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Synthesis, Structure, and Properties of Binuclear Nickel(II) Complex with Hydrogen Bond and π···π Interaction

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A binuclear nickel complex {[$Ni_2(H_3bptc)_2(bpmp)(H_2O)_4$]·$2H_2O$} (**1**) [$H_4bptc$ = biphenyl-2,3,3',5'-tetracarboxylic acid, bpmp = 1,4-*bis*(2-pyridylmethyl)pipyrazine] was obtained by hydrothermal reaction. Single crystal X-ray diffraction analysis shows that complex **1** crystallizes in triclinic space group P-1 with cell parameters a = 10.4630(11) Å, b = 10.9057(12) Å, c =13.3948(15) Å, α = 73.8070(10)°, β = 72.0600(10) °, γ = 67.7310(10)°, V = 1322.6(2) Å^3, M_r = 593.18, Z = 2, R_1 = 0.0418, and wR_2 = 0.1056. In complex **1**, both Ni ions are six-coordinated to form slightly distorted octahedral coordination geometry. The binuclear symmetric nickel(II) unit containing main ligand H_3bptc^- and auxiliary ligand bpmp is further extended *via* hydrogen bonds and π···π interactions (d = 3.8454 Å) into a 3D supramolecular structure. In addition, complex **1** is also characterized by elemental analyses, IR spectra and thermogravimetric analyses.

Keywords: Dinuclear Ni(II) complex, Hydrogen bond, Crystal structure.

INTRODUCTION

The crystal engineering of supramolecular architectures based on metal-organic frameworks (MOFs) has been rapidly expanding in recent years owing to their novel and diverse topologies and potential applications in host-guest chemistry, catalysis, electrical conductivity, and magnetism[1]. Therefore, the exploitation of new organic linkers plays a vital role in constructing coordination polymers with superior properties. Tetracarboxylate ligands, possessing four potential coordination groups, have been used as ideal organic linkers for building metal-organic frameworks[2-7]. As a member of polycarboxylate ligands, H_4bptc has a rich variety of coordination modes with four carboxylic groups, which may be completely or partially deprotonated upon the pH and help to construct novel coordination polymers with various dimensions and connections. On the other hand, it is a flexible ligand because two phenyl rings can rotate around the C-C single bond, which can be used to construct intriguing coordination polymers because of the non-coplanarity of two phenyl rings[8]. Furthermore, in the process of forming hydrogen bond, multi-carboxylate ligands have been proved to be good candidates because they can be regarded not only as hydrogen-bonding acceptors but also as hydrogen-bonding donors, depending upon the number of deprotonated carboxylic groups[9].

Recently, the "mix-ligand" method in the design of high dimensional metal-organic frameworks has aroused chemists' attention[10,11]. In view of excellent coordination capability of 1,4-*bis*(2-pyridylmethyl)pipyrazine and the good H-donor/acceptor nature of multicarboxylate anions, we employed 1,4-*bis*(2-pyridylmethyl) (bpmp) and 2,3,3',5'- biphenyltetracarboxylic acid (H_4bptc) as mixed organic building units to synthesize a novel supermolecular compound {[$Ni_2(H_3bptc)_2(bpmp)(H_2O)_4$]·$2H_2O$} which was obtained by the assembly of binuclear Ni(II) units *via* hydrogen-bonding and π···π stacking interactions.

EXPERIMENTAL

2,3,3',5'-Biphenyltetracarboxylic acid (H_4bptc) was synthesized according to the literature[12,13]. Other starting materials were of reagent quality and obtained from commercial sources without further purification.

Fourier-transform infrared (FT-IR) spectra (4000-600 cm^{-1}) were collected in the solid state on a Varian 800 FT-IR spectrometer. Elemental analyses (C, H, and N) were carried out on a FLASH 2000 elemental analyzer. High resolution dynamic thermogravimetric analysis (TGA) were performed under N_2 and recorded on a SDT Q600 Thermogravimetric Analyzer with a heating rate of 10 °C per minute.

Synthesis of complex 1: A mixture of H_4bptc (0.033 g, 0.1 mmol), $NiCl_2·6H_2O$ (0.024 g, 0.1 mmol), bpmp (0.027 g, 0.1 mmo1), and H_2O (10 mL) was adjusted to pH 6.5 with 1 M NaOH solution and then heated in a 25 mL Teflon-lined vessel at 165 °C for 4 days, followed by slow cooling (5 °C h^{-1})

TABLE-1
CRYSTAL DATA AND STRUCTURE FOR **1**

Empirical formula	$C_{24}H_{26}N_2O_{12}Ni$	Volume (Å^3), Z	1322.6(2), 2
Formula weight	593.18	Absorption coefficient (mm^{-1})	0.800
Crystal system	Triclinic	F(000)	616
Space group	P-1	Calculated density (g cm^{-3})	1.489
a(Å)	10.4630(11)	R(int)	0.0261
b(Å)	10.9057(12)	Goodness-of-fit on F2	1.066
c(Å)	13.3948(15)	Final R indices ($I > 2\sigma(I)$)	R1 = 0.0418, wR2 = 0.1056
α(°)	73.8070(10)	R indices (all data)	R1 = 0.0558, wR2 = 0.1144
β(°)	72.0600(10)	θ range (°)	2.42 to 25.00
γ(°)	67.7310(10)	Reflections collected	9525
Crystal size (mm)	0.41 × 0.35 × 0.26	Independent reflections	4622

to room temperature.After filtration and washing with H_2O, green block crystals were collected and dried in air (yield about 31.2 % based on bpmp). Anal. Calcd. (%) for $C_{24}H_{26}N_2O_{12}Ni$: C, 48.60; H, 4.39; N, 4.73. Found (%): C, 48.56; H, 4.41; N, 4.74.

X-ray crystallography: The X-ray intensity data for complex **1** were collected on a Bruker SMART APEX CCD diffractometer with MoK_α radiation (λ = 0.71073 Å) at 296 (2) K. The crystal structure was solved by direct methods and refined employing full-matrix least-squares on F^2 (SHELXTL-97). The non-hydrogen atoms were refined with anisotropic displacement parameters, while hydrogen atoms were placed in geometrically calculated positions. Crystal data and refinement conditions are shown in Table-1, and selected bond lengths and angles are listed in Table-2.

TABLE-2
SELECTED BOND LENGTHS (Å) AND
BOND ANGLES (°) FOR COMPLEXES **1**

Bond	d (Å)	Angel	θ (°)
Ni(1)-O(3)	2.049(2)	O(3)-Ni(1)-N(2)	176.62(10)
Ni(1)-N(2)	2.063(3)	O(3)-Ni(1)-O(4)	86.35(9)
Ni(1)-O(4)	2.074(2)	O(4)-Ni(1)-O(8)	164.77(9)
Ni(1)-O(8)	2.084(2)	N(2)-Ni(1)-N(1)	80.87(10)
Ni(1)-N(1)	2.141(2)	O(8)-Ni(1)-O(7)	60.93(8)
Ni(1)-O(7)	2.215(2)	N(1)-Ni(1)-O(7)	158.82(9)

RESULTS AND DISCUSSION

Crystal structure of complex 1: As shown in Fig. 1, the binuclear unit contains two H_3bptc^-, one bpmp molecule, two symmetry equivalent Ni(II) ions, two coordinated water molecules and two lattice water molecules. Both Ni(1) and Ni(1A) coordinated to two oxygen atoms of one carboxylic group from one H_3bptc-ligand, two nitrogen atoms from one bpmp molecule and two oxygen atoms from two water molecules to form a slightly distorted octahedral coordination geometry (relevant bond lengths and bond angels are illustrated in Table-1). Ni(1) connected with Ni(1A) by bpmp ligand, with a Ni(1)···Ni(1A) distance of 6.1196(7) Å. In H_4bptc ligand, only one carboxylic group participate in coordinating to Ni and the other three carboxylic groups can form hydrogen bonds with water molecules of complex 1 by hydroxide radicals. All four nitrogen atoms of bpmp ligand coordinate to two Ni ions, respectively.

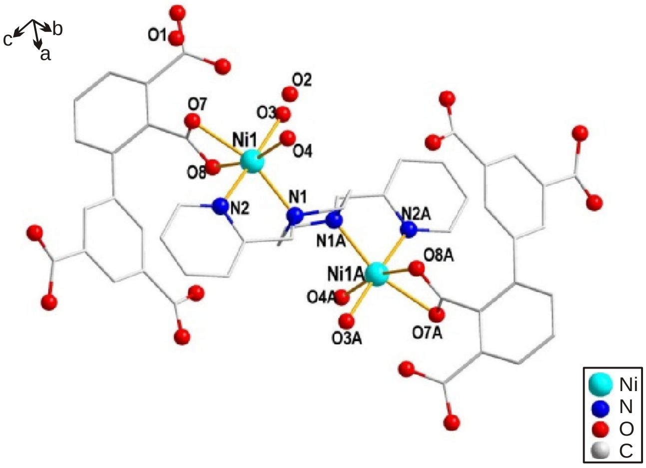

Fig. 1. Coordination environments of Ni(II) in complex **1** and hydrogen atoms are omitted for clarity

This binuclear Ni(II) units are linked each other by multitudinous hydrogen bonds and π···π interaction, which lead to the formation of three-dimensional supramolecular network (Figs. 2 and 3). These hydrogen bonds can be divided into four categories in compound **1**: lattice water molecules O(1W) and O(2W) serve as either H-donor or H-accepter and interact with the carboxylate oxygen atoms O(6), O(7), O(10) and O (12) of H_3bptc- anions *via* hydrogen bonds [O(1W)…O(7) 1.78 Å, O(1W)…O(10) 1.794 Å, O(2W)…O(6) 1.850(4)Å, O(12)…O(2w)1.732 Å]. Similarly, coordinated water molecules serve as H-donor connect with O(5), O(11), O(6) and O(6#5) (#5: -x + 1, -y + 1, -z + 1) of H_3bptc-anions by hydrogen bonds [O(3W)…O(6#5) 1.798 Å, O(3W)…O(6) 1.908 Å, O(4W)…O(5) 1.978 Å, O(4W)…O(11) 1.799 Å]. Another two kinds of hydrogen bonds exist between the carbonyl oxygen atoms of uncoordinated H_3bptc-anions [O(5)…O(9) 1.825Å] and between lattice water molecules [O(1w)…O(2) 1.869 Å], respectively.

As shown in Fig. 3, benzene ring A and B in the stacking structure are almost planar and array in a sliding mode, which further extension of structure through π···π interactions produces a 3D stacking network with centroid-centroid distance being 3.8454 Å. This π-stacking plays an important role to stabilize the packing of complex **1** or form 3D supermolecular structure[3].

IR spectra: Compound **1** shows broad OH stretching bands at 3330-3540 cm^{-1} showing the presence of water molecules

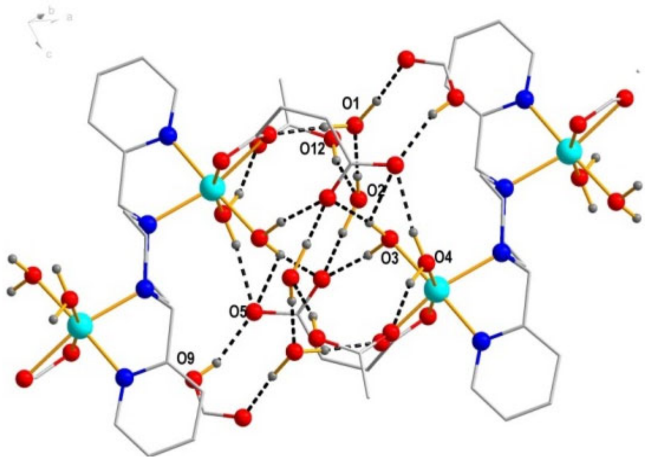

Fig. 2. Intermolecular hydrogen bonds between two neighbouring binuclear Ni(II) units

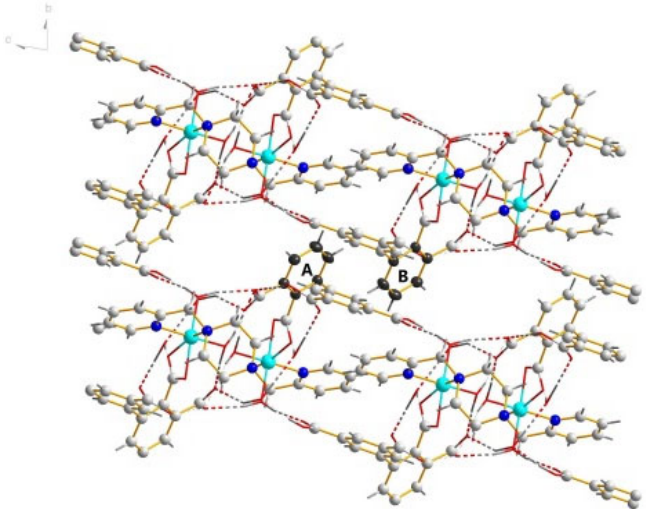

Fig. 3. 3D structure formed by hydrogen bonds and π···π interaction

in the compound. The absorption bands resulting from the skeletal vibrations of the aromatic ring are observed in the 1261-1538 cm^{-1} region[13]. The IR spectra of complex **1** shows characteristic bands of carboxylate groups at 1526 cm^{-1} for the asymmetric stretching and at 1386 cm^{-1} for symmetric stretching. The separation (Δ) between ν_{as}(-COO-) and ν_{s}(-COO-) are 140 cm^{-1}, indicating that carboxylate is coordinated with Ni atoms in a 1,3-bidentate bridging fashion[1]. The presence of the characteristic bands at around 1682 cm^{-1} in compound **1** attributed to the protonated carboxylic group indicates that deprotonation of the H_4bptc ligand is incomplete[11]. These results are also confirmed by single-crystal structure analysis.

Thermal stability analyses: The thermal stability of complex **1** was investigated by thermogravimetric analysis from 18 to 800 °C under nitrogen with a heating rate of 10 °C min^{-1} (Fig. 4). It shows three successive steps in the decomposition process of 1. A total weight loss of 6.14 % occurred over the temperature below 83 °C, corresponding to the loss of two lattice water molecules (calcd. 6.07 %), followed by one-step weight losses of 6.70 % in the range 83-161 °C consistent with the removal of two coordinated water molecules (calcd. 6.07 %). After that, there is a period of heat stability in the range 161-370 °C. The last thermal decomposition process is from 370 to 430 °C with weight loss of 62.08 % corresponding to the decomposition of H_3bptc-and coordinated bpmp ligand (calcd. 61.88 %). The remaining weight may be attributed to the formation of NiO (Obsd. 22.28 %, Calcd. 23.19 %)[14].

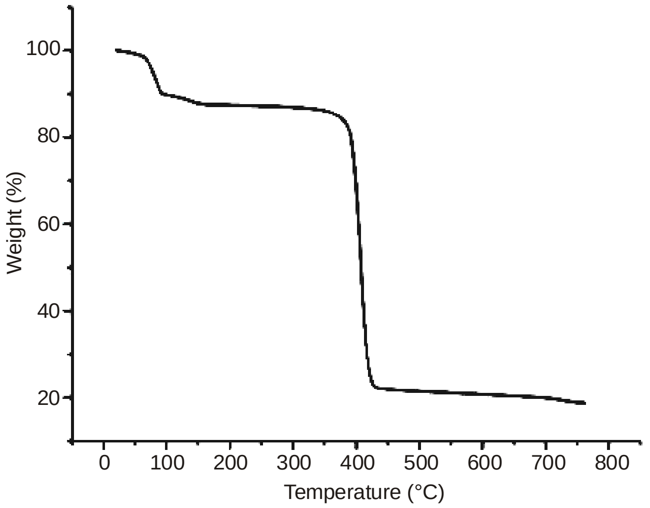

Fig. 4. TG curves for complex **1**

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