



Hydrothermal Synthesis and Crystal Structure of Zn(II) Coordination Polymer with Rigid 4,4'-azobispyridine

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Abstract: The new metal complex with phenylsuccinic acid (H_2psa) and 4,4'-azobispyridine (4,4'-abpy), $\{[Zn(psa)(H_2O)_3(\mu-4,4'-abpy)](H_2O)\}_n$ (**I**), was synthesized by hydrothermal process. The structure of **I** has been characterized by IR spectra, elemental analysis, and single crystal X-ray diffraction. Single crystal X-ray analysis reveals that the psa ligand O-coordinated to the Zn(II) ion and distorted octahedral geometry of Zn(II) ion is completed by bridging 4,4'-abpy and three aqua ligands.

Keywords: Coordination polymers, 4,4'-azobispyridine, phenylsuccinic acid, Zn complexes.

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INTRODUCTION

Although it was stated that coordination polymers had emerged in 1960s, it has attracted attention via leading reports on the findings of the porous structures and associated functionalities since 1990s (1). Since the past decade, the interest in searching for the coordination polymers has aroused profoundly for the immediate increase in the publication ratio and number about them. Coordination polymers which are known as 1D, 2D and 3D are considered structurally interesting, especially 1D polymers have intriguing electrical, optical and magnetic properties (2). For 1D chains, self-assembly of metal ions that have specific directionality and functionality with organic ligands that have appropriate functional groups is relatively simple; however, this simplicity leads to corporate structural features at the metal centers or in the backbone of the bridging ligands (3). We have studied on the metal-phenylsuccinate-azobispyridine system, in which 4,4'-azobispyridine (4,4'-abpy) has a structure with a π conjugated system and two

coordinatively active nitrogen atoms in which pyridine nitrogens are more basic and are more accessible for polynuclear arrangements for steric reasons (4-12). Furthermore, azobispyridine complexes are used as electro-optical devices for reversible data storage, in indicators, therapeutic and drug delivery agents, and photochemical switches. Even if H_2psa displays coordination capabilities of the two carboxylate groups and an amazing phenyl ring side group, that is presumed to modulate and affect the orientation relationship (13), in fact there are still few studies on H_2psa . In addition, more interesting coordination polymers can be obtained through enforcing it as a configurationally asymmetric bridging ligand. The aim of this work was to prepare new coordination polymers of phenylsuccinate complexes of Zn(II) metal ion with 4,4'-azobispyridine by hydrothermally process, and to analyze their structural and spectroscopic characteristics using single crystal X-ray diffraction and IR technique.

EXPERIMENTAL

Materials and measurements

All chemicals used were of analytical reagent quality. The 4,4'-abpy ligand was synthesized by oxidation of the 4-aminopyridine with NaOCl according to literature (Kirpal-Reiter method) (15). Elemental analysis was performed by standard methods at IBTAM (İnönü University Scientific Research Centre). The IR spectrum was recorded on a Bruker Tensor 27 FT/IR spectrophotometer using KBr pellets and operating at 4000-400 cm^{-1} . The X-ray diffraction data of the complex were collected with a Bruker Kappa Apex2duo diffractometer. The structures were solved and refined by full-matrix least-squares techniques on F^2 by using the SHELXT-2015 program (16). The absorption corrections were done by the multiscan technique. All non-hydrogen atoms were refined anisotropically. All non-water hydrogen atoms were included in the refinement process by using a riding model.

Synthesis of the complex

$\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (24 mg, 0.11 mmol), phenylsuccinic acid (21 mg, 0.11 mmol) and 4,4'-abpy (20 mg, 0.11 mmol) were placed into 10 mL of distilled H_2O in a pyrex bottle. The bottle was sealed and heated in an oven at 120 $^\circ\text{C}$ for 72 h, and then cooled slowly to 25 $^\circ\text{C}$. Red blocks of **1** (33 mg, 58%) were isolated after washing with distilled water and acetone, and finally drying in air. Anal. Calc. for $\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_8\text{Zn}$: C, 46.75; H, 4.71; N, 10.90. Found: C, 47.09; H, 4.27; N, 10.12%. IR (cm^{-1}): 3505 (mb), 3433 (m), 3104 (w), 3053 (w), 2976 (w), 2911 (w), 1611 (s), 1583 (s), 1491

(m), 1423 (s), 1367 (s), 1226 (m), 1168 (m), 1051 (m), 1026 (m), 846 (s), 741 (m), 704 (m), 680 (s), 566 (m), 526 (w).

RESULT AND DISCUSSION

Vibrational Analysis

The elemental analysis results and selected IR data are consisted with assigned formulation. The observation of the IR spectrum of **1** was performed by considering the most important internal vibrations of carboxylate, phenyl and azo groups, and water molecules.

The bands of stretching vibrations $\nu(\text{O}-\text{H})$ were found at 3433 cm^{-1} for compound **1**, indicating that the water molecules exist within the structures. Because of the $\nu(\text{CH})$ vibrations of aromatic and aliphatic groups, the relatively weak bands are above and below 3000 cm^{-1} , respectively. The absorption bands of the carbonyl groups of **1** in which psa is O-coordinated (monodentate) are found out as strong bands at 1583 cm^{-1} and 1611 cm^{-1} respectively (14,17). It is considered that intra- and intermolecular hydrogen bonding interactions involving the carbonyl group shift this band to higher frequencies. The bands of symmetric $\nu_s(\text{COO})$ stretch was found at 1367 cm^{-1} for **1**. The values of $\Delta\nu[\nu_{\text{as}}(\text{COO}) - \nu_s(\text{COO})]$ in the the complex (more than 200) fall within the range for a vibrational mode associated with a monodentate ligand (18). The bands centered around 1423 cm^{-1} are assigned to the $\text{N}=\text{N}$ vibrations of the 4,4'-abpy ligand. $\text{C}=\text{N}$ vibrations of 4,4'-abpy appear at ca. 1583 cm^{-1} .

Crystal Structure

The crystal data, experimental details and refinement details of complex are given in Table 1. Selected bond distances, angles and hydrogen band geometries are listed in Tables 2-3, respectively.

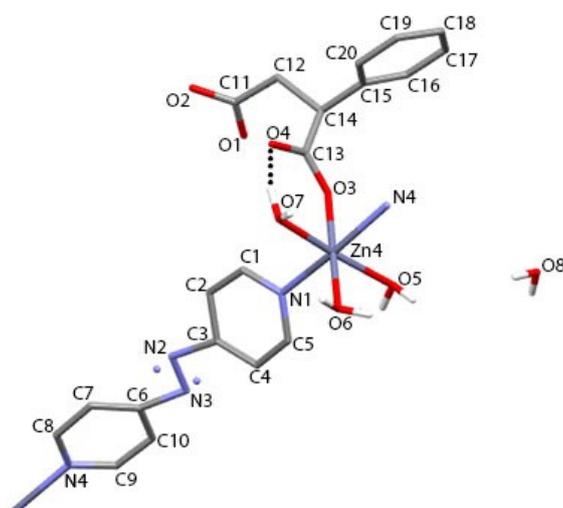


Figure 1. The crystal structure of **I** displaying the atom-labelling scheme.

Table 1. Crystal data and structure refinement parameters for complex **I**.

Crystal data	1
Empirical formula	C ₂₀ H ₂₄ N ₄ O ₈ Zn
Formula weight	513.83
Crystal system	Monoclinic
T (K)	100 (2)
λ (Å)	0.71073
Space group	P2 ₁ /n
a (Å)	12.676(4)
b (Å)	9.681(2)
c (Å)	19.455(6)
β (°)	108.716(9)
V (Å ³)	2261.3(11)
Z	4
D _c (g cm ⁻³)	1.5091
μ (mm ⁻¹)	1.14
Measured ref.	75543
Independent ref.	5634
θ Range (°)	0.963–1.00
Crystal size (mm)	0.15 × 0.11 × 0.1

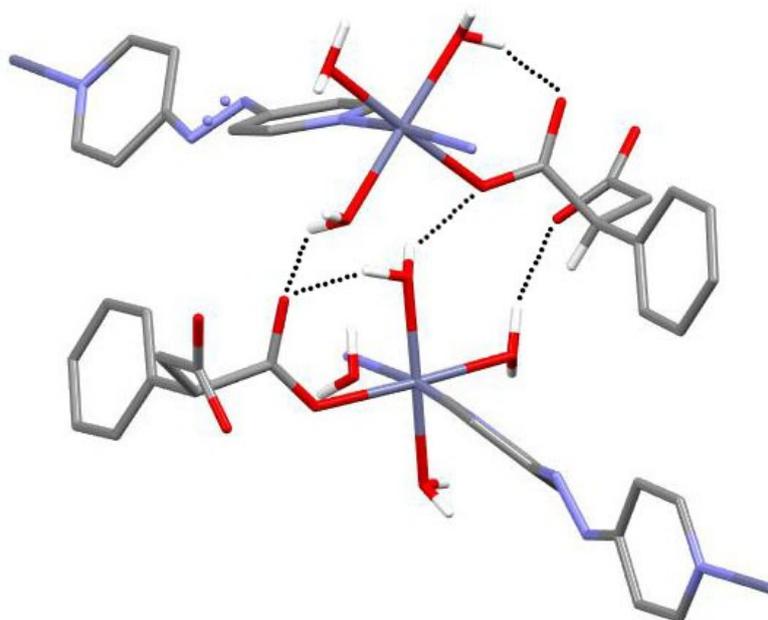
R_{int}	0.088
S	1.05
$R, R_w[I > 2\sigma(I)]$	0.067, 0.189
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} (\text{e}\text{\AA}^{-3})$	2.5, / -0.89

Table 2 Selected bond distances and angles for complex **I** (\AA , $^\circ$)

Bond distance	\AA	Bond distance	\AA
Zn4-O5	2.074	Zn4-O6	2.110
Zn4-N1	2.148	Zn4-O3	2.188
Bond angle	$^\circ$	Bond angle	$^\circ$
O5-Zn4-N1	95	O6-Zn4-N1	106
O7-Zn4-O3	92.6	O6-Zn4-O3	177.6
			6

According to the X-ray structural analysis, **I** crystallized in the monoclinic space group of $P2_1/n$. The asymmetric unit comprises of a Zn(II) atom, one half of the abpy, one PSA ligand as monodentate, three aqua ligands and one the lattice water molecule. (Figure 1.) The zinc settles with an octahedral geometry with

the PSA units and three aqua ligands on the equatorial plane and the axial sites are filled by two symmetry-related μ -abpy ligands ($\text{Zn-N} = 2.148(3) \text{ \AA}$) and subsequently, together with the the bridging abpy ligands, compose a one-dimensional coordination polymer. (Figure 2.).

**Figure 2.** Hydrogen-bonding for **I**

Contrary to expectations, PSA ligand is coordinated monodentate via carboxylate oxygen. The azo N atoms of 4,4'-azobispyridine was found to be distorted, probably due to unresolved disorder.

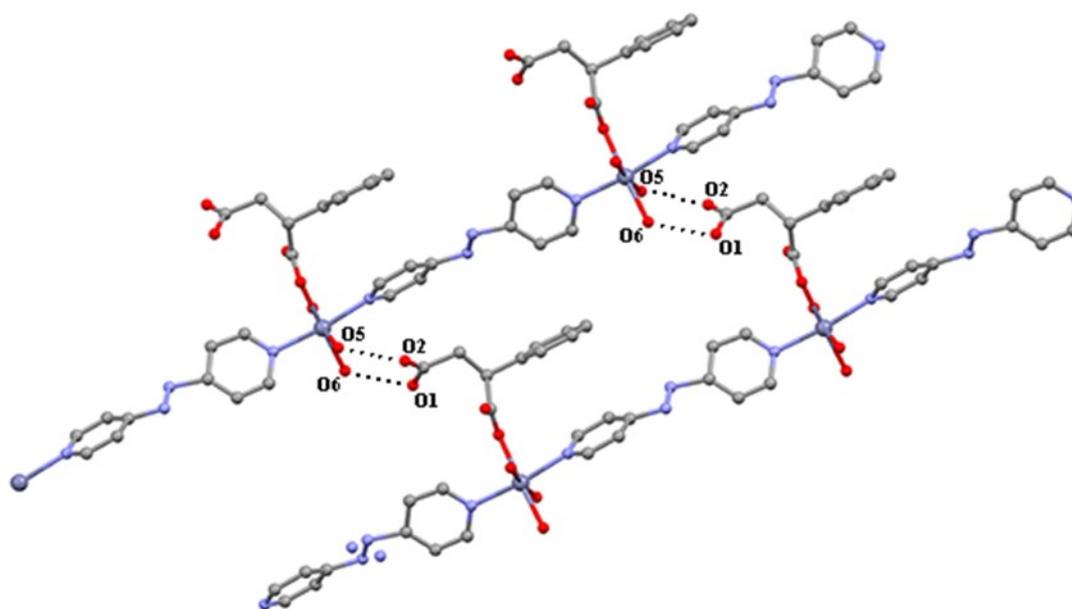
Table 3. Hydrogen-bond parameters for complex **I** (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
O5—H5A...O4	0.87	2.06	2.795(4)	141.4
O5—H5B...O2 ⁱ	0.87	1.87	2.649(5)	148.8
O7—H7A...O4 ⁱⁱ	0.87	1.82	2.628(4)	153.7
O6—H6A...O1 ⁱⁱⁱ	0.87	1.91	2.744(5)	160.4
O6—H6B...O1 ⁱ	0.87	1.95	2.815(5)	169.0
O8—H8B...O2 ⁱ	0.85	1.96	2.803(9)	172.5

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

The crystals are stabilized by intra- and intermolecular hydrogen bonding. As shown in Figure 2, adjacent complex units are connected by O5—H5A...O4, O5—H5B...O2ⁱ, O6—H6A...O1ⁱⁱⁱ and O8—H8B...O2ⁱ hydrogen bonding between aqua and carboxy oxygen atom of phenylsuccinate

ligands. 1D coordinasyon polymer units are connected by O5—H5B...O2ⁱ and O6—H6B...O1ⁱ hydrogen bonds between aqua and carboxy oxygen atom of phenylsuccinate ligands (Figure 3).

**Figure 3.** View of the infinite 1D chain structure of **I**.

CONCLUSIONS

As a summary, the title coordination polymer, $\{[Zn(psa)(H_2O)_3(\mu-4,4'-abpy)](H_2O)\}_n$, has been hydrothermally prepared by utilizing phenylsuccinic acid and 4,4'-azobispyridine ligands. X-ray structural analysis and IR data display that the complex compose a one-dimensional coordination polymer together with the the bridging abpy ligands. It is examined that phenylsuccinate-azobispyridine system should be a good candidate to achieve the desired multifunctionalities in coordination polymer.

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