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Hydro/ Solvothermal Synthesis and Crystal Structure of New Ni(II) Coordination Polymer Containing Pamoic Acid and Ethylenediamine Mixed Ligands : $\{[Ni(\mu\text{-}pam)(en)_2]\cdot H_2O\}_n$

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Abstract: The new coordination polymers arranged from flexible pamoic acid, namely $\{[Ni(\mu\text{-}pam)(en)_2]\cdot H_2O\}_n$ (**1**), (H2pam= pamoic acid, en= ethylenediamine), have been synthesized under hydro/ solvothermal conditions and characterized by elemental analysis, simultaneous TG, DTA techniques, IR spectroscopy, and X-ray crystallography. X-ray single crystal structure analysis of **1** shows that the Ni(II) ions are bridged by pamoic acid ligands to generate 1-dimensional (1D) coordination polymer running parallel to the direction, with the Ni···Ni separation is 14.057 Å. Adjacent 1D chains are connected by N-H···O and O-H···O hydrogen bonds to establishing 3 dimensional (3D) supramolecular network.

Keywords: Hydro/ solvothermal synthesis, coordination polymers, pamoic acid, X-ray crystallography.

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INTRODUCTION

Metal–organic frameworks and coordination polymers, which are called abbreviation MOFs and CPs respectively, have expanded rapidly the last two decades because of promising materials for wide applications. CPs are described as running coordination units extending in all three directions in space. Also, MOFs are defined as a subclass of coordination polymers, with the special feature that they have durable and permanent porosity (1). Cps and MOFs are investigated mainly for fuel gas storage (2-4), separation and purification (5, 6) as well as heterogeneous catalysis (7-9) owing to their low density and high surface area.

As a flexible dicarboxylic acid, pamoic acid is formed of two naphthalene portions which are bound up with a methylene group, which gives hope to facility for creating extraordinary frameworks. This frameworks have different size permanent pores. Magnetic, photoluminescent, and fluorescence properties of new CPs with pyridine derivatives and pamoic acid mixed ligands are investigated (10-14).

In this study at first, the experiment was carried out under hydrothermal conditions with pamoic acid and ethylenediamine ligands were used to obtain the Ni(II) complex, but coordination polymer could not be obtained. Then, to increase the solubility of pamoic acid, chloroform was added with water as a solvent and the experiment was repeated under the hydro/ solvothermal conditions. Coordination polymer was obtained as $\{[Ni(\mu\text{-}pam)(en)_2]\cdot H_2O\}_n$ (1), whose structure is shown in Figure 1. New CPs structure (**1**) exhibits one dimensional chains. This adjacent one dimensional chains are attached by N-H···O and O-H···O hydrogen bonds to forming 3 dimensional (3D) supramolecular network. The structure of the complex **1** is identified by elemental analyses, thermal analyses, IR spectroscopy, and single crystal X-ray diffraction techniques.

MATERIALS AND METHODS

Materials and Physical Measurements

Pamoic acid (Sigma-Aldrich), ethylenediamine (Sigma-Aldrich), $Ni(NO_3)_2.6H_2O$ (Carlo Erba), and chloroform (Merck) were used.

Elemental analysis of compound **1** was carried out by using a CHNS-932 Elemental Analyzer at IBTAM (İnönü University Laboratory). An IR spectrum of **1** was carried out by Perkin-Elmer FT-IR 100 spectrometer in the region of 4000–400 cm^{-1} (at room temperature). The thermal analysis measurements (TG, DTA and DTG) of 1 was carried out by using Perkin-Elmer Diamond Thermal Analysis Instrument with heating rate 10 °C min^{-1} in the temperature range of 30–800 °C (in the static air atmosphere) using platinum crucibles at Eskişehir Osmangazi University.

Preparation of Complex {[Ni(μ-pam)(en)$_2$]·H$_2$O}$_n$ (1)

A mixture of pamoic acid (0.05 g, 0.13 mmol) and $Ni(NO_3)_2.6H_2O$ (0.038 g, 0.13 mmol) were stirred in a mixture of water (10 mL) / chloroform (5 mL) at room temperature for 30 min and then ethylenediamine (0.0086 mL, 0.13 mmol) was added to the mixture. The mixture was placed in a Pyrex bottle and heated at 100 °C for 72 h to obtain Brown-purple crystals. Yield: 0.049 g (65%); Anal. Calc. (found) for $C_{27}H_{32}N_4O_7Ni$: C, 55.59 (55.81); H, 5.53 (5.69); N, 9.52 (10.02); m.p: decomposed without melting.

X-Ray Crystallography

A suitable crystal of **1** was selected for data collection which was performed on a D8-QUEST diffractometer equipped with a graphite-monochromatic Mo-K$_\alpha$ radiation at 296 K. The structure solved methods are given in supplementary materials and details of data collection and crystal structure determinations are given in **Table S1**.

RESULTS AND DISCUSSION

Description of Crystal Structure 1

Selected bonds and angles for **1** are collected in **Table 1** and hydrogen-bond parameters (Å, °) are given in **Table 2**. The X-ray structural analysis reveals that **1** crystallizes in the orthorhombic Fddd space group. The molecular structure of **1** with the atom labeling is shown in **Figure 1**. The asymmetric unit of **1** is formed of one Ni(II) ion, pamoic acid ligand, two ethylenediamine ligand and water molecule. The pamoic acid ligand has the centre of symmetry at the mid-point of the central C-CH$_2$-C angle. The Ni(II) ion is located on a centre of symmetry and is coordinated by two oxygen atoms [Ni1-O1=2.1286(17) Å] from two different pamoic acid ligands and four nitrogen atoms [Ni1-N1=2.087(2) Å and Ni1-N2=2.097(2) Å] from two different ethylenediamine ligands, thus showing a distorted octahedral coordination geometry.

The Ni(II) ions are bridged by pamoic acid ligands to create 1-dimensional coordination polymer running parallel to the [110] direction, with the Ni···Ni separation is 14.057 Å (**Figure 2**). Adjacent 1-dimensional (1D) chains are attached by N-H···O and O-H···O hydrogen bonds to forming 3 dimensional (3D) supramolecular network (**Figure 3**).

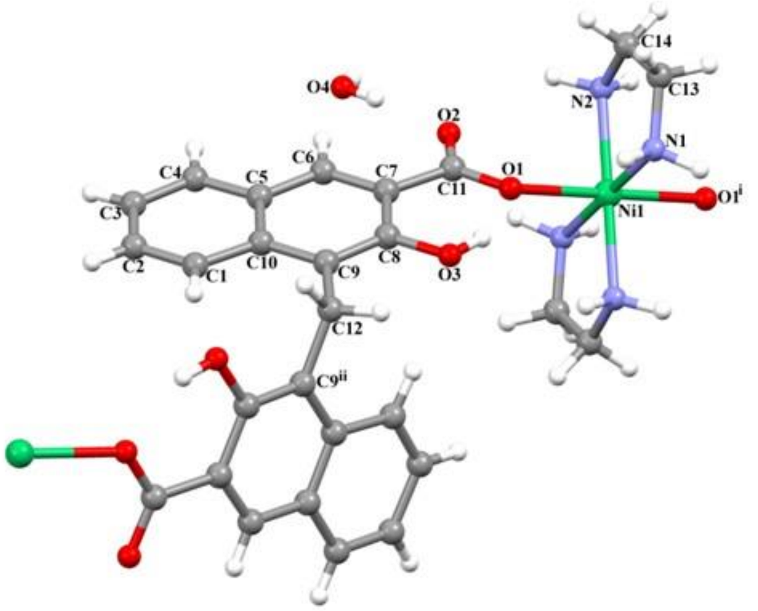

Figure 1: The molecular structure of **1** showing the atom numbering scheme. [(i) -x+3/2, -y+1, -z+3/2; (ii) -x+3/4, -y+3/4, z]

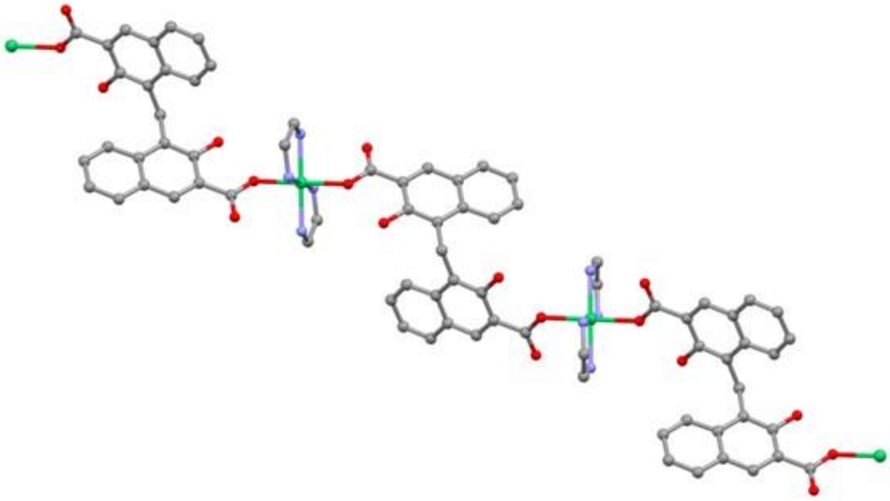

Figure 2: An infinite 1D layer in **1.**

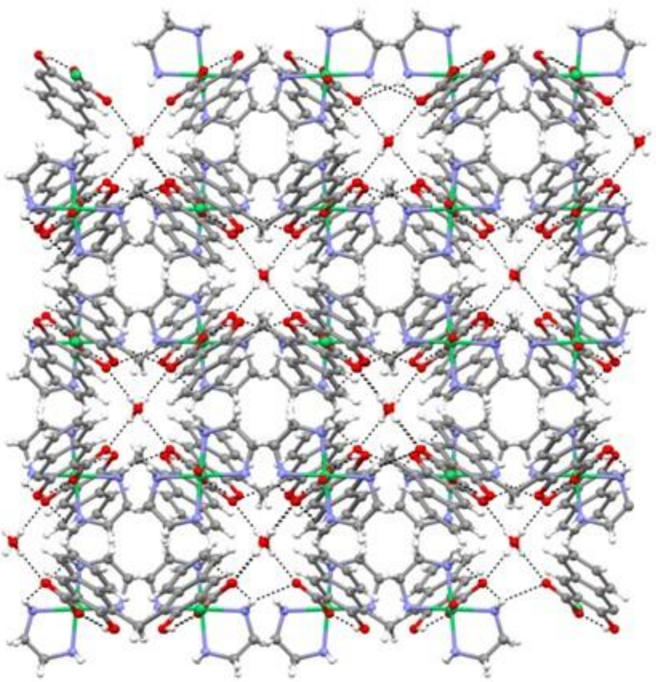

Figure 3: 1D chains are attached by N-H···O and O-H···O hydrogen bonds to forming 3D supramolecular network in **1.**

Table 1 Selected bond distances for **1** (Å, º)

N1-Ni1	2.087(2)	N2-Ni1	2.097(2)	O1-Ni1	2.1286(17)
N1-Ni1-N2	82.83(8)	N1-Ni1-O1	87.62(8)	N1-Ni1-O1^{i}	92.38(8)
N2-Ni1-O1^{i}	87.43(7)	N2-Ni1-O1	92.57(7)		

Symmetry code: (i) -x+3/2, -y+1, -z+3/2.

Table 2 Hydrogen-bond parameters (Å, º)

D-H· · ·A	**D-H**	**H···A**	**D···A**	**D-H···A**
N1—H1B···O2^{i}	0.97	2.43	3.160 (3)	131
N2—H2B···O2	0.97	2.29	3.044 (3)	134
N2—H2B···O2^{iii}	0.97	2.42	3.213 (3)	139
O3—H3A···O1	0.82	1.80	2.543 (2)	149
O4—H4A···O2^{iv}	0.76 (3)	2.05 (3)	2.806 (2)	168

Symmetry codes: (i) −x+3/2, −y+1, −z+3/2; (iii) −x+5/4, −y+5/4, z; (iv) x, −y+5/4, −z+5/4.

IR Spectroscopy and Thermal analysis

In the FT-IR spectra of **1**, the broad bands observed at 3454 cm^{-1} are due to the m(O–H) stretching vibrations of water molecule. For **1**, N–H stretching vibrations are observed in the ranges 3356 and 3290 cm^{-1} and aromatic and aliphatic C–H stretching vibrations are observed in the ranges 3067 cm^{-1} and 2933–2873 cm^{-1} respectively. In the FT-IR spectra of **1**, C=O groups are characteristic for pamoic acid ligand. The strong band observed at 1645 cm^{-1} is attributed to the C=O stretching vibrations of the pamoic acid ligand (C=O stretching vibrations for pamoic acid is 1650 cm^{-1}) (**Fig. S1**).

The thermal analysis of 1D coordination polymer (**1**) was performed by thermal analysis methods (TG, DTA and DTG) in the temperature range of 30-800 ^{o}C. The thermal curves for **1** are given in **Fig. 4**. Thermal decompositions of new coordination polymer (**1**) proceed in the three stages. In the first stages, **1** loses one crystal water molecule in the temperature range of 184-244 ^{o}C [found (calcd.): 3.75% (3.08%)]. 1D chains are attached by O-H···O hydrogen bonds to forming 3D supramolecular network in compound **1** so water molecules firmly bound to crystal lattice with hydrogen bonds and separated from the structure at high temperature. The second stage is concerned with the release of two ethylenediamine ligands as a weak exothermic peak on the DTA curve [DTA_{max}= 300 ^{o}C] between 245 and 334 ^{o}C with a mass loss of 21.79% (calcd. 20.61%) for **1**. In the last stage (334-467 ^{o}C), a strong exothermic peak (DTA_{max}= 395 ^{o}C) is associated with the burning of the pamoic acid ligands. Finally, the product is found to be NiO [found (calcd.): 10.60 (12.80)].

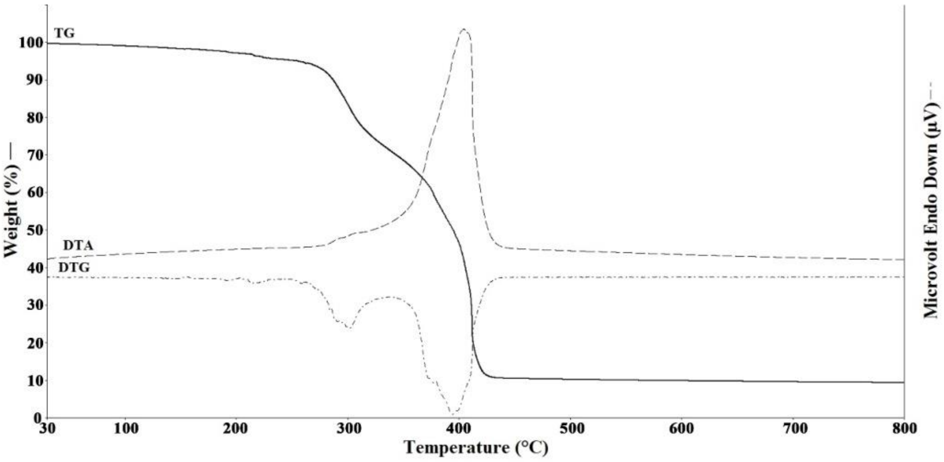

Fig.4 The TG, DTG and DTA curves of **1**

CONCLUSION

In this study, $\{[Ni(\mu\text{-}pam)(en)_2]\cdot H_2O\}_n$ (**1**) was synthesized and characterized. The unrepeatable **1** under hydrothermal conditions was synthesized under hydro / solvothermal conditions by adding chloroform to increase the solubility of pamoic acid. In the complex, the behavior of pamoic acid was an anionic ligand and ethylenediamine was a neutral ligand. New coordination polymer structure exhibits 1D adjacent chains which are attached by N-H···O and O-H···O hydrogen bonds to forming 3D supramolecular network.

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