A Double Chain Metal-organic Framework Constructed by Tetrameric Nickel(II) Units and 1,3,5-Benzenetricarboxylic Trianions

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Abstract. Hydrothermal reaction of nickel sulfate, 1,3,5-benzenetricarboxylic acid and deprotonation agent ethylenediamine yields a metal-organic framework $[Ni_4(\mu^3-OH)_2(H_2O)_{10}(BTC)_2] \cdot H_2O$, which consists of double chains constructed from tetrameric nickel(II) units and 1,3,5-benzenetricarboxylic trianions. Hydrogen bonds and π - π stacking interactions among these chains result in

Introduction

In the last decade, metal-organic frameworks have been investigated extensively due to their potential applications in many areas [1-10]. 1,3,5-benzenetricarboxylic acid (H₃BTC) is one type rigid ligand and has been proved to be versatile for construction of porous materials [11-16]. Recently, our group also reported two BTC-based porous metal-organic frameworks Zn(BTC) · NH₂(CH₃)₂ · DMF and $[Ni(HBTC)(4,4'-bipy) \cdot 3DMF]$ (DMF = N,N'-dimethvlformamide, 4,4'-bipy = 4,4'-bipyridine) prepared under solvothermal conditions [17, 18]. As a part of our ongoing research, we investigated the reactions of Ni²⁺ ions and H₃BTC under hydrothermal condition. A compound formulated as $[Ni_4(\mu^3-OH)_2(H_2O)_{10}(BTC)_2] \cdot H_2O$ (1) has been isolated, which consists of one-dimensional (1D) double chains built up of tetrameric nickel(II) units and 1,3,5-benzenetricarboxylic trianions. Synthesis, structure and magnetic property of the compound are reported here.

Experimental Section

Materials and general methods

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed

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the three-dimensional structure of the compound. Magnetic study reveals there are ferromagnetic interactions among the Ni^{2+} ions of each Ni_4 units in the compound.

Keywords: Metal-organic framework; Double chain; 1,3,5-Benzenetricarboxylic acid; Nickel; Magnetic properties

on a Perkin-Elmer 240C elemental analyzer. IR spectrum was recorded in the range 400–4000 cm⁻¹ on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N₂ with a heating rate of 10 °C/min. Powder X-ray diffraction measurement was performed on a Rigaku D/MAX-3 instrument with Cu-K α radiation in the angular range $2\theta = 3-90^{\circ}$ at 293 K. Magnetic susceptibility data were collected over the temperature range 2-300 K at a magnetic field of 5000 Oe on a Quantum Design MPMS-5 SQUID magnetometer.

Preparation of 1

A mixture of NiSO₄·6H₂O (1.5 mmol, 0.394 g), H₃BTC (1 mmol, 0.210 g), ethylenediamine (1.5 mmol, 0.1 mL) and water (10 mL) was sealed in a Teflon-lined autoclave and heated at 160 °C for 4 days, followed by slow cooling to room temperature. Compound **1** was collected as green block crystals with a yield about 0.255 g (77 % based on Ni). $C_{18}H_{30}Ni_4O_{25}$ (881.26); C 24.21 (calc. 24.53); H 3.71 (3.43) %.

X-ray crystallography

Diffraction intensities for compound 1 was collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo-K α monochromated radiation ($\lambda = 0.71073$ Å) at 283 K. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. H atoms on C atoms are placed in calculated positions and refined in the riding model approximation with C-H = 0.93 Å and $U_{\rm iso}(\rm H) = 1.2$ $U_{\rm eq}(\rm C)$. H atoms for coordinated water molecule and hydroxide ion were located in a difference Fourier map, and fixed with lengths of O-H bonds in the range of 0.83 to 0.87 Å and $U_{\rm iso}(\rm H) = 1.2$



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 Table 1
 Crystal data and structure refinement parameters for 1.

| C ₁₈ H ₃₀ Ni ₄ O ₂₅ |
|---|
| 881.26 |
| 283(2) |
| 0.71073 |
| monoclinic |
| C2/c (No. 15) |
| 19.862(4) |
| 13.024(3) |
| 13.120(3) |
| 125.98(3) |
| 2746.4(10) |
| 4 |
| 3.12-25.00 |
| $-23 \le h \le 23, -15 \le k \le 15, -15 \le l \le 15$ |
| 1800 |
| 2.131 |
| 2.814 |
| 10457 |
| 2409 |
| 1719 |
| 0.1128 |
| 2409 / 0 / 217 |
| 1.103 |
| $R1 = 0.0621^{a}, wR2 = 0.1212^{b}$ |
| $R1 = 0.0924^{\rm a}, wR2 = 0.1373^{\rm b}$ |
| 0.696 and -0.874 |
| |

^{a)} $R1 = \Sigma ||F_o| - |F_c||\Sigma |F_o|$. ^{b)} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 |\Sigma w(F_o^2)^2|^{1/2}; w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, where $P = (Max (F_o^2, 0) + 2F_c^2)/3$, a = 0.0423, b = 23.62.

Table 2 Selected bond lengths /Å and angles /° for1.

| Ni(1)-O(7) | 1.994(5) | Ni(1)-O(1W) | 2.074(5) |
|---|---|---|--|
| Ni(1)-O(5) | 2.033(5) | Ni(1)-O(1) | 2.105(5) |
| Ni(1)-O(2W) | 2.064(5) | Ni(1)-O(3W) | 2.120(5) |
| Ni(2)-O(6) | 2.023(5) | Ni(2)-O(7)#1 | 2.064(5) |
| Ni(2)-O(2) | 2.054(5) | Ni(2)-O(4W) | 2.070(5) |
| Ni(2)-O(7) | 2.059(5) | Ni(2)-O(5W) | 2.149(5) |
| O(7)-Ni(1)-O(2W) O(5)-Ni(1)-O(2W) O(7)-Ni(1)-O(1W) O(5)-Ni(1)-O(1W) O(2W)-Ni(1)-O(1W) O(7)-Ni(1)-O(1) O(7)-Ni(1)-O(1) O(7)-Ni(1)-O(1) O(6)-Ni(2)-O(2) O(6)-Ni(2)-O(7) O(2)-Ni(2)-O(7) | $\begin{array}{c} 88.54(19)\\ 93.9(2)\\ 93.9(2)\\ 171.3(2)\\ 88.7(2)\\ 94.65(19)\\ 90.72(19)\\ 94.4(2)\\ 174.4(2)\\ 174.4(2)\\ 90.18(19)\\ 92.01(19) \end{array}$ | O(2W)-Ni(1)-O(1) O(1W)-Ni(1)-O(3W) O(5)-Ni(1)-O(3W) O(2W)-Ni(1)-O(3W) O(1W)-Ni(1)-O(3W) O(1W)-Ni(1)-O(3W) O(1)-Ni(1)-O(3W) O(4W)-Ni(2)-O(5W) O(2)-Ni(2)-O(4W) O(7)#1-Ni(2)-O(4W) | 174.2(2) 86.2(2) 176.4(2) 82.0(2) 91.0(2) 89.6(2) 86.2(2) 85.9(2) 86.9(2) 97.4(2) 175.5(2) |
| O(6)-Ni(2)-O(7)#1 | 96.7(2) | O(6)-Ni(2)-O(5W) | 87.8(2) |
| O(2)-Ni(2)-O(7)#1 | 88.6(2) | O(2)-Ni(2)-O(5W) | 90.3(2) |
| O(7)-Ni(2)-O(7)#1 | 82.79(19) | O(7)-Ni(2)-O(5W) | 176.0(2) |
| O(6)-Ni(2)-O(4W) | 87.7(2) | O(7)#1-Ni(2)-O(5W) | 94.02(19) |

Symmetry transformations used to generate equivalent atoms: #1 - x + 1/2, -y + 1/2, -z.

 $U_{eq}(O)$. The lattice water (O6W) molecule is disordered at two positions and set half-occupied, hydrogen atoms on which were not located. Details of the crystal data and final structure refinements of the compound 1 are summarized in Table 1. Selected bond lengths and angles for 1 are listed in Table 2 and hydrogen bond parameters are in Table 3. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 646309. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (internat.) + 44-1223-336-033;

Table 3Hydrogen bond parameters for 1.

| D-H···A | $\mathrm{d}(D\mathrm{-H})/\mathrm{\mathring{A}}$ | $d(H^{\dots}A)/\mathring{A}$ | $d(D^{\dots}A)/\mathring{A}$ | ∠(DHA) /° |
|-----------------------------|--|------------------------------|------------------------------|-----------|
| O1W-H1A…O6W | 0.85 | 1.96 | 2.806 (17) | 175 |
| O1W-H1B····O3 ⁱ | 0.84 | 2.00 | 2.628 (7) | 132 |
| O3W-H3A···O3 ⁱ | 0.83 | 2.16 | 2.789 (8) | 133 |
| O3W-H3A…O4 ⁱⁱ | 0.83 | 2.45 | 2.964 (8) | 121 |
| O7-H1…O6W | 0.84 | 2.43 | 3.18 (2) | 149 |
| O7-H1···O6W ⁱⁱⁱ | 0.84 | 2.54 | 3.320 (19) | 156 |
| O5W-H5A···O3 ^{iv} | 0.87 | 2.07 | 2.745 (7) | 134 |
| O2W-H2A···O5W ^v | 0.84 | 2.01 | 2.755 (7) | 147 |
| O4W-H4A…O1 | 0.84 | 2.06 | 2.781 (7) | 143 |
| O5W-H5B…O1vi | 0.85 | 2.27 | 3.012 (7) | 145 |
| O2W-H2B····O4 ⁱⁱ | 0.84 | 1.85 | 2.652 (7) | 158 |
| | | | | |

Symmetry codes: (i) x+1/2, -y+3/2, z+1/2; (ii) -x+1/2, -y+3/2, -z; (iii) -x+1, y, -z+1/2; (iv) -x, -y+1, -z; (v) -x+1/2, -y+1/2, -z; (vi) -x+1/2, y-1/2, -z+1/2.

e-mail: deposit@ccdc.cam.ac.uk). The powder X-ray diffraction pattern for bulk sample of 1 agrees well with that simulated from the single-crystal data. The diffraction peaks on both experimental and simulated patterns match well in positions, indicating its phase purity. (see Supporting information Fig. 2S)

Results and Discussion

Synthesis and structure

The key for good yield of **1** is the quantity of the deprotonation agent ethylenediamine (en) added into the reaction system. We noted that if excessive en was added, only homogeneous purple solution can be obtained after reaction. It may be solution of stable complex $[Ni(en)_3]^{2+}$. We attempted to prepare **1** with NaOH, KOH or some other organic amine (such as piperazine and triethylene diamine) instead of en, however, failed. It may be related the coordination peculiarity and deprotonation ability of en.

Single-crystal X-ray diffraction study reveals that compound 1 consists of 1D double chains, which are constructed by tetrameric nickel units $[Ni_4(CO_2)_4(\mu^3-OH)_2(H_2O)_{10}]$ (Ni₄) and BTC ligands. There are two crystallographic independent nickel (Ni1, Ni2) centers and one type of BTC ligand in the structure. Ni1 coordinate with two carboxyl O atoms from two BTC ligands, a hydroxide ion (O7) and three additional water molecules (O1W, O2W, O3W), adopting a slight distorted octahedral coordination with lengths of Ni-O bonds ranging from 1.994(5) to 2.120(5) Å. (Fig. 1)



Fig. 1 Perspective view of the Ni_4 unit. All H atoms have not been shown for clarity.



Fig. 2 Perspective view of the double chain with Ni_4 units represented by polyhedra. All H atoms have not been shown for clarity.

Ni2 coordinate with two carboxyl O atoms from two BTC ligands, two hydroxide ions and two additional water molecules (O4W, O5W), a slight distorted octahedral coordination too, with lengths of Ni-O bonds ranging from 2.023(5) to 2.149(5) Å. Two Ni1 and two Ni2 atoms, which are both related by an inversion center, respectively, are locked by four carboxyl groups and two hydroxide ions, forming a Ni₄ unit. In the Ni₄ unit, each carboxyl group is chelating two Ni atoms in di-monodentate fashion and each hydroxide ion is bridging three Ni atoms. For each BTC ligand in 1, two carboxyl groups are coordinated with four Ni atoms from two Ni₄ units, while the other one is deprotonated too, however, uncoordinated with any Ni atom. Two such BTC ligands are together bridging two Ni₄ units, with their benzene rings separated about 3.3025 Å [19], and each Ni₄ unit connects four BTC ligands, resulting in a unique 1D double chain along a axis. (Fig. 2) Hydrogen bond interactions among the uncoordinated carboxyl O atoms and water molecules from neighboring chains (O1W-O3 =2.628(7) Å, O2W-O4 = 2.652(7) Å, O3W-O3 = 2.789(8) Å, O3W-O4 = 2.964(8) Å) result in a two-dimensional layer along *ab* plane. (see Supporting information Fig. 3S) Such layers further stack along c axis, forming the three-dimensional structure of 1 through hydrogen bonds and π - π stacking interactions. Hydrogen bonds between adjacent layers are among the water molecules and carboxyl O atoms from neighboring layers (O5W-O1 = 3.012(7) A, O5W-O3 = 2.745(7) Å), and π - π stacking interactions derive from the benzene rings among adjacent layers separated about 3.167 A. There is one type of channel along c axis in the structure after the layers stacking, where one lattice water molecule per formula (O6W) resides. (Fig. 3) It is stabilized by hydrogen bond interactions with surrounding hydroxide ions and water molecules (O1W) (O6W-O1W = 2.806(1) A, O6W-O7 = 3.180(2) or 3.320(1) Å.

Magnetic property

The variation of the molar magnetic susceptibility χ_m was investigated for 1 in the temperature range 2-300 K. At room temperature, the product $\chi_m T$ value (4.46 cm³ K mol⁻¹) is slightly lower than the expected value (4.71 cm³ K mol⁻¹, assuming g = 2.17 [20]) of four noninteracting S = 1 Ni²⁺ ions in a tetrameric unit. When temperature



Fig. 3 Perspective view of 3D supramolecular structure of 1 stacked by double chains along c axis. Lattice water molecules are represented by space filling model. All H atoms have not been shown for clarity.



Fig. 4 Temperature dependence of $\chi_m T$ for 1.

decreases, the product $\chi_m T$ continuously increase and reach a maximum (6.19 cm³ K mol⁻¹) at 9 K, followed by an abrupt drop of $\chi_m T$ value to 4.11 cm³ K mol⁻¹ at 2 K. (Fig. 4) The maximum is obviously lower than the value (11.77 cm³ K mol⁻¹) of a totally populated nonuple ground state for each Ni₄ unit. These results indicate weak ferromagnetic interactions exist among the intra-cluster Ni²⁺ ions. The sudden decrease of $\chi_m T$ in low temperature range may be for the zero-field splitting of the Ni²⁺ ions or/and weak antiferromagnetic interactions among these Ni₄ units [21, 22]. The magnetic data of **1** obey the Curie-Weiss law in the temperature range measured, and fitting of the data gives values of C = 4.41 cm³ K mol⁻¹ and $\theta = 3.12$ K.



Fig. 5 TG curve of compound 1.

Thermogravimetric analysis

The thermogravimetric analysis (TGA) curve recorded at 20-600 °C reveals that there are two step weight losses for compound **1**. (Fig. 5) The first stage occurred between 20 and 360 °C is corresponded to the detachment of one lattice water and ten coordinated water molecules per formula. (weight loss: calc., 22.4 %; found, 21.9 %) The second step from 360 to 445 °C results from the breaking down of BTC ligands. Final species is corresponded to NiO from 445 to 600 °C. (weight: calc., 33.9 %; found, 34.3 %)

Conclusion

Structure analysis of **1** provides some information for our future works. Though the ligand H_3BTC can be totally deprotonated in the reaction system, its carboxyl groups did not exhibit strong coordination ability with Ni²⁺ ions. Consequently, some coordination sites of the Ni²⁺ ions were occupied by water molecules, which prevent the metalorganic framework from extending into higher dimensions. It is also suggested that when lower dimensional metal-organic framework is formed, hydrogen bonds and π - π stacking interactions play an important role in growing of the crystalline compound.

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