

Synthesis, crystal structure and thermal stability property of Ni(aze)(4,4'-bipy)(H₂O) based on longer-spanning azelaic acid and 4,4'-bipyridine ligands

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Abstract: One new three-dimensional (3D) supramolecular longer-spanning azelaic acid (H₂aze) complex: Ni(aze)(4,4'-bipy)(H₂O) (4,4'-bipy = 4,4'-bipyridine) has been synthesized using hydrothermal conditions and characterized by elemental analysis, IR spectroscopy, UV spectrum, powder X-ray diffraction, TG analysis and single crystal X-ray diffraction. Structural analysis reveals that the title complex is six-coordinate and connected by the azelaic acid and 4,4'-bipy ligands to generate a 2D planar structure, further linked through the interaction of hydrogen bond of C-H...O to form a 3D supramolecular structure.

Supporting information: FT-IR, UV-Vis, X-Ray, Cif file

Keywords: Nickel complex, thermal stability property, 4,4'-bipyridine, azelaic acid.

1. INTRODUCTION

Metal-organic frameworks (MOFs) have become an increasingly important research field in recent years due to their intriguing structural diversity and promising applications such as gas storage, catalysis, ion exchange, magnetism and photoactive materials [1–5]. The MOF materials are normally realized by deliberate design of the ligands with adjustable connectivity and/or the judicious selection of metal ions with a specific coordination tendency, such as solvents used, reaction temperature, pH value and so on. However, to accurately predict and further control the framework array of a given crystalline product remain a considerable challenge at this stage. In all these MOFs, α,ω -dicarboxylates have been widely used as ligands in constructing metal-organic frameworks because they possess interesting features, such as: (i) a wide range of organic linker species [6], (ii) the possibility to obtain mono- or di-anionic forms [7], (iii) the ability to bridge metal transition ions to generate various discrete polynuclear complexes [8], (iv) α,ω -dicarboxylate anions afforded a variety of supramolecular motifs, where the discrete metal-oxygen polyhedron could be interconnected by organic linkers into 1 to 3D arrangements [9–11]. To our knowledge, complexes constructed by such flexible α,ω -dicarboxylate ligands, such as succinate, glutarate, adipate and suberic acid have been extensively reported [12–15]. But reports on the nickel complex with azelaic acid (H₂aze) are very rarely.

In order to enrich the molecular structure of the different longer-spanning flexible α,ω -dicarboxylate ligands, we firstly synthesize a new complex Ni(aze)(4,4'-bipy)(H₂O).

2. EXPERIMENTAL

All starting materials were obtained commercially and used without further purification. Reagent-grade solvents were used without further purification.

All synthetic manipulations were carried out at room temperature. The infrared spectra were recorded on a JASCO FT/IR-480 PLUS Fourier Transform spectrometer with pressed KBr pellets in the range 200–4000 cm⁻¹. The elemental analyses for C, H, and N were carried out on a Perkin Elmer 240C automatic analyzer. UV-Vis absorption spectrum diffuse reflection was recorded with a UV-Vis/NIR/NIR spectrophotometer of JASCO V-570 in the range of 200–2500 nm (solid sample). Thermogravimetric analyses (TGA) were performed under N₂ atmosphere at 1 atm with a heating rate of 10 °C/min on a Perkin Elmer Diamond TG. X-ray powder diffraction (PXRD) patterns were obtained on a Bruker Advance-D8 equipped with Cu K α radiation, in the range 5° < 2 θ < 50°, with a step size of 0.02° (2 θ) and a count time of 2 s per step.

2.1. Preparation of Ni(aze)(4,4'-bipy)(H₂O)

Ni(Ac)₂·6H₂O (0.0490 g, 0.2 mmol), 4,4'-bipy (0.0781 g, 0.5 mmol), H₂aze (0.0753 g, 0.4 mmol) and 15 mL H₂O were mixed in a 25 mL beaker with stirring for 3 h. The mixture was sealed in a Teflon-lined stainless-steel vessel under autogenous pressure and heated to 120 °C for 3 days, then cooled to room temperature. Green crystals suitable for X-ray diffraction were obtained. Yield: 0.0377 g, 45% (based on Ni). Anal. Calc. for C₁₉H₂₄N₂O₅Ni (419.11): C, 54.45; H, 5.77; N, 6.68. Found: C, 54.51; H, 5.82; N, 6.72. IR (KBr pellet, v/cm⁻¹): 3046(s), 2927(m), 2850(m), 1607(s), 1539(s), 1490(m), 1457(m), 1408(s), 1335(w), 1313(m), 1218(m), 1201(m), 1098(w), 1067(w).

2.2. Crystallography

Suitable single crystal of the title complex was mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromatized Mo K α radiation ($\lambda=0.71073$ Å). All the measured independent reflections ($I > 2s(I)$) were used in the structural analyses, and semi-

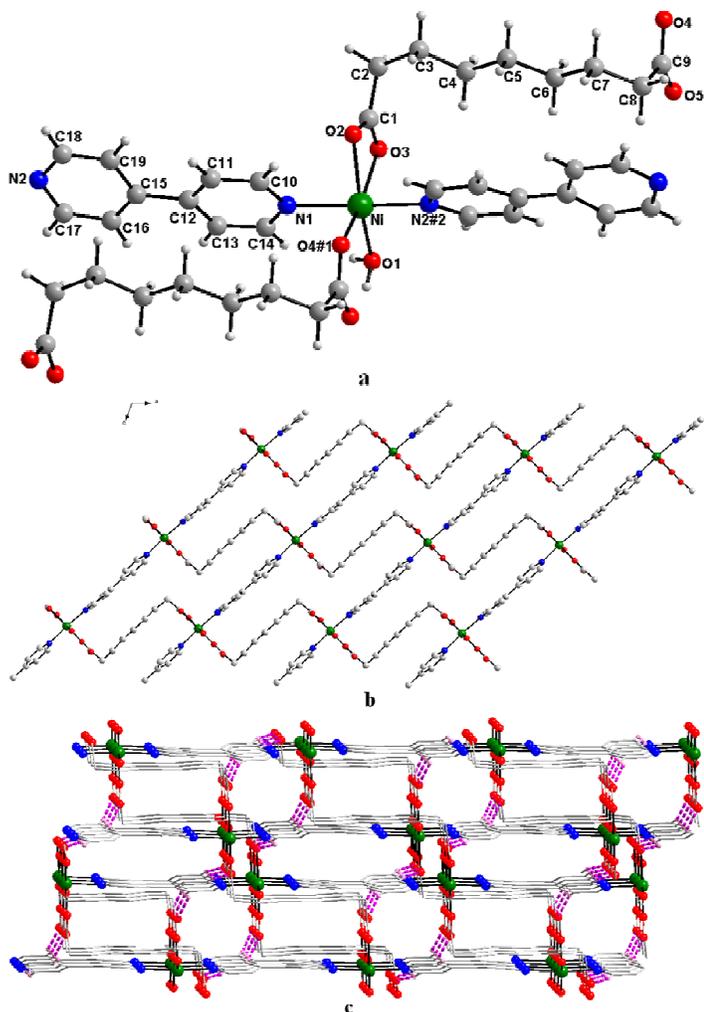


Figure 1: (a) The coordination environment of the title complex; Symmetry operations #1: $x+1, y, z$; #2: $x-1/2, -y+3/2, z+1/2$. (b) The 2D structure of the title complex (All H atoms were omitted for clarity); (c) The 3D hydrogen bonding network structure of the title complex (part of H atoms were omitted for clarity).

empirical absorption corrections were applied using SADABS program [16]. Crystal structure was solved by the direct method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon and nitrogen were fixed at calculated positions and refined by using a riding model. All calculations were performed using the SHELX-97 program [17]. The crystal belongs to monoclinic crystal system, $P2_1/n$ space group with $a=11.234(2)$, $b=11.134(2)$, $c=16.208(3)$ Å, and $\beta=108.27(3)^\circ$ (Table S1). The selected bond lengths and bond angles around metal atoms of the title complex are listed in Table S2.

3. RESULTS AND DISCUSSION

The asymmetric unit of the title complex contains one six-coordinated nickel ion, one H_2 aze ligand, one 4,4'-bipy ligand and one coordinated water molecule (Figure S1). The coordination environment around the nickel ion is shown in Figure 1a. The center metal Ni(II) is surrounded by four oxygen atoms and two nitrogen atoms to form a NiN_2O_4 distorted octahedral geometry, in which three oxygen atoms (O2, O3 and O4#1) are from two H_2 aze ligands and one (O1) is from a coordinated wa-

ter molecule, two nitrogen atoms (N1, N2#2) are from two 4,4'-bipy ligand. Therein Ni-O bond average length is 2.090(4) Å and Ni-N bond average length is 2.112(4) Å, which are similar with that of the related reported [18]. The H_2 aze ligand regards as a m_2 -bridging linker, exhibiting two types of coordinated modes: bidentate and monodentate linking modes. Adjacent Ni atoms are connected by the H_2 aze ligand to form an infinite 1D "M" chain along "a" axis direction (Figure 1b). At the same time, adjacent Ni atoms are also connected by the 4,4'-bipy ligand to form an infinite 1D straight line chain along c axis direction (Figure 1b). Simultaneity, these chains further form a 2D planar structure, that further linked through the interaction of hydrogen bond of $C16-H16A \cdots O5\#3$ (0.23482 nm, 159° , #3: 1-x, 2-y, 1-z) and $C18-H18A \cdots O3\#4$ (0.24507 Å, 172° , #4: 3/2-x, y-1/2, 1/2-z) to form a 3D hydrogen bond network structure in Figure 1c.

The IR spectrum of the title complex exhibits strong absorption bands at 3046 cm^{-1} , showing the presence of the O-H stretching vibration. The absorption peaks at about 2927 and 2850 cm^{-1} are due to the stretching vibrations of the C-H ($-CH_3, -CH_2-$). The absorption at 1607 cm^{-1} is due to the deformable vibration of O-H. The absorptions at 1539 and 1408 cm^{-1} are due to the asymmetric and symmetric stretching vibrations of C=O, which generate red shift through comparison of that of corresponding to the free H_2 aze ligand ($1698, 1407\text{ cm}^{-1}$). Additionally, the bands at $1456, 1416, 1335$ and 1313 cm^{-1} are attributed to the stretching vibrations of the C=N and C=C for the title complex. Moreover, there are several absorption peaks in the range of $1218-1067\text{ cm}^{-1}$, which are assigned to the stretching vibrations of the C-C and C-N. The IR spectra of the title complex and free H_2 aze ligand are shown in Figure S2 and S3, respectively.

The electronic absorption spectra of the title complex are recorded in Figure S4. Bands at 210 and 268 nm are attributed to the $\pi-\pi^*$ transition of 4,4'-bipy ligand. Peak at 418 nm is due to the intra-ligand charge transitions from ligand to metal (LMCT) with $d \rightarrow d^*$ transition (${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$) [19]. Besides, the broad peaks at 706 and 1194 nm could be caused by the $d \rightarrow d^*$ transition of Ni^{2+} cation (${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{2g}$) [19].

Additionally, the composition of the title complex is confirmed by elemental analysis and X-ray powder diffraction (PXRD)

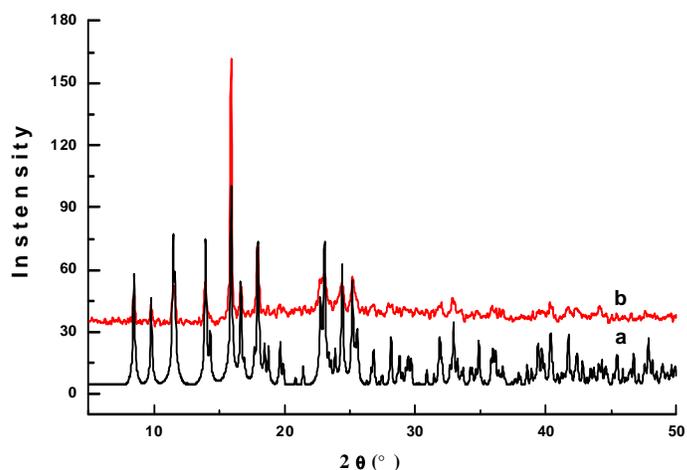


Figure 2: The simulation (a) and experimental (b) XRD spectrum of the title complex

was used to confirm the phase purity of the bulk materials (Figure 2). The experiment results prove that all the peaks presented in the measured patterns closely match the simulated patterns generated from single crystal diffraction data.

To examine the thermal stability of the coordination polymers, thermogravimetric analysis (TGA) were carried out under N₂ atmosphere of the title complex (Figure 3) in the temperature range of 30–1000 °C. Thermal decomposition of the title complex proceeded with three distinct weight losses between 188 and 992 °C. The first weight loss 5.04% was attributed to the departure of one coordinated water molecule (calc.: 4.30 %) in the temperature range of 188–220 °C. The second weight loss 37.88% corresponded to the release of one 4,4'-bipy ligand (calc.: 37.27%) occurred from 220 to 531 °C. The third weight loss 32.87% ascribed to the reduction of the azelaic acid residue (C₈H₁₄O₂, calc.: 33.93%) in the range of 531–992 °C. Finally, the residue could correspond to nickel oxide and carbon residue (obs.: 22.32%; calc.: 24.50%).

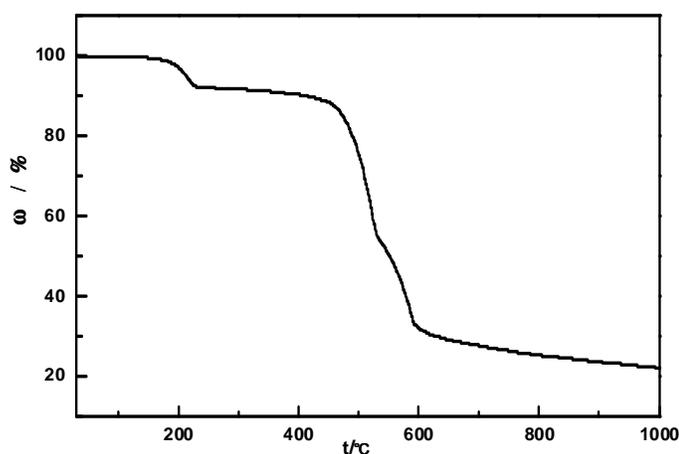


Figure 3: The TG curve for the title complex

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