

Synthesis and Crystal Structure of Ni(II) Complex with 3-Hydroxyadamantane-1-carboxylic Acid and 4,4'-Bipyridine

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A novel dinickel(II) complex $[\text{Ni}_2(\text{HOC}_{10}\text{H}_{14}\text{COO})_4(\text{H}_2\text{O})(4,4'\text{-bipy})_2]\cdot 7\text{H}_2\text{O}$ (**1**), consisting of monodentate and bidentate coordinated 3-hydroxyadamantane-1-carboxylic acid ($\text{HOC}_{10}\text{H}_{14}\text{COO}^-$) ligand, 4,4'-bipyridine (4,4'-bipy) and water molecules, has been synthesized under hydrothermal conditions and characterized by FTIR spectrum, thermogravimetric analysis and single-crystal X-ray diffraction. It crystallizes in the monoclinic system, space group Pc with $a = 1.1995(3)$ nm, $b = 2.0489(4)$ nm, $c = 1.7595(3)$ nm, $\beta = 132.978(10)^\circ$, $V = 3.1637(11)$ nm³, $Z = 2$, $M_r = 1354.80$, $F(000) = 1440$, $D_c = 1.422$ g cm⁻³, $\mu(\text{MoK}\alpha) = 0.674$ mm⁻¹, the final $R = 0.0614$ and $wR = 0.1012$ for 4245 observed reflections ($I > 2\sigma(I)$). The structure reveals that the complex forms a robust twofold interpenetrated diamond structure net. CCDC: 720487.

Key Words: Ni(II) complex, 3-Hydroxyadamantane-1-carboxylic acid, 4,4'-Bipyridine, Crystal structure.

INTRODUCTION

Secondary building units (SBUs) are molecular complexes and cluster entities in which ligand coordination modes can be utilized in the transformation of these fragments into extended porous networks using polytopic linkers. Consideration of the secondary building units and linkers leads to prediction of novel porous materials with robust structures and high porosity. The great interest in the design and synthesis of coordination polymers with secondary building units is an attractive synthetic approach due to their intriguing network topologies and promising applications in fields such as catalysis, gas storage, molecular magnets, optoelectronic devices, sensors, *etc.*¹⁻⁸. By the choice of versatile bridging organic ligands and appropriate metal ions, numerous 1D⁹, 2D^{10,11} and 3D¹² coordination polymers have been synthesized so far. 2D honeycomb and 3D diamond nets are especially popular because of their high symmetry and aesthetic sense.

In general, the architectures of such supramolecular networks are built-up using multidentate organic ligands containing O- and/or N-donors. To our best of knowledge, one of the best strategies for the rational synthesis of high-dimensional coordination polymer is using the 4,4'-pyridine as a bridging ligand. And with that in mind we choose 4,4'-bipyridine connect with Ni(II) in an attempt to prepare a novel network complex.

Adamantane-1-carboxylic acid has a highly-symmetric and steady structure, which is an effective cure for virus. For

instance, it has an obvious effect on controlling the exuviating the influenza A virus¹³. The fascinating structures of adamantane-1-carboxylic acid complexes coupled with their special functionality catch a lot of chemists' interests¹⁴⁻¹⁷. Recently, we have reported copper and cadmium complexes with 3-hydroxyadamantane-1-carboxylic acid and 1,10-phenanthroline^{18,19}. To the best of our knowledge, the polymer complex using 4,4'-bipyridine as the linker and 3-hydroxyadamantane-1-carboxylic acid as filling agent has not been reported up to the present time. As an extension of our work in this field, we report the synthesis, thermogravimetric analysis and single crystal X-ray diffraction of a new dinickel(II) complex $[\text{Ni}_2(\text{HOC}_{10}\text{H}_{14}\text{COO})_4(\text{H}_2\text{O})(4,4'\text{-bipy})_2]\cdot 7\text{H}_2\text{O}$ (**1**).

EXPERIMENTAL

3-Hydroxyadamantane-1-carboxylic acid was synthesized as reported²⁰ and recrystallized in water and decoloured with activated carbon before using. Other reagents were of analytical grade quality and were used without further purification. Elemental analyses were carried out on Elementar Vario EL III elemental analyzer. The FTIR spectra were obtained from KBr pellets in the range 4000-400 cm⁻¹ with a Nicolet NEXUS 670 FTIR spectrometer. Thermal analyses were carried out using Mettler-Toludolo TGA/SDTA 851e thermal analyzer at a heating rate of 10 °C min⁻¹ from 30 to 800 °C in air atmosphere. Diffraction data were collected at 293(2) K on a Bruker APEXII

CCD diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.071073$ nm).

Synthesis of the Ni(II) complex: A mixture of 3-hydroxyadamantane-1-carboxylic acid (0.3924 g, 2 mmol), Ni(OH) $_2$ (0.0927 g, 1 mmol), 4,4'-bipyridine (0.1562 g, 1 mmol) and water (16 mL) was sealed in a 25 mL stainless steel reactor with a Teflon liner and heated at 433 K for 3 days. On completion of the reaction, the reactor was cooled slowly to room temperature over 3 days. Then the mixture was filtered, giving green single crystals suitable for X-ray analysis. Yield: 91 %. m.p. 201.5–202.0 °C Anal. calcd. for C $_{64}$ H $_{92}$ N $_4$ O $_{20}$ Ni $_2$ (%): C, 56.73; H, 6.84; N, 4.14. Found: C, 57.86; H, 6.91; N, 4.19. IR (KBr, cm $^{-1}$): 3305–3407 (s), 3189 (s), 1622 (s), 1541 (s), 1453 (s), 1399 (s).

Crystal structure determination: A single crystal of the present Ni(II) complex with dimensions of 0.30 mm \times 0.09 mm \times 0.08 mm was selected and mounted on a glass fiber and collected diffraction data on a Bruker Smart APEX II CCD diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.071073$ nm). A total of 16057 reflections were collected in the range of $1.97 < \theta < 27.68^\circ$, of which 11678 were independent ($R_{int} = 0.0947$) and 4246 observed reflections with $I > 2\sigma(I)$ were used in the structure analysis. Corrections for L_p factors and empirical absorption. The structures were solved by direct methods using SHELXS-97 21 and refined with fullmatrix least-squares technique on the F^2 (SHELXL-97 22). The final $R = 0.0614$ and $wR = 0.1012$ [$I > 2\sigma(I)$] ($w = 1/[\sigma^2(F_o)^2 + (0.0000P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$, $S = 0.621$ and $(\Delta/\sigma)_{max} = 0.000$). The maximum and minimum peaks in the final difference Fourier map are 436 and -470 nm $^{-3}$, respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon atoms were positioned geometrically and constrained to ride on their parent atoms. The hydroxyl hydrogen atoms were located in a difference map and refined isotropically. H atoms of waters were found in difference electron-density syntheses and were partly refined using the rigid-body model (AFIX 3). Crystal data and structure refinement parameters are listed in Table-1. The selected bond lengths and bond angles are given in Table-2.

RESULTS AND DISCUSSION

The FTIR spectra of **1** shows absorption bands resulting from the skeletal vibrations of the heteroaromatic rings in 1600–1400 cm $^{-1}$ regions, which verifies the presence of 4,4'-bipyridine. Comparing to the infrared spectra of free 3-hydroxyadamantane-1-carboxylic acid, the characteristic sharp band centered at about 1708 cm $^{-1}$ for $\nu(C=O)$ is vanished and there are four new peaks appear: 1622 cm $^{-1}$ for $\nu_{as}(COO^-)$ and 1399 cm $^{-1}$ for $\nu_s(COO^-)$ of monodentate COO^- ; 1541 and 1453 cm $^{-1}$ for the absorption of bidentate COO^- . This shift suggests the coordination modes of carbonyl oxygen with metal ions. And the broad band at about 3305 cm $^{-1}$ is the characteristic absorption peak of $\nu(OH)$, which proves there are water molecule in this compound. Moreover, the presence of $\nu(Ni-O)$ stretching vibration at 445 cm $^{-1}$ indicates the formation of metal complex.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR **1**

Empirical formula	C $_{64}$ H $_{92}$ N $_4$ O $_{20}$ Ni $_2$
Formula weight	1354.80
Crystal size (mm)	0.300 \times 0.090 \times 0.080
Colour/Shape	Green/block
Temperature (K)	296(2)
Crystal system	Monoclinic
Space group	Pc
a (nm)	1.1995(3)
b (nm)	2.0489(4)
c (nm)	1.7595(3)
β ($^\circ$)	132.978(10)
V (nm 3)	3.1637(11)
Z	2
Dc (g cm $^{-3}$)	1.422
μ (mm $^{-1}$)	0.674
F(000)	1440
θ range ($^\circ$)	$1.97 \leq \theta \leq 27.68^\circ$
Limiting indices	$-15 \leq h \leq 15, -26 \leq k \leq 23, -21 \leq l \leq 22$
Reflections collected	16057
Independent reflections	11677 [$R_{int} = 0.0947$]
Data/restraints/parameters	11677 / 2 / 811
Goodness of fit on F^2	0.612
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0614, wR_2 = 0.1012$
R indices (all data)	$R_1 = 0.1596, wR_2 = 0.1361$
$\Delta\rho_{max}, \Delta\rho_{min}$ (e nm $^{-3}$)	436 and -470

TABLE-2
SELECTED BOND LENGTHS (nm) AND ANGLES ($^\circ$)

Bond	Dist.	Bond	Dist.
Ni(1)-O(10)	0.1992(5)	Ni(2)-O(4)	0.1993(5)
Ni(1)-O(1)	0.2057(5)	Ni(2)-O(7)	0.2036(5)
Ni(1)-O(5)	0.2095(5)	Ni(2)-O(11)	0.2056(5)
Ni(1)-N(1)	0.2103(7)	Ni(2)-O(1W)	0.2107(5)
Ni(1)-N(2)	0.2102(6)	Ni(2)-N(4)	0.2117(7)
Ni(1)-O(1W)	0.2126(5)	Ni(2)-N(3)	0.2135(6)
Angle	($^\circ$)	Angle	($^\circ$)
O(10)-Ni(1)-O(1)	174.6(2)	O(4)-Ni(2)-O(11)	92.7(2)
O(10)-Ni(1)-O(5)	88.5(2)	O(7)-Ni(2)-O(11)	90.2(2)
O(1)-Ni(1)-O(5)	89.2(2)	O(4)-Ni(2)-O(1W)	93.7(2)
O(10)-Ni(1)-N(1)	91.6(3)	O(7)-Ni(2)-O(1W)	90.0(2)
O(1)-Ni(1)-N(1)	90.8(2)	O(11)-Ni(2)-O(1W)	88.00(19)
O(5)-Ni(1)-N(1)	179.9(2)	O(4)-Ni(2)-N(4)	89.3(2)
O(10)-Ni(1)-N(2)	88.1(2)	O(7)-Ni(2)-N(4)	87.1(2)
O(1)-Ni(1)-N(2)	86.9(2)	O(11)-Ni(2)-N(4)	88.6(2)
O(5)-Ni(1)-N(2)	85.9(2)	O(1W)-Ni(2)-N(4)	175.6(2)
N(1)-Ni(1)-N(2)	94.2(2)	O(4)-Ni(2)-N(3)	90.5(2)
O(10)-Ni(1)-O(1W)	94.4(2)	O(7)-Ni(2)-N(3)	86.7(2)
O(1)-Ni(1)-O(1W)	90.5(2)	O(11)-Ni(2)-N(3)	175.7(3)
O(5)-Ni(1)-O(1W)	90.5(2)	O(1W)-Ni(2)-N(3)	88.9(2)
N(1)-Ni(1)-O(1W)	89.4(2)	N(4)-Ni(2)-N(3)	94.3(2)
N(2)-Ni(1)-O(1W)	175.5(2)	Ni(2)-O(1W)-Ni(1)	114.4(3)
O(4)-Ni(2)-O(7)	175.3(2)	—	—

Description of the structure: A single-crystal X-ray diffraction study of this complex reveals the formation of an diamond network constructed from 3-hydroxyadamantane-1-carboxylic anions, 4,4'-bipyridine molecules and Ni(II) cations. The perspective drawing of the molecules with partly atom-labeling scheme is shown in Fig. 1. The structure of **1** is constructed by dinickel centre unit and each unit consists of a

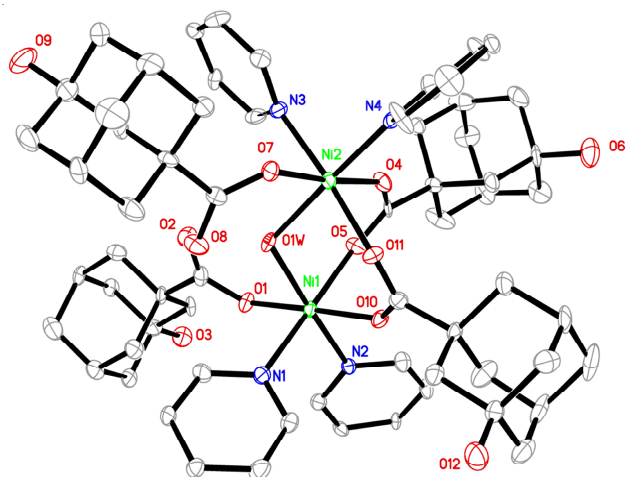


Fig. 1. Thermal ellipsoid diagram of asymmetric unit of compound **1** (30 % probability). Hydrogen atoms and lattice water molecules are omitted for clarity

pair of Ni(II) centres, four 3-hydroxyadamantane-1-carboxylic acid anions ($\text{HOC}_{10}\text{H}_{14}\text{COO}^-$), one water molecule and two bridging 4,4'-bipy ligands. Four $\text{HOC}_{10}\text{H}_{14}\text{COO}^-$ ligands bind to each pair of Ni(II) centre in a flat, two of which bridge the two Ni(II) centres as bidentate bridging ligand, while the other two coordinate to a single Ni(II) centre in monodentate mode. The binuclear unit is further supported by a hydrogen bonding interactions involving the non-coordinated oxygen atoms of the two monodentate $\text{HOC}_{10}\text{H}_{14}\text{COO}^-$ ligands and a bridging water molecule. Two half parts of 4,4'-bipyridine coordinate Ni(1) and Ni(2) from the upside and underside. One coordinate water molecule bridges the Ni(1) and Ni(2) with a similar bond length [$\text{Ni}(1)\text{-O}(1\text{W}) = 0.2126(5)$ nm, $\text{Ni}(2)\text{-O}(1\text{W}) = 0.2107(5)$ nm]. The structure demonstrated that both of the Ni(II) ions coordinate in a distorted octahedral geometry. The Ni-O (from carboxylic and water oxygen) distances are all within the range 0.1992(5)-0.2126(5) nm and the Ni-N distances are almost the same. The central dinickel separation [$\text{Ni}(1)\cdots\text{Ni}(2) = 0.35591(6)$ nm] are similar to the similar complex reported²³. The selected bond lengths and angles for Ni(II) complex **1** are listed in Table-1.

Interestingly, if the coordinate water molecules and the $\text{HOC}_{10}\text{H}_{14}\text{COO}^-$ ligands were omitted, then the left part forms a diamond network. The network model is demonstrated in Fig 2(a). The binuclear centre with the bridging water molecule can be regard as nodes. Four bridging 4,4'-bipy ligands link this binuclear unit to equivalent units and extended in space infinitely to form a diamond-like polymeric structure. The "diamond" stretches along the b-axis in consequence of the arrangement of binuclear units and the angles of N-Ni-N bonds are smaller than $109^\circ 28'$ [$\text{N}(4)(i)\text{-Ni}(2)\text{-N}(3) = 94.3(2)^\circ$, $\text{N}(1)\text{-Ni}(1)\text{-N}(2) = 94.2(2)^\circ$].

Fig. 2(b) illustrates the diamond network structure with the $\text{HOC}_{10}\text{H}_{14}\text{COO}^-$ ligands viewed after a tiny rotation of Fig. 1(a) along the b-axis. The $\text{HOC}_{10}\text{H}_{14}\text{COO}^-$ ligands occupy most spaces of the network. Further analysis of the interpenetrated work voids using the SQUEEZE routine within PLATON²⁴ reveals that lattice water filled the residue space up. This represents *ca.* 13 % of the unit cell volume, which is different with similar reported compound¹².

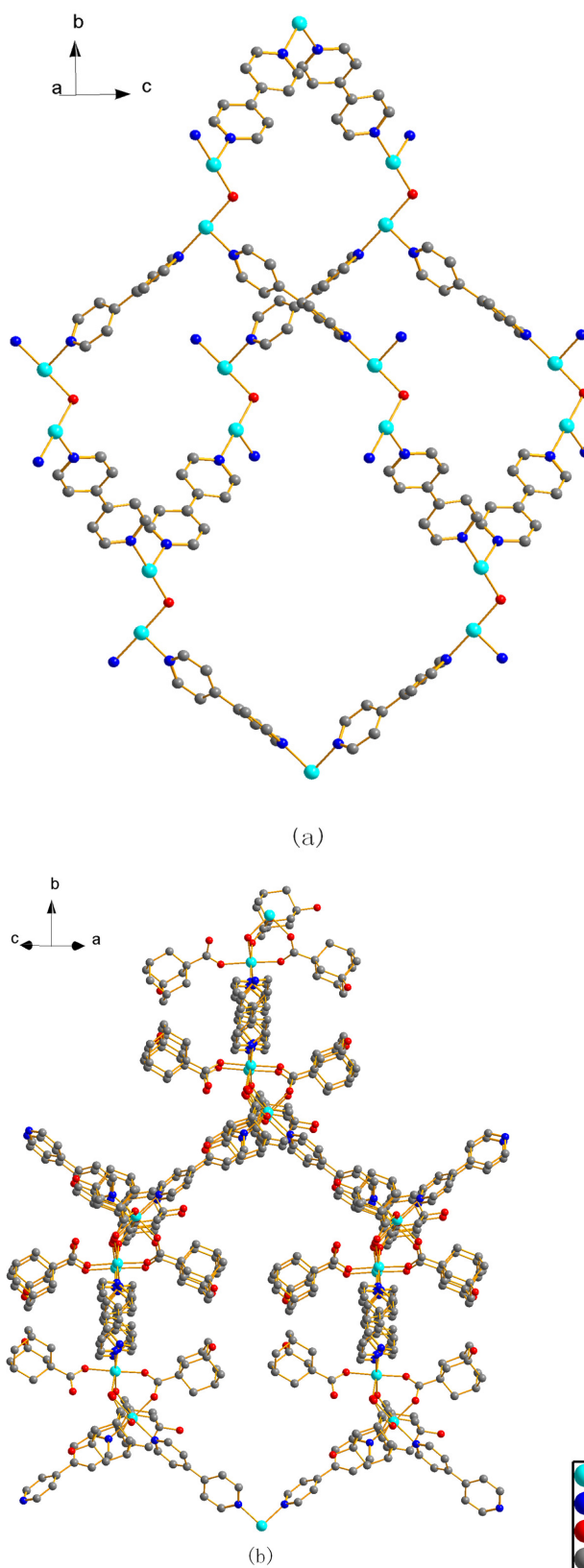


Fig. 2. (a) The diamond-like network structure viewed along the a-axis. (b) The diamond-like network structure viewed from another angle. The H atoms and lattice water molecules are omitted for clarity

Another feature of compound **1** is that the nickel cations are bridged by 4,4'-bipyridine to form twofold interpenetrated diamond structure net (Fig. 3). The single one of the two same twofold interpenetrated nets can be specified by (6,4)-connected

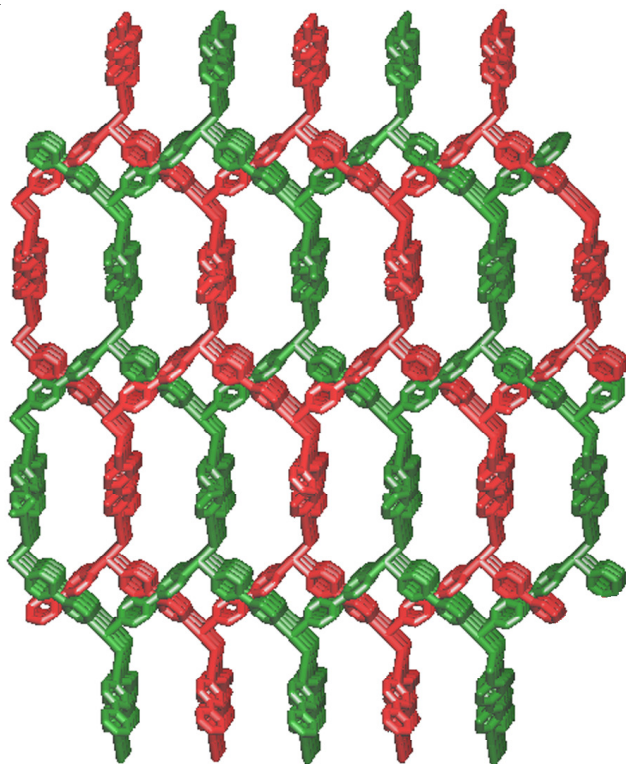


Fig. 3. The two-fold interpenetrated diamond structure net

net, where the 4 indicates the number of different pairs of connections radiating from one node to its neighbors and 6 is the number of these nodes in the shortest ring. The interpenetrated diamond net indicates the stable of the complex.

Thermogravimetric analysis: Thermogravimetric analysis shows that the Ni(II) complex undergoes three weight losses upon heating (Fig. 4). The first is a 9.58 % weight loss at the range of 45 to 190 °C, corresponding to loss of lattice water (theoretical value 9.31 %). The second stage is a 1.07 % weight loss at 210-240 °C, which corresponds to the loss of a coordinated

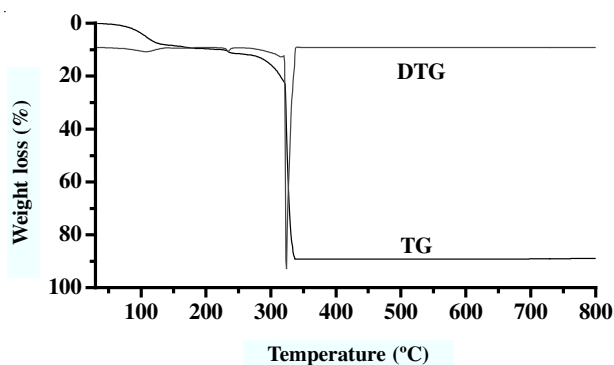


Fig. 4. TG-DTG curves of complex 1

water (calcd. 1.33 %). The release of 4,4'-bipy molecules and $\text{HOC}_{10}\text{H}_{14}\text{COO}^-$ ligands led to the third stage of weight loss of ca. 78.70 % (calcd. 78.33 %) from 240 °C to 337 °C. Finally, the remaining mass of 11.02 %, seems likely to correspond to NiO (calcd. 11.03 %).

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