in 1:2 mole ratio, resulted in the formation of $[\text{Zn}(\text{pydc}\cdot\text{H}_2)_2]\cdot 2\text{H}_2\text{O}$ complex.⁵ Literature survey on this complex showed that no X-ray crystal data has been reported to date. Here, we wish to report the synthesis and X-ray crystal data of an ionic Zn(II) complex which resulted from the reaction between LH_2 and ZnCl_2 in water. The Zn(II) ionic complex includes dianionic and monoanionic forms of $\text{pydc}\cdot\text{H}_2$ simultaneously and one pyridinium cation, as counter ion, that causes hydrogen bondings. The resulting ionic Zn(II) complex would assemble into layers by hydrogen-bonds ($\text{O}\cdots\text{H}\cdots\text{O}^-$) and ($^+\text{N}\cdots\text{H}\cdots\text{O}^-$).

Preparation: To a solution of ZnCl_2 (0.124 g, 0.9 mmol) in water (20 cm^3) was added a solution of LH_2 (0.5 g, 1.8 mmol)¹ in water (150 cm^3) and the resulting light yellow solution was stirred for 15 min. After two days, light yellow crystals were obtained (Scheme 1). The crystals were collected, washed with fresh distilled water and dried. The pure light yellow block-

shaped crystals $[\text{pyda}\cdot\text{H}][\text{Zn}(\text{pydc})(\text{pydc}\cdot\text{H})]\cdot 3\text{H}_2\text{O}$ (0.4101 g) were obtained in 80.7% yield.

The X-ray data were collected by graphite-monochromated Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal and experimental data are listed in Table 1. The structure was solved by direct methods using SHELXS-97.⁶ The non-hydrogen atoms were refined anisotropically by the full matrix least-square method. The hydrogen atoms were obtained from a difference Fourier map and some of the hydrogen atoms were included in the ideal position with fixed isotropic U values equal to 1.2 times that of the atom they are attached to. The final atomic coordinates of the non-hydrogen are listed in Table 2. The selected bond distances and angles are given in Table 3. The molecular structure of the title compound is shown in Fig. 1 together with the atom-labeling scheme.

The central metal ion is coordinated by four oxygen atoms (O_1 , O_3 , O_5 , O_7) and two nitrogen atoms (N_1 , N_2). The two $\text{O}_1\text{-Zn-O}_3$ and $\text{O}_7\text{-Zn-O}_5$ angles are 152.65° and 151.09° , respectively. This shows that the four carboxylate groups of

Table 1 Crystal and experimental data

Formula: $\text{C}_{19}\text{H}_{21}\text{N}_6\text{O}_{11}\text{Zn}$
Formula weight = 560.78
Crystal system: triclinic
Space group: $P\bar{1}$ $Z = 2$
$a = 6.9482(10) \text{ \AA}$ $\alpha = 102.603(2)^\circ$
$b = 10.4796(15) \text{ \AA}$ $\beta = 93.925(2)^\circ$
$c = 16.678(2) \text{ \AA}$ $\gamma = 104.354(2)^\circ$
$V = 1138.4(3) \text{ \AA}^3$
$D_x = 1.636 \text{ g/cm}^3$
Absorption coefficient = 1.50 mm^{-1}
$F(000) = 576$
Crystal dimensions (mm): $0.25 \times 0.1 \times 0.1$
$R = 0.0401$
$R_w = 0.0857$
θ range for data collection: 2.07 to 28.73°
Goodness-of-fit = 1.043
Largest diff. Peak and hole: 0.393 and $-0.507 \text{ e \AA}^{-3}$
No. of reflections used = 5153
No. of parameters = 346
Measurement: Bruker SMART
Program system: SHELXS-97, SHELXL-97, Bruker SHELXTL
Structure determination: direct method
Refinement: full-matrix least-squares of F^2

Scheme 1 The synthetic method for $[\text{pydc}\cdot\text{H}][\text{Zn}(\text{pydc})(\text{pydc}\cdot\text{H})]\cdot 3\text{H}_2\text{O}$ complex.

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Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for non hydrogen atoms

Atom	x	y	z	U_{eq}
Zn	2900(1)	1937(1)	2789(1)	24(1)
C(1)	1858(5)	-478(3)	3461(2)	27(1)
C(2)	2084(4)	-987(3)	2551(2)	22(1)
C(3)	1884(5)	-2317(3)	2162(2)	25(1)
C(4)	2106(5)	-2621(3)	1324(2)	26(1)
C(5)	2504(5)	-1603(3)	907(2)	25(1)
C(6)	2691(4)	-279(3)	1348(2)	21(1)
C(7)	3142(5)	970(3)	999(2)	24(1)
C(8)	6910(5)	3209(3)	3833(2)	26(1)
C(9)	5890(5)	4341(3)	3878(2)	23(1)
C(10)	6646(5)	5657(3)	4337(2)	25(1)
C(11)	5423(5)	6533(3)	4348(2)	29(1)
C(12)	3533(5)	6074(3)	3896(2)	26(1)
C(13)	2888(5)	4726(3)	3450(2)	20(1)
C(14)	865(5)	4044(3)	2931(2)	25(1)
C(15)	2933(5)	3006(3)	8647(2)	24(1)
C(16)	3071(5)	3060(3)	7833(2)	30(1)
C(17)	2893(5)	1862(3)	7242(2)	31(1)
C(18)	2604(5)	626(3)	7443(2)	28(1)
C(19)	2519(4)	595(3)	8268(2)	24(1)
O(1)	2078(3)	801(2)	3704(1)	28(1)
O(2)	1488(4)	-1316(2)	3881(1)	40(1)
O(3)	3526(3)	2093(2)	1523(1)	26(1)
O(4)	3082(4)	800(2)	239(1)	39(1)
O(5)	6147(3)	2119(2)	3337(1)	30(1)
O(6)	8486(3)	3499(2)	4374(1)	31(1)
O(7)	499(3)	2773(2)	2646(1)	26(1)
O(8)	-254(3)	4766(2)	2819(1)	29(1)
N(1)	2491(4)	1(2)	2151(1)	20(1)
N(2)	4066(4)	3891(2)	3446(1)	20(1)
N(3)	2254(4)	-540(2)	8544(2)	34(1)
N(4)	3030(4)	4074(2)	9266(2)	36(1)
N(5)	2697(4)	1776(2)	8838(1)	22(1)
O(9)	9340(4)	1465(3)	4613(2)	55(1)
O(10)	7437(4)	3578(2)	1309(1)	34(1)
O(11)	1458(5)	688(3)	787(2)	53(1)

Table 3 Selected bond lengths ($\text{\AA}$) and angles ($^\circ$)

Zn-N(1)	2.015(2)
Zn-N(2)	2.032(2)
Zn-O(1)	2.1552(19)
Zn-O(3)	2.2166(18)
Zn-O(5)	2.322(2)
Zn-O(7)	2.0903(19)
N(1)-Zn-N(2)	165.24(9)
N(1)-Zn-O(7)	116.16(9)
N(2)-Zn-O(7)	77.90(9)
N(1)-Zn-O(1)	77.08(8)
N(2)-Zn-O(1)	105.10(8)
O(7)-Zn-O(1)	102.97(8)
N(1)-Zn-O(3)	75.56(8)
N(2)-Zn-O(3)	101.37(8)
O(7)-Zn-O(3)	89.10(7)
O(1)-Zn-O(3)	152.65(7)
N(1)-Zn-O(5)	92.72(8)
N(2)-Zn-O(5)	73.21(8)
O(7)-Zn-O(5)	151.09(8)
O(1)-Zn-O(5)	83.75(8)
O(3)-Zn-O(5)	97.53(8)

Fig. 1 Molecular structure of the Zn(II) complex with the atom labeling.

two $[\text{pydc}]^{2-}$ and $[\text{pydc}\cdot\text{H}]^-$ anions are oriented in a flattened tetrahedral arrangement around the Zn(II) atom. The dianionic $[\text{pydc}]^{2-}$ unit and monoanionic $[\text{pydc}\cdot\text{H}]^-$ unit are almost perpendicular to each other (*i.e.*, $\text{O}_3\text{-Zn-N}_2\text{-C}_9$ torsion angle is -97.7° , $\text{N}_2\text{-Zn-O}_3$ and $\text{N}_2\text{-Zn-O}_1$ angles are 101.37° and 105.10° , respectively). The geometry of the zinc atom is distorted octahedral. The molecular structure consists of monomeric units $[\text{pyda}\cdot\text{H}][\text{Zn}(\text{pydc})(\text{pydc}\cdot\text{H})]\cdot 3\text{H}_2\text{O}$ in which the two $[\text{pydc}]^{2-}$ and $[\text{pydc}\cdot\text{H}]^-$ moieties act as tridentate ligands. The protonated position in the cationic counter ion is the pyridine nitrogen atom, while the two protons in the ligand LH_2 are located at the two $-\text{NH}_2$ nitrogen positions. The intermolecular forces which exist between anionic and cationic units in the Zn(II) complex consist of both H-bonding and ion-pairing. Three uncoordinated water molecules increase the number of H-bonding in the crystal lattice. The data found in this work for the unit $[\text{pyda}\cdot\text{H}]^+$ are quite similar to the previous data reported for the $[\text{pyda}\cdot\text{H}_2]^+$ moiety.¹ The metal-ligand bond distances of the title compound are consistent with those found in $\text{K}_2\text{Zn}[\text{NH}(\text{CH}_2\text{CO}_2)]$ ($\text{Zn-N} = 2.16 \text{ \AA}$; $\text{Zn-O} = 2.03 \text{ \AA}$, $2.12 \text{ \AA}$).⁷ In $[\text{pyda}\cdot\text{H}][\text{Zn}(\text{pydc})(\text{pydc}\cdot\text{H})]\cdot 3\text{H}_2\text{O}$ the Zn-N distance is $2.023 \text{ \AA}$, and the average of Zn-O distances is $2.196 \text{ \AA}$. The $\text{N}_1\text{-Zn-N}_2$ angle (axial) is 165.24° , which shows a significant deviation from linearity. The Zn atom is positioned at the inversion center of the molecule. The structure is strongly stabilized by a complicated network of hydrogen bonds. Hydrogen coordinates, isotropic displacement parameters, bond angles, bond lengths and torsional angles are available as supplementary materials.

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