

## Ni(II) Complex Extended Structures Sustained by Hydrogen Bonding, $\pi$ - $\pi$ and C-H $\cdots$ $\pi$ Interactions

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The complex  $[\text{Ni}(\text{NAA})_2(\text{im})_6](\mathbf{1})$  (where  $\text{H}_2\text{NAA} = \alpha$ -naphthylacetic acid and im = imidazole) has been synthesized under solvothermal conditions. The complex fully characterized by IR spectroscopy, elemental analysis and single crystal X-ray diffraction. In complex  $\mathbf{1}$ , Ni(II) is coordinated by six N atoms with an octahedral coordination geometry. This mononuclear complex is further extended into three-dimensional structure *via*  $\pi$ - $\pi$ , C-H $\cdots$  $\pi$  and hydrogen bonding interactions. The thermal stable property of complex  $\mathbf{1}$  is also reported

**Keywords:** Hydrogen bond, C-H $\cdots$  $\pi$  Interaction,  $\pi$ - $\pi$  Interaction, Thermal stable property.

### INTRODUCTION

The rational design and synthesis of novel coordination polymers have achieved considerable progress in the field of supramolecular chemistry and crystal engineering, owing to their potential applications in gas storage, sensor technology, separation processes, ion exchange, luminescence, magnetism catalysis and nonlinear optics (NLO) and optical limiting capability, as well as their intriguing variety of architectures and topologies<sup>1,2</sup>. The structures of supermolecular complexes rely on several factors, but to select suitable bi- or multi-dentate bridging ligands is no doubt the key factor because it has an obvious influence on the topologies of coordination polymers. However, the assembly reaction not only relies on the interactions between a metal ion and a ligand with rich coordination chemistry,  $\pi$ - $\pi$  and C-H $\cdots$  $\pi$  stacking interactions are also one of the most powerful non-covalent intermolecular interactions in determining the supramolecular architectures, which can result in infinite frameworks of one, two and three dimensions. In recent years the self-assembly of supramolecular architectures by exploiting non-covalent forces including hydrogen bonding, aromatic  $\pi$ - $\pi$  and C-H $\cdots$  $\pi$  stacking interactions, *etc.* has been one of the focuses of solid-state chemistry<sup>3</sup>. The significance of hydrogen bonding has long been recognized in crystal engineering<sup>3,4</sup>, and has emerged to be the most powerful tool among the directional interactions in non-covalent synthesis, which is operative in determining the molecular conformation and supramolecular arrangement in solids<sup>5-8</sup>. In addition,

through-space interactions between aromatic molecules, such as  $\pi$ - $\pi$ , C-H $\cdots$  $\pi$  stacking and metal-ligand coordination interactions have been used. Since these interactions control a variety of molecular recognition and self-assembly processes, they are responsible for crystal packing and the understanding of them contributes to the comprehension of collective properties and allows the design of new supramolecular structures with special physical and chemical properties and functions<sup>9</sup>.  $\alpha$ -Naphthylacetic acid possesses one carboxyl group, which can be used for coordination. In addition,  $\alpha$ -naphthylacetic acid and imidazole may introduce additional  $\pi$ - $\pi$ , C-H $\cdots$  $\pi$  and hydrogen bond interactions in stabilizing the structures of metal-organic frameworks. So, we chose  $\alpha$ -naphthylacetic acid and imidazole to react with corresponding Ni(II) salt under solvothermal conditions  $[\text{Ni}(\text{NAA})_2(\text{im})_6](\mathbf{1})$ .

### EXPERIMENTAL

All reagents commercially available were of reagent grade and used without further purification. Solvents were purified according to the standard methods. C, H and N elements analyses were carried out on a Perkin-Elmer 240C elemental analyzer. FT-IR spectra were recorded on a Vector 22 FT-IR spectrophotometer by using KBr pellet in the range of 4000-400  $\text{cm}^{-1}$ . Thermogravimetric analyses were carried out with a SDT Q600 instrument under 100.0 mL/min flowing nitrogen and ramp rate of 10.00  $^\circ\text{C}/\text{min}$  from 50 to 800  $^\circ\text{C}$ .

**Synthesis of complex  $[\text{Ni}(\text{NAA})_2(\text{im})_6](\mathbf{1})$ :**  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (124.3 mg, 0.5 mmol), imidazole (34 mg, 0.05 mmol) were

TABLE-1  
CRYSTALLOGRAPHIC DATA FOR COMPLEX

m.f.	$C_{42}H_{42}N_{12}NiO_4$	Z	1
Formula weight	837.59	T/K	298(2)
group	$P_1$	$D_c/(g/cm^3)$	1.352
Crystal system	triclinic	F(000)	438
a (Å)	8.1792(11)	$\mu/mm^{-1}$	0.529
b (Å)	9.1130(13)	$R_{int}$	0.0308
c (Å)	14.195(2)	unique reflections	3603
$\alpha$ (°)	96.5550(10)	obsd reflns	2701
$\beta$ (°)	96.530(3)	R1(all data)	0.0631
$\gamma$ (°)	98.955(2)	wR2 (all data)	0.1021
$V/\text{Å}^3$	1029.0(2)	Goodness of fit on $F^2$	1.019

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad wR = \frac{[\sum w(|F_o|^2 - |F_c|^2)]^2}{\sum w(F_o)^2}]^{1/2}, \quad \text{where } w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP], \quad P = (F_o^2 + 2F_c^2)/3.$$

TABLE-2  
SELECTED BOND LENGTHS (Å) AND ANGLES (DEG) FOR COMPLEX

N1-Ni1	2.121(2)	N3-Ni1	2.125(2)
N5-Ni1	2.1118(19)	N5-Ni1#1	2.1118(19)
1N1-Ni #1	2.121(2)	N3-Ni1#1	2.125(2)
N5-Ni1-N5#1	180.000(1)	N5-Ni1-N1#1	89.83(8)
N5-Ni1-N1	90.17(8)	N5#1-Ni1-N1#1	90.17(8)
N5-Ni1-N1#1	89.83(8)	N1-Ni1-N1#1	180.0
N5-Ni1-N3#1	91.19(8)	N5-Ni1-N3	88.81(8)
N1-Ni1-N3	89.56(7)	N1-Ni1-N3#1	90.44(7)
N5#1-Ni1-N3#1	88.81(8)	N5-Ni1-N3#1	91.19(8)
N1-Ni1-N3#1	90.44(7)	N1#1-Ni1-N3#1	89.56(7)
N3-Ni1-N3#1	180.0		

Symmetry transformation used to generate equivalent atoms: #1: -x, 2 - y, -z;

added to 10 mL  $H_2O$  and after being stirred at room temperature for 0.5 h, 10 mL of  $\alpha$ -naphthylacetic acid (186 mg, 1 mmol) methyl in alcohol solution was added to the solution. The mixture was homogenized and transferred into a sealed Teflon-lined solvothermal bomb (volume: 25 mL) and heated to 423 K for 3 days. After cooling to room temperature, title compound was obtained and finally washed with distilled water and followed by absolute ethanol (yield: 48.5 % based on  $C_4H_6O_4Ni \cdot 4H_2O$ ). Anal. calcd. (%) for  $C_{42}H_{42}N_{12}O_4Ni$ : C, 60.17; H, 5.01; N, 20.01; Found (%): C, 59.96; H, 5.12; N, 19.67. IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ): 3134, 3050, 3010, 2921, 2689, 2627, 1582, 1536, 1496, 1448, 1375, 1326, 1253, 1185, 1145, 1071, 940, 900, 830, 786, 748, 665, 624, 539.

**X-ray structure determinations:** The crystal data collection for complex **1** were carried out on a Bruker Smart Apex II CCD at room temperature, using graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques with SHELXL-97<sup>10,11</sup>. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. The hydrogen atoms were generated geometrically. Details of the crystal parameters, data collection and refinement for complexes **1** are summarized in Table-1. Selected bond lengths and angles with their estimated standard deviations for complexes **1** are listed in Table-2 and hydrogen-bonding parameters in Table-3. Crystallographic data for the structure of complex **1** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC- 846978.

TABLE-3  
DISTANCE (Å) AND ANGLES (DEG) OF  
HYDROGEN BONDS FOR THE COMPLEX **1**

D-H $\cdots$ A	Distance (D $\cdots$ A)	Angle (D-H-A)
N2-H2A $\cdots$ O1	2.643(4)	165
N4-H4A $\cdots$ O2#1	2.727(3)	160
N6-H6A $\cdots$ O2#2	2.745(3)	163

## RESULTS AND DISCUSSION

**Structure description:** The crystallographic analysis reveals title complex **1** is a single molecule coordination compound as shown in Fig. 1a, which illustrates the coordination diagram with atomic numbering scheme. Each Ni(II) atom is six-coordinated by six nitrogen atoms from six different imidazole molecules with an octahedral coordination geometry (Fig. 1). The  $NAA^-$  does not take part in coordinating to Ni(II) center, only acting as counter anion. The lengths of Ni(II)-N are in a range from 2.1118(19) to 2.125(2) Å, which means that the Ni(II) atom adopts a distorted octahedral coordination geometry. The packing structure shows a three-dimensional supramolecular network formed *via* intermolecular  $\pi$ - $\pi$ , C-H $\cdots$  $\pi$ , N-H $\cdots$ O hydrogen bonds weak stacking interactions. First, interactions of edge-to-face type interaction exist between imidazole ring centroid and C atom of imidazole with a distance of about 4.439 Å<sup>12</sup>, which links single molecule units to give rise to one dimensional structure (Fig. 2). The hydrogen bonds N6-H6A $\cdots$ O2N2-H2A $\cdots$ O1 and N4-H4A $\cdots$ O2 connects neighbor chain units to form 2D layer structure (Fig. 3) (Table-3). Further, two-dimensional network of **1** is

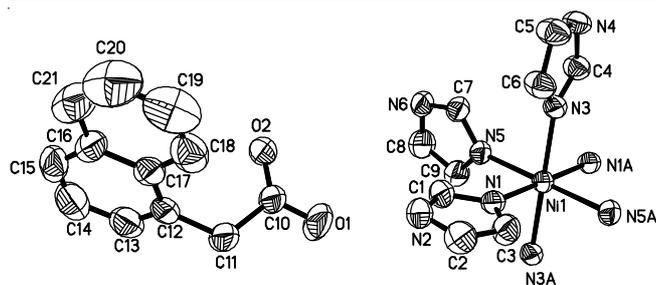


Fig. 1. ORTEP view of coordination environment of Ni(II) atom in **1** with 50 % probability displacement, the hydrogen atoms omitted for clarity. N1A, N3A, N5A:  $-x, 2 - y, -z$

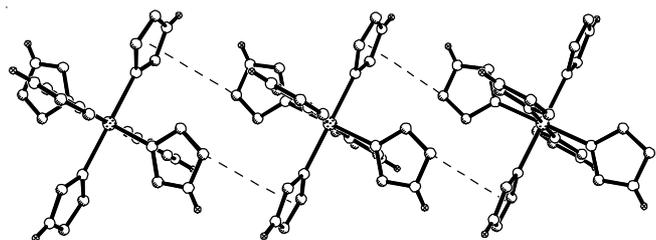


Fig. 2. 1D chain structure in title complex

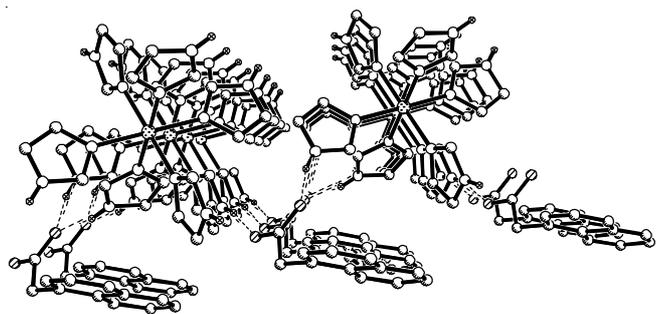


Fig. 3. 2D layer structure in title complex

linked together to generate three-dimensional structure by  $\pi \cdots \pi$  interactions (Fig. 4). The distances of benzene ring centroids between neighbor layers are  $4.091 \text{ \AA}$ .<sup>12</sup>

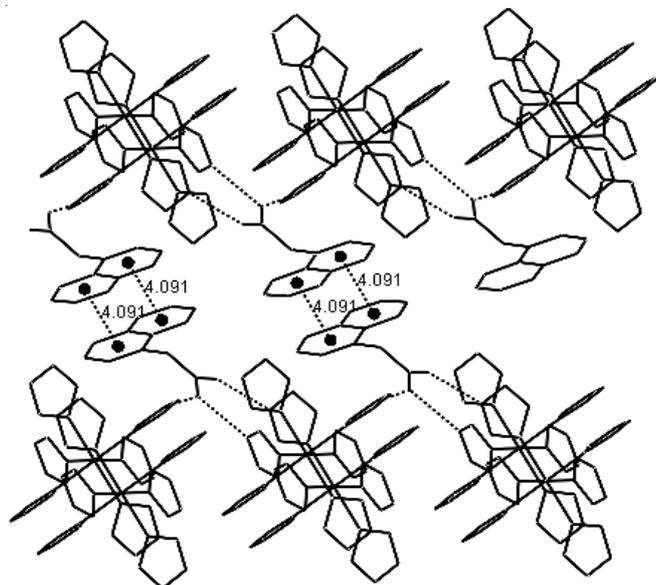


Fig. 4. Crystal packing diagram for title complex

**TG Analysis:** Thermogravimetric experiments were performed to explore thermal stabilities (Fig. 5). In order to examine the thermal stability of complex **1**, a thermogravimetric analysis (TGA) was carried out in the range of room temperature -  $800 \text{ }^\circ\text{C}$ . The TGA curve shows that the thermolytic pathway for complex degradation involves only one step (Fig. 5). The weight loss of 80.53 % below  $381 \text{ }^\circ\text{C}$  is assigned to the liberation of all six coordinated imidazole molecules and two naphthalene molecules owing to decomposition of the ligand naphthaleneacetate, which is in agreement with the calculated value (79.37 %). The residual mass is nickel acetate.

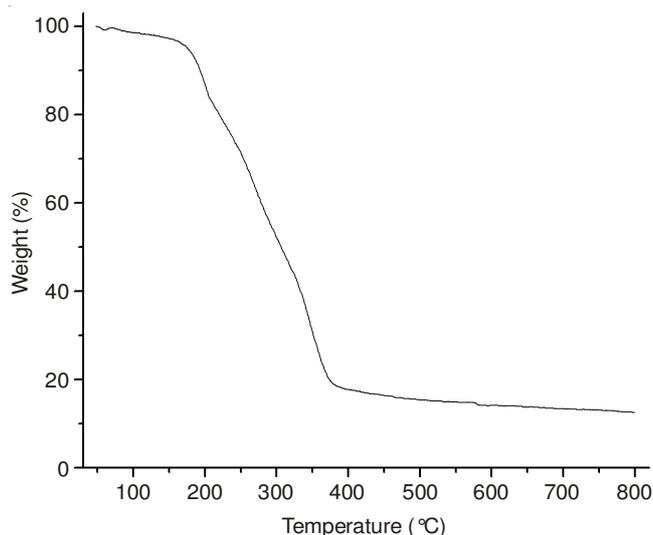


Fig. 5. TG curve of title complex

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