


Short Note

Solvent-Mediated Synthesis of M(II)-Coordination Polymer Part 1: Crystal Structure of Poly(1,2-di(4-pyridyl)ethylene- k^2N,N')-bis(1,4-benzenediacetato- k^4O,O',O'',O''')zinc(II)], $C_{22}H_{18}ZnN_2O_4$

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Abstract: An interaction of water-methanol solution of sodium 1,4-benzenediacetate (bda) and 4,4'-bipyridylethylene (bpee) with aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ at room temperature yielded colourless crystals of **1** after three weeks in a sealed glass tube. The compound with composition $C_{22}H_{18}ZnN_2O_4$ crystallizes in monoclinic space group $P2_1/c$, with the following cell dimensions: $a = 10.4566(2)$, $b = 13.3085(2)$, $c = 13.7189(2)$ Å, $\beta = 101.491(1)^\circ$. In the structure of **1**, two Zn(II) neighbours are connected by two bda ligands adopting chelating and bidentate-bridging coordination modes to form a dimeric unit ($Zn_2O_8N_4$) with the Zn–Zn distance of 4.0432(6) Å. The carboxyl-bridged dimeric units are extended along the [001] direction by bpee co-ligands and further linked by bda ligand to form a three-dimensional network structure. The IR shows the characteristic bands of the carboxylates at 1611/1507 cm^{-1} and 1424/1373 cm^{-1} , respectively, for asymmetric and symmetric stretching $-CO_2^-$ vibrations. The separation $\Delta[\nu_{asym}(CO_2^-) - \nu_{sym}(CO_2^-)]$ values of 187 and 134 cm^{-1} are indicative of chelating and bidentate bridging coordination modes of the carboxylate to the metal centre.

Keywords: coordination polymer; crystal structure metal-organic frameworks; solvent diffusion

1. Introduction

In recent times, metal–organic framework (MOF) materials have received a great deal of attention not only for their unique properties, but also for their potential applications owing to their diversity in topological architectures [1–4]. Metal–organic frameworks consist of a metal ion linked by organic ligands to form one-, two-, or three-dimensional network structures [5,6]. A number of carboxylate ligands with aromatic backbones are frequently used in the design of metal–organic frameworks with desirable properties. Versatile carboxylate ligands derived from 1,4-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, or pyridine-2,4-dicarboxylic acid are commonly used owing to their abundant carboxylate groups possessing high affinity to metal cations [7–9]. Other functionalized ligands such as 1,2-bis(4-pyridyl)ethylene, 1,4-benzenediacetic acid, 4,4'-bipyridylethene, or 3-nitro-1,2-benzenedicarboxylic acid have also been extensively used under diverse synthetic conditions to prepare MOFs [10–17], which are used in several applications [18–22]. The interest in the use of phenylenediacetic acid as ligand in the synthesis of coordination polymers stems from the presence of the flexible $-CH_2-$ spacer that enables the $-CO_2^-$ units to freely bend

and rotate to meet the requirements of the coordination geometries of metal ions in the assembly process [23]. Researchers have made use of the flexible nature of phenylenediacetate along with different auxiliary ligands in preparing one-, two-, and three-dimensional structures [24–28]. In particular, Wang and coworkers [24,25] investigated a synthetic system containing various divalent metal acetates, 1,2-phenylenediacetate and 1,3-bis(4-pyridyl)propane co-ligand. Zhang et al. [23] reported on the structural diversities of divalent metal complexes of 1,3-phenylenediacetate with organo-nitrogen co-ligands, in which the structural characteristics of auxiliary ligands vary from chelating to bridging. However, reports on the coordination polymers of 1,4-phenylenediacetate are scant [26,27]. In this study, we were interested in using one long chain linker 4,4-bipyridylethylene (bpee) with $-\text{CH}=\text{CH}-$ (ethylenic) functionalities as N-donors and 1,4-benzenediacetic acid (bda) to synthesize a coordination polymer. We have been able to prepare a zinc(II)-coordination polymer, $\text{C}_{22}\text{H}_{18}\text{ZnN}_2\text{O}_4$, **1**, with a three-dimensional structure, incorporating the two ligands, via solvent diffusion technique.

2. Results and Discussion

The zinc(II)-coordination polymer was prepared by layering an aquo-methanol solution of the ligand on top of aqueous solution of the metal ion in a glass tube and allowing to stand at room temperature for three weeks. Compound **1** crystallizes in monoclinic space group $P2_1/c$ (Table S1). The zinc atom is six-coordinated in a distorted octahedral manner (Figure 1a). The bda ligand is tetradentate, with one carboxylate group coordinating to the zinc centre in a bidentate-bridging fashion via O1 and O2, while the other is bidentately chelating via O3 and O4. Two symmetry-related bpee ligands coordinating via N1 and N2 at the apical positions complete the sixth coordination. What is especially noteworthy about this compound is that the two Zn(II) neighbours are connected by two bda ligands through μ_2 -oxo bridge carboxylic oxygen atoms to form an eight-membered cyclic dimer (Zn_2bda_2) with the Zn–Zn distance of 4.0432(6) Å. The carboxyl-bridged dimeric units are extended along the [010] direction by bpee co-ligands to produce 1D coordination polymer with Zn–bpee–Zn separation of 13.7189(6) Å. All the Zn–O bond lengths are between 2.020(4) and 2.384(5) Å ($\text{Zn}-\text{O}_{\text{av}} = 2.140(3)$) and the Zn–N bond lengths are in the range of 2.172(3)–2.185(3) Å (Table S2) and are in agreement with similar compounds in the literature [14–17,21–28]. The polymeric corrugated chains are connected by chelating bda into 2D layered structure as shown in Figure 1b. The second bda ligand connects the layer into a 3D network (Figure 1c). In the isomeric structure reported by Zhang et al. [23], the zinc centre is in four coordination and the 1,3-phenylenediacetate ligand shows *trans-trans*-configuration and adopts bis(monodentate) coordination. Furthermore, in the structural diversity for a series of metal(II) complexes based on flexible 1,2-phenylenediacetate and dipyridyl-type co-ligand reported by Xin et al. [25], the phenylenediacetate anions also adopt a bis(monodentate) coordinated mode that bridges the adjacent Zn(II) atoms to yield an undulating $[\text{Zn}(\text{phda})]_n$ chain. In the present compound, the metal centre is in six coordination and the 1,4-phenylenediacetate ligand bidentately bridges two Zn atoms and the other bidentately chelates one Zn atom. The difference between these compounds is due to the effect of ligand isomerism. The topology of the present compound is similar to $[\text{Co}(\text{phda})(\text{dpe})]_n$ characterized as a six-connected self-penetrated network with (4^86^68) rob topology. It is interesting to note that although the synthesis was solvent-mediated, the solvent molecules could not be located in the lattice.

The infrared spectrum of the as-synthesized compound (Figure S2) shows the characteristic bands of the carboxylates at $1611/1507\text{ cm}^{-1}$ and $1424/1373\text{ cm}^{-1}$, respectively, for asymmetric and symmetric stretching $-\text{CO}_2^-$ vibrations. The separation $\Delta[\nu_{\text{asym}}(\text{CO}_2^-) - \nu_{\text{sym}}(\text{CO}_2^-)]$ values of 187 and 134 cm^{-1} are indicative of chelating and bidentate bridging coordination modes of the carboxylate to the metal centre [29]. The in-plane C–H bending vibrations of the aromatic ring are observed at $1197-1062\text{ cm}^{-1}$, while the out-of-plane C–H bending vibrations appeared in the region $959-721\text{ cm}^{-1}$. Bands in the region $637-451\text{ cm}^{-1}$ are due to Zn–O vibrations.

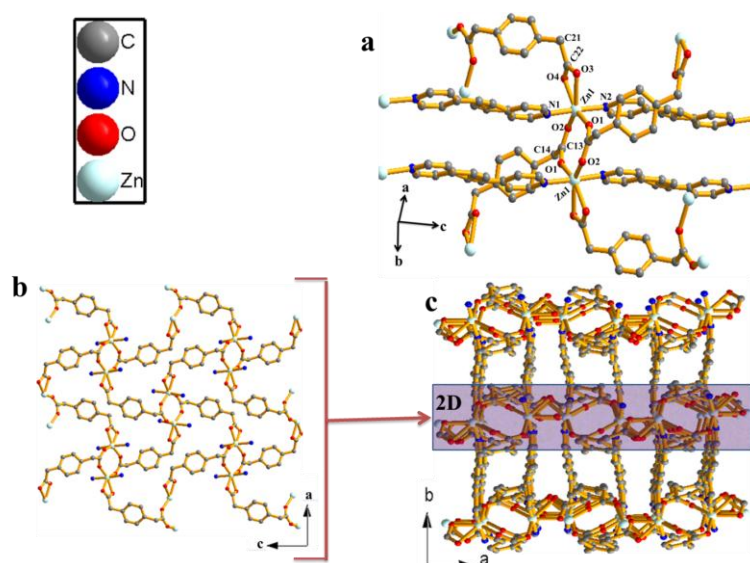


Figure 1. (a) Zn(II) dimeric unit of compound **1**. (b) 2D sheets of compound **1** observed along the b-crystallographic axis). (c) 3D nonporous networks of **1** assembled by connecting 2D layers (hydrogen are omitted for clarity).

3. Materials and Methods

3.1. Materials

The materials were obtained commercially and used without further purification. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 4,4'-bipyridylethelene, 1,4-benzenediacetic acid, distilled water, ethanol, methanol, and acetone were purchased from the Aldrich Chemical Co. (St. Louis, MO, USA).

3.2. Methods

3.2.1. Synthesis of $\text{C}_{22}\text{H}_{18}\text{ZnN}_2\text{O}_4$, **1**

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.50 mmol, 0.149 g) was dissolved in 50 mL of water with constant stirring. Sodium 1,4-benzenediacetate (Na-bda) (0.25 mmol, 0.060 g) and 4,4'-bipyridylethelene (bpee) (0.25 mmol, 0.045 g) were dispersed in 25 mL mixture of water (H_2O) and methanol (CH_3OH) (7:3), respectively, and sonicated for 15 min to make a homogeneous solution. Water/methanol mixture of the ligands (Na-bda and bpee) (2 mL) was slowly and carefully layered on top of the aqueous metal ion [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] solution (2 mL) using the 2 mL buffer solution of water and methanol (7:3) in a crystal tube, which was sealed and left uninterrupted at room temperature. Colourless block type single crystals were grown at the junction of the two different solvents after three weeks. The crystals, which were separated and washed with water and methanol, were found to be air-stable and insoluble in a wide spectrum of solvent. A bulk amount of the compound was synthesized by direct mixing of the corresponding ligands (sodium 1,4-benzenediacetate and 4,4'-bipyridylethelene) solution with a water-methanol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ under stirring for 24 h. Yield: 82%. The PXRD pattern of **1** compared with the simulated pattern from single crystal analyses is presented in Figure S3. Anal. Calcd. For $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_4\text{Zn}$: C, 60.08; H, 4.13; N, 6.37. Found: C, 60.21; H, 4.08; N, 6.41%.

3.2.2. Physical Measurements

The elemental analysis of the compound was carried out on a Thermo Fisher Flash 2000 Elemental Analyzer (ThermoFisher Scientific Warrington, UK). Fourier transformed IR spectroscopic investigation was carried out using a KBr pellet on Bruker IFS-66v (Bruker, Ettlingen, Germany).

3.2.3. Single-Crystal X-ray Diffraction.

A good single crystal of compound **1** was mounted on a thin glass fiber with commercially available super glue. X-ray single-crystal structural data were collected on a Bruker Smart-CCD diffractometer (Bruker AXS, GmbH, Germany) equipped with a normal focus and a 2.4 kW sealed tube X-ray source with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 30 mA. The program SAINT [30] was used for the integration of diffraction profiles, and absorption correction was made with the SADABS [31] program. The structure was solved by SIR 92 [32] and refined by the full-matrix least-squares method using SHELXL [33]. All the hydrogen atoms were fixed by HFIX and placed in ideal positions. The stilbene-type C=C atoms were positionally disordered. The potential solvent accessible area or void space was calculated using the PLATON [34] multipurpose crystallographic software. All crystallographic and structure refinement data of compound **1** is summarized in Table S1. Selected bond lengths and angles for compounds **1** are given in Tables S2, supporting information. All calculations were carried out using SHELXL 97, PLATON, SHELXS 97, and WinGX system, Ver 1.80.05 [35]. Crystal Data for C₂₂H₁₈ZnN₂O₄ (M = 439.77 g/mol): monoclinic, space group P2₁/c (no. 14), a = 10.4566(2) Å, b = 13.3085(2) Å, c = 13.7189(2) Å, $\beta = 101.491(1)^\circ$, V = 1870.88(5) Å³, Z = 4, T = 293(2) K, $\mu(\text{Mo K}\alpha) = 1.346 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.561 \text{ g/cm}^3$, 27316 reflections measured ($3.6^\circ \leq 2\theta \leq 25.9^\circ$), 3791 unique (Rint = 0.060) which were used in all calculations. The final R1 was 0.0400 (I > 2 σ (I)) and wR2 was 0.1557 (all data).

4. Conclusions

We have successfully constructed a Zn(II) coordination polymer under solvent diffusion condition by employing mixed linkers system of 4,4'-bipyridylethene and 1,4-benzenediacetic acid. The compound [Zn(bpee)(bda)]_n, **1**, has a 3D network. We are currently investigating these mixed linkers system with first row transition elements with a view to unravel their magnetic properties; the results will be published elsewhere.

Supplementary Materials: The following are available online at <http://www.mdpi.com/1422-8599/2017/3/M952>, Figure S1: Asymmetric unit of **1**, Figure S2: Infrared spectrum of **1**, Figure S3: Simulated and experimental XRD powder patterns for compound **1**, Table S1: Crystallographic data and structural refinement parameters for compound **1**, Table S2: Selected bond distances and bond angles in **1**. "CCDC 1566264" contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

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Author Contributions: S.A.A. and O.E.O. conceived and designed the experiments; S.A.A. performed the experiments; S.A.A. and A.A.A. analyzed the data; A.A.A. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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