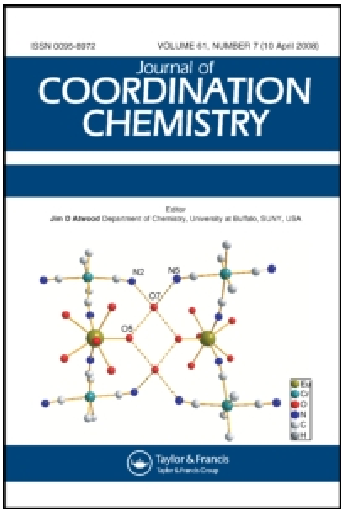

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Synthesis and characterization of a nickel-organic framework encapsulating hetero-chiral helical water chains in the 1-D channels

Cui-Juan Wang[a]; Ping-Di Ren[a]; Zhi-Bin Zhang[a]; Yi-Fang[a]; Yao-Yu Wang[b]
[a] Department of Chemistry and Chemical Engineering, School of Life Science and Bioengineering, SouthWest JiaoTong University, Sichuan 610031, P.R. China [b] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Department of Chemistry, Northwest University, Shaanxi 710069, P.R. China

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Synthesis and characterization of a nickel-organic framework encapsulating hetero-chiral helical water chains in the 1-D channels

CUI-JUAN WANG*†, PING-DI REN†, ZHI-BIN ZHANG†,
YI-FANG† and YAO-YU WANG*‡

†Department of Chemistry and Chemical Engineering, School of Life Science and
Bioengineering, SouthWest JiaoTong University, Chengdu, Sichuan 610031, P.R. China
‡Key Laboratory of Synthetic and Natural Functional Molecule
Chemistry of Ministry of Education, Department of Chemistry,
Northwest University, Xian, Shaanxi 710069, P.R. China

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A porous coordination polymer based on nickel(II) and rigid multitopic ligands, $\{[\mathrm{Ni(dpdapt)(BDC)(H_2O)}]\cdot 3.5\mathrm{H_2O}\}_n$ (**1**) (dpdapt = N, N′-di(2-pyridyl)-2,4-diamino-6-phenyl-1,3,5-triazine), has been synthesized and characterized. Compound **1** crystallizes in the space group *C*2/*m* and possesses a 3-D open framework with 1-D rhombic hydrophilic channels, in which hetero-chiral helical water chains are located. Two 1-D water chains are further stabilized by hydrogen-bonding interactions with the host, inducing a 10-oxygen ring propagated along the channel. TGA, PXRD analyses, and magnetic properties have also been studied.

Keywords: Nickel; Rigid multitopic ligands; MOFs; Hydrophilic channels; Water chains

1. Introduction

The design and construction of metal-organic frameworks (MOFs) is of interest in supramolecular chemistry and crystal engineering with the promise of being able to design new materials with tailor-made properties [1–3]. Coordination polymers also constitute a fascinating branch of fundamental structural chemistry [4]. Transition-metal clusters were linked *via* polycarboxylate organic anions to form coordination polymers exhibiting large cavities and low densities [5]. However, crystal engineering of MOFs has challenges including control of the architecture of building blocks and

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*Corresponding authors. Email: ejuan6046@163.com; wyaoyu@nwu.edu.cn

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functionalization of the pores for a special target material [6]. Water chains appear to be important [7, 8] in control of proton fluxes in a variety of biomolecules and also to facilitate selective permeation of water across membranes. However, hydrogen-bonded chains of water molecules in abiological molecules are rare [9]. Rational design of MOFs for property oriented crystal engineering is of high interest [10, 11].

Rigid multitopic ligands are often employed to construct MOFs with special topologies due to the predictability of the resulting networks. We reported five copper(II) compounds with mononuclear and chain structures based on N,N′-di(2-pyridyl)-2,4-diamino-6-phenyl-1,3,5-triazine (dpdapt) and H_2dhbd (2, 3-dihydroxybutanedioic dianion) [12]. To extend our work, here terephthalic acid (BDC = 1, 4-benzene dicarboxylate) is our coligand, which has been widely used in constructing MOFs by Férey *et al.* [13a], Rosy *et al.* [13b], Li *et al.* [13c, d], and others. BDC is a long bridging spacer, propitious to connect dpdapt with large cavities and multicarboxylates generate diverse coordination modes, which provide for structures of high dimensions. As a result, large cavities, rich topologies, and dimensionalities of coordination polymers may result from these two ligands.

Herein, we describe the synthesis and characterization of the porous coordination polymer $\{[\mathrm{Ni(dpdapt)(BDC)(H_2O)}]\cdot 3.5\mathrm{H_2O}\}_n$ (**1**), which forms 1-D polymeric chains, which form a 2-D layer in the *bc* plane with superposition. Layers are accumulated along the *c*-axis yielding a 3-D framework with 1-D open rhombic hydrophilic channels. A remarkable feature for the compound is the presence of two hetero-chiral helical water chains in these hydrophilic channels.

2. Experimental

2.1. *Materials and physical measurements*

All reagents and solvents were commercially available and used as received. Infrared spectra as KBr pellets were recorded on a Nicolet 170SX FT-IR spectrophotometer from 4000 to 400 $\mathrm{cm^{-1}}$. Electronic spectra were taken on a Cary 300 Bio UV-Visible spectrophotometer from 200 to 800 nm at ambient temperature. Elemental analysis was conducted with a Perkin–Elmer model 240C instrument. Thermal analysis was performed on a NETZSCH STA 449C microanalyzer in nitrogen at a heating rate of 10°C $\mathrm{min^{-1}}$.

2.2. *Synthesis of* $\{[\mathrm{Ni(dpdapt)(BDC)(H_2O)}]\cdot 3.5\mathrm{H_2O}\}_n$ *(1)*

A mixture of $\mathrm{Ni(NO_3)_2}$ (0.5 mmol), dpdapt (0.5 mmol), terephthalic acid sodium (0.5 mmol), and water (10 mL) was stirred for 30 min in air, then transferred and sealed in a 25 mL Teflon-lined autoclave, which was heated at 130°C for 96 h. After the sample was slowly cooled to room temperature, green block crystals of **1** were filtered off, washed with distilled water, and dried at ambient temperature (yield: 78% based on dpdapt). Anal. Calcd for $\mathrm{C_{27}H_{30}N_7NiO_{8.50}}$: C, 50.10; H, 4.67; N, 15.14. Found: C, 50.02; H, 4.56; N, 15.26%. IR (KBr, $\mathrm{cm^{-1}}$) ν: 3305 m, 3066 m, 1640 m, 1581 s, 1468 s, 1435 s, 1384 s, 1239 w, 1157 w, 839 w, and 770 m.

Table 1. Crystallographic parameters for **1**.

Crystal data	$\{[\mathrm{Ni(dpdapt)(BDC)(H_2O)}]\cdot 3.5\mathrm{H_2O}\}_n$
Empirical formula	$C_{27}H_{30}N_7NiO_{8.50}$
Formula weight	647.29
Crystal system	Monoclinic
Space group	$C2/m$
Unit cell dimensions (Å, °)	
a	20.1767(1)
b	18.3953(1)
c	9.7443(7)
β	105.393(5)
V (Å^3)	3486.9(4)
Z	4
D_{Calcd} (g cm^{-3})	1.233
μ(mm^{-1})	0.609
$F(000)$	1348
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0691, 0.1696
R_1, wR_2 (all data)	0.1046, 0.2003

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Ni(1)–N(3)	2.020(5)
Ni(1)–O(1)	2.074(3)
Ni(1)–O(1A)#1	2.074(3)
Ni(1)–N(1)	2.089(4)
Ni(1)–N(1A)#1	2.089(4)
Ni(1)–O(3)	2.096(5)
N(3)–Ni(1)–O(1)	90.82(2)
N(3)–Ni(1)–O(1A)#1	90.82(2)
O(1)–Ni(1)–O(1A)#1	88.28(2)
N(3)–Ni(1)–N(1A)#1	83.97(2)
O(1)–Ni(1)–N(1A)#1	171.54(2)
N(3)–Ni(1)–N(1)	83.97(2)
O(1)–Ni(1)–N(1)	85.15(1)
O(1A)#1–Ni(1)–N(1)	171.54(2)
N(1A)#1–Ni(1)–N(1)	100.9(2)
N(3)–Ni(1)–O(3)	177.28(2)
O(1)–Ni(1)–O(3)	91.16(3)
N(1A)#1–Ni(1)–O(3A)	94.29(2)
N(1)–Ni(1)–O(3)	94.29(2)

Symmetry codes: #1: x, $-y$, z.

2.3. *Crystallographic data collection and structure determination*

Single-crystal X-ray diffraction of **1** was performed on a BRUKER SMART 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection. Crystallographic data were collected with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 296(2) K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-97 and SHELXL-97 [14, 15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions. Crystal data, data collection, and refinement parameters are shown in table 1 and selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Structure of* $\{[Ni(dpdapt)(BDC)(H_2O)]\cdot 3.5H_2O\}_n$ *(1)*

Single-crystal X-ray diffraction reveals that **1** crystallizes in the monoclinic space group *C2/m*. Each crystallographic unit consists of one nickel(II), one dpdapt, one 1,4-BDC, one coordinated water, and 3.5 lattice water molecules. Each nickel has a slightly distorted octahedral environment with equatorial plane with two oxygens from two different carboxylates (Ni(1)–O 2.074(3) Å) and two nitrogens of dpdapt (Ni(1)–N 2.089(4) Å). Nitrogens from the triazine ring and another coordinated water occupy the apical sites, as shown in figure 1. The axial Ni–O distance (Ni(1)–O(3) 2.096(5) Å) is longer than those in the equatorial plane. For 1,4-BDC, the two carboxylates are monodentate to Ni. The Ni atoms are linked to form chains running along the *b* direction (figure 2). The dpdapt groups, grafted on chains, are like lateral arms protruding from two sides. In the packing arrangement of **1**, two chains are interconnected with interweaving arrangement generating a pseudo-interlaced double chain in the *bc* plane (figure 3a). The close of chains is achieved *via* π–π stacking interactions between phenyl rings, with separation of 3.8 Å between ring centroids. Two chains are connected by π–π stacking interactions (the nearest distance is 3.339 Å) between triazine rings, making a 2-D layer in the *bc* plane like a butterfly (figure 3b). Furthermore, the layers are accumulated along the *c*-axis yielding a 3-D framework with 1-D open rhombic hydrophilic channels.

A notable feature for the compound is the presence of two hetero-chiral helical water chains in these hydrophilic channels. Among various types of water clusters, 1-D chain arrangement is of interest because of their occurrence in biological processes related to water and ion transport [16, 17]. As shown in figure 4(a), the left-handed (M) helical water chain with a pitch of 9.744 Å running along crystallographic 2_1 screw axis, and

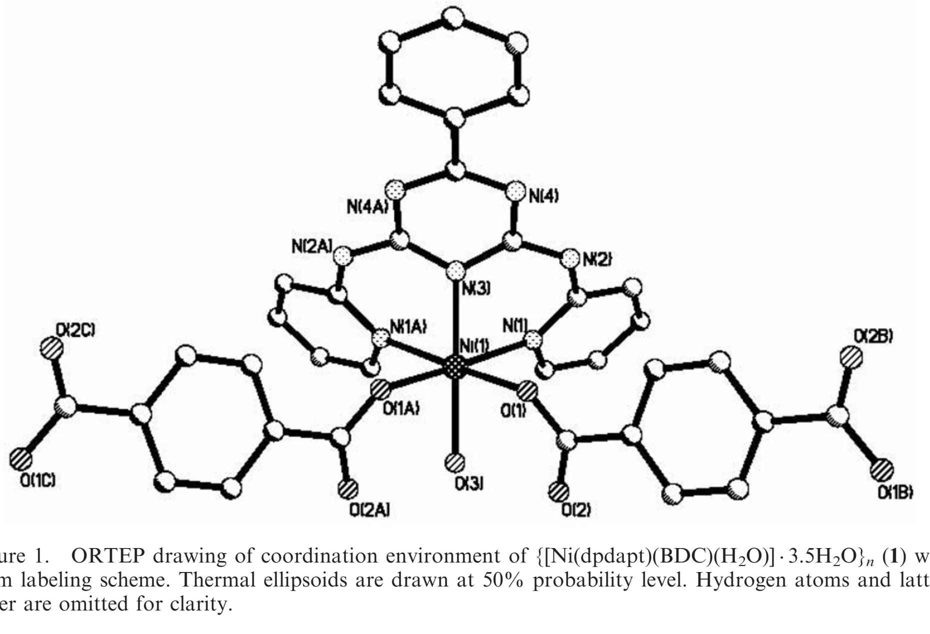

Figure 1. ORTEP drawing of coordination environment of $\{[Ni(dpdapt)(BDC)(H_2O)]\cdot 3.5H_2O\}_n$ (**1**) with atom labeling scheme. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms and lattice water are omitted for clarity.

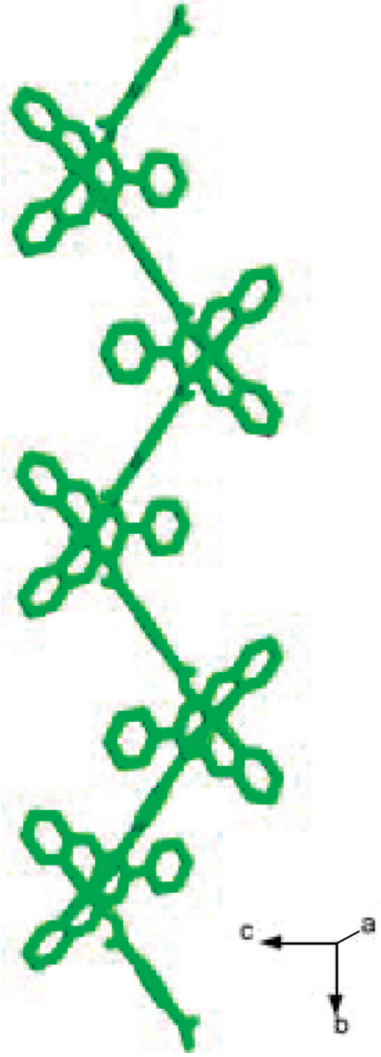

Figure 2. View of a polymeric chain of **1** along the crystallographic *b*-axis (hydrogen atoms and lattice water are omitted for clarity).

two types of lattice water molecules (OW(5), OW(4)) in the water chain are arranged in an AABB (OW(5) · · · OW(5) · · · OW(4) · · · OW(4)) fashion. The water chains are stabilized by hydrogen bonds. The interatomic distance and angles for the hydrogen-bonding interactions in water are presented in table 3. Each water in the chain forms two hydrogen bonds, one as a donor and the other as an acceptor, with OW(5) · · ·OW(5) · · · OW(4) · · · OW(4) distances being 2.838(2), 2.945(1), and 2.849(1) Å, respectively. The angles OW(5)–OW(5)–OW(4) and OW(5)–OW(4)–OW(4) in the water helix are 120.55(2) and 116.72(2)°, respectively. Moreover, the right-handed (P) helical water chain in this channel with 2_1 screw axis also connects with OW(5) and OW(4) in AABB fashion by hydrogen bonds. The hetero-chiral water chain coexistence in one channel constitutes a potentially important form of water that is poorly understood [18].

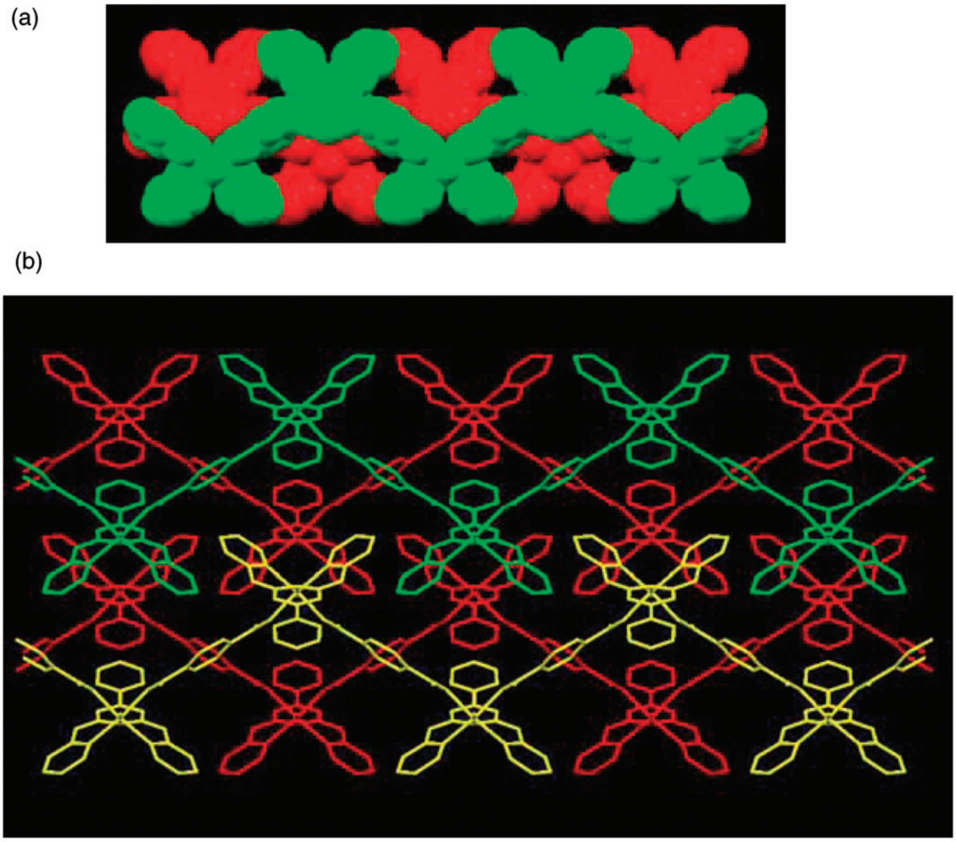

Figure 3. (a) A perspective view of pseudo-interlaced double chains in the *bc* plane. (b) A 2-D layer in the *bc* plane like a butterfly. Hydrogen atoms and lattice water are omitted for clarity.

Many fundamental biological processes appear to depend on unique properties of water chains [19]. However, the structural constraints in stabilizing 1-D water chains have not been fully illustrated [20]. The two 1-D water chains are further stabilized by OW(5)$\cdots$O(2) and OW(5)$\cdots$O(2A) (2.834(2) Å) hydrogen bonds between water molecules and non-coordinated carboxylate oxygen O(2), with intermolecular hydrogen bonds O(2)$\cdots$O(3) (coordinated water), thus inducing a 10-membered oxygen ring (OW(5)$\cdots$O(2)$\cdots$O(3)$\cdots$O(2A)$\cdots$OW(5)$\cdots$OW(5)$\cdots$O(2A)$\cdots$O(3)$\cdots$O(2)$\cdots$OW(5)). The OW(6) appends to this oxygen ring by hydrogen bond interaction (2.770 Å) with O(3). Figure 4(b) shows the packing of 10-membered oxygen rings propagated along the channel, emphasizing the left (purple) and right (yellow) handed helices. Channels in **1** possess approximate dimensions of 17.04 × 17.04 Å (atom-to-atom), occupied by water chains (figure 5). Calculations using PLATON [21] reveal that the open channels constitute about 37.1% (1292.0 Å^3 out of 3486.9 Å^3) of the crystal volume.

3.2. *Magnetic properties*

The temperature dependence of the magnetic susceptibility χ_M and $\chi_M T$ for **1** are shown in figure 6. The experimental $\chi_M T$ value at 300 K is 1.11 cm^3 mol^{-1} K, slightly

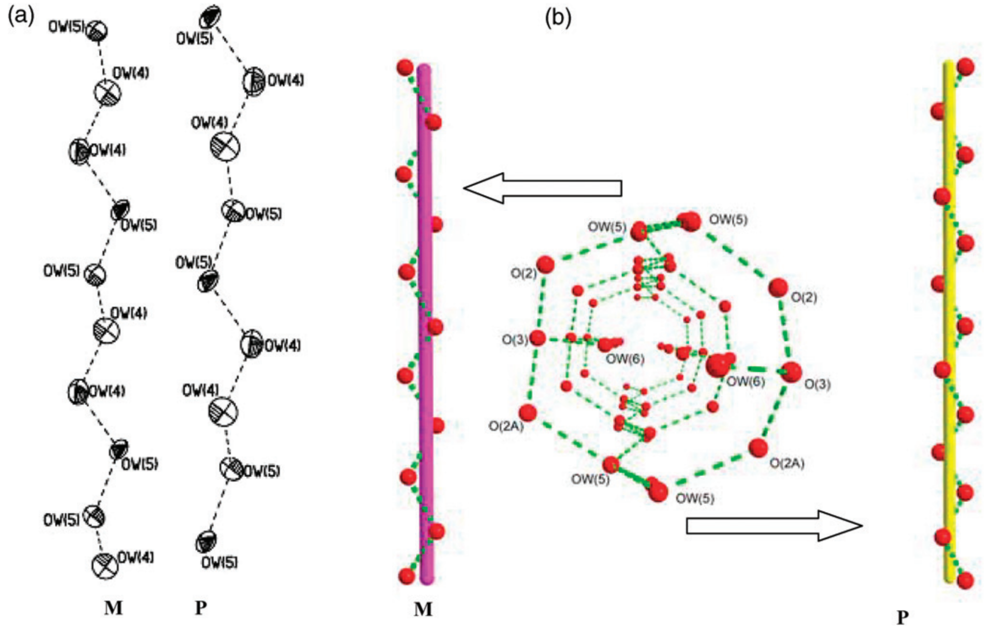

Figure 4. (a) A view of the two hetero-chiral helical water chains in the 1-D channel. The left (M) is a left-handed helical chain with 2_1 screw axis and the right (P) is a right-handed helical chain running along the *c*-axis, (b) the packing of the 10-membered oxygen ring propagated along the channel, emphasizing the left (purple) and right (yellow) handed helix chains.

Table 3. Hydrogen-bonded parameters in **1**.

O–H···O	O···O (Å)	∠O···O···O	
OW5–H5WA···OW4	2.945(1)	OW5···OW5···OW4	120.55(2)
OW5–H5WB···OW5	2.838(2)	OW5···OW4···OW4	116.72(2)
OW4–H4WB···OW4	2.849(1)		
OW4–H4WA···OW5	2.945(1)		
OW6–H6WA···O3	2.770(3)		
OW5–H5WA···O2	2.834(2)		

larger than the spin value expected for nickel(II) ($1.0\,\mathrm{cm^3\,mol^{-1}\,K}$). The $\chi_M T$ value gradually decreases with decrease in temperature, suggesting the presence of antiferromagnetic interactions between nickel(II) centers. Fitting this curve to the Curie–Weiss law $[1/\chi_M = (T-\theta)/C]$ gives a Curie–Weiss constant $C = 1.12\,\mathrm{cm^3\,K\,mol^{-1}}$, and a Weiss temperature θ of $-0.5\,\mathrm{K}$ for **1** with an agreement factor $R = 1.7\times10^{-4}$, where $R = \Sigma[(1/\chi_M)_{\mathrm{obs}} - (1/\chi_M)_{\mathrm{calc}}]^2/\Sigma[(1/\chi_M)_{\mathrm{obs}}]^2$. The χ_M data are interpreted using the isotropic nickle(II) chain spin Hamiltonian ($S = 1$ and $H_{\mathrm{chain}} = -J\Sigma(S_iS_{i+1})$ [22]) and fitted to equation (1) by neglecting zero-field splitting and the Haldane gap effect [23].

$$\chi_M^J = \frac{N\beta^2 g^2 S(S+1)}{3kT}\frac{1+u}{1-u}$$

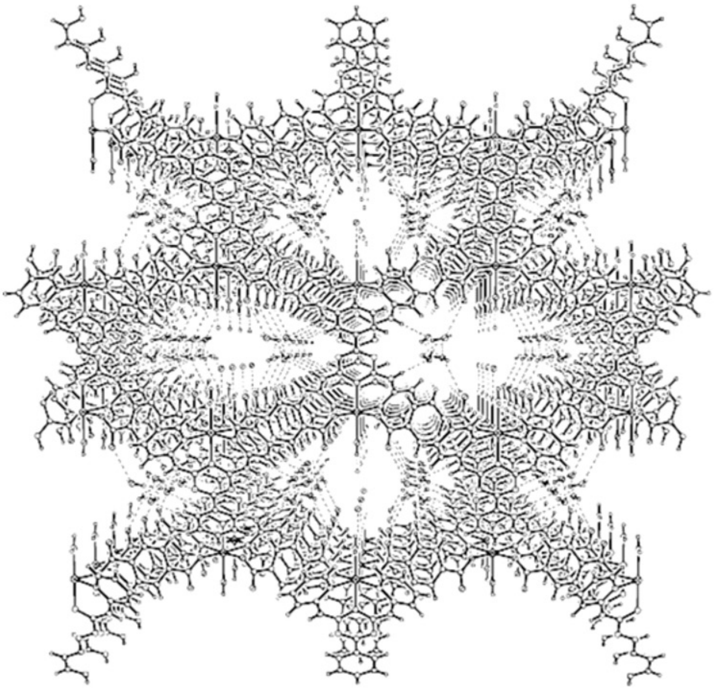

Figure 5. The packing arrangement of **1** along the *c* axis with water molecules in the channels.

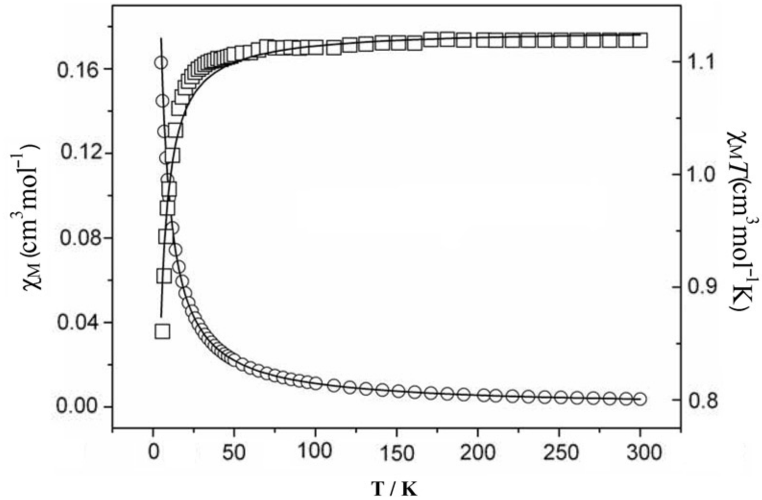

Figure 6. Experimental (○ and □) and fitted (–) curves showing the temperature dependence of χ_M and $\chi_M T$ for **1**.

where

$$u = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right] \tag{1}$$

This expression fits very well with the experimental susceptibilities of **1**, giving $g = 2.12$ and $J = -0.95\,\mathrm{cm}^{-1}$, where the J value is very low, and in agreement with the value of θ deduced above. The magnetic interaction is very weak, which may be due to the large intramolecular Ni $\cdots$ Ni distance ($\geq$11.3 Å) [24].

3.3. *TGA analyses and PXRD patterns*

The existence of guest molecules in the porous framework inspired us to investigate the thermal stability of the framework. Thermogravimetic anslyses (TGA) showed that **1** lost 13% of total weight in the temperature range of 50–140°C, corresponding to the loss of 3.5 lattice water molecules and one coordinated water (expected 12.5%). When the temperature is above 330°C, the product begins to decompose and oxidize. The residual percentage weight (observed 15.6%) at the end of the decomposition of the complex is consistent with the formation of NiO (expected 13.2%). The powder X-ray diffraction (PXRD) pattern of a dehydrated sample of **1** was compared with that of an as-synthesized solvent-containing sample (figure S1). The PXRD pattern after heating shows that the shapes and intensities of some reflections are only slightly changed relative to that of the original sample. This means that guest loss does not result in symmetry change or cavity volume collapse.

4. Conclusion

In summary, we have developed a strategy for constructing MOFs, $\{[\mathrm{Ni(dpdapt)(BDC)(H_2O)}]\cdot 3.5\mathrm{H_2O}\}_n$. Compound **1** exhibits a thermally stable 3-D architecture formed by chains and π–π stacking interactions, featuring 1-D pores enclosing unusual helical water chains. The stability of water chains is derived from hydrogen-bonding interactions between neighboring water molecules along the chain as well as H-bonding interactions with carboxylate. Our results provide an effective route for preparation of supramolecular architectures relevant to biopolymers.

Supplementary material

Figure of powder X-ray diffraction patterns and X-ray crystallographic data in CIF format for the structure reported in this article has been deposited with the Cambridge Crystallographic Data Centre. CCDC No. 655398 for **1**. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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