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A novel helical chainlike nickel(II) coordination polymer containing 1D trigonal channels with water molecule guests

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ABSTRACT

A novel 1D helical nickel coordination polymer, $[Ni(TAU)_2(4,4'\text{-bipy})]_n \cdot 2nH_2O$ (TAU = taurine, 4,4′-bipy = 4,4′-bipyridine), was synthesized and its crystal structure has been determined by X-ray diffraction. Each helix interlinks with six adjacent helices through extensive hydrogen bonds to form 3D supramolecular structure, in which 1D trigonal microporous channels filled with water guest molecules exist within the polymer coils. The framework remains intact on removal of guest water molecules which is proved by XPRD and TGA. Variable temperature magnetic susceptibility indicates weak anti-ferromagnetic interactions between the Ni(II) ions.

Recently, the assembly of metal-organic open frameworks (MOFs) has attracted great attention; MOFs with various network topologies have been prepared by using metal ions and organic building blocks [1]. MOFs with the flexible or rigid microporous channels have potential applications in selective molecular recognition and separation [2], physical gas storage [3], sensors [4], ion-exchange [5] and heterogeneous catalysis [6]. Chirality is also central in the assembly and construction of biological and chemical materials, both in their natural and synthetic forms. Among the chiral materials, there is strong interest in the design of chiral coordination polymers [7]. In many cases chiral coordination polymers are prepared with chiral ligands, which is a reliable method to introduce chirality to the structure but the preparation of chiral ligands is a laborious task [6,8]. Another approach is to form a chiral structure using chiral arrangement of achiral components [9].

Although it is not yet possible to prepare fully predictable metal-organic frameworks, the selective combination of metal centers, bridging ligands and co-ligands is an effective strategy for rational design and creative synthesis of desired frameworks. Thus, in designing extended porous coordination polymers and helical coordination polymers, the judicious selection of the properties of the ligands, such as shape, functionality, flexibility, symmetry, length, and substituent group is crucial to the construction of target polymers [10]. Despite the simple and common formula, the rigid rod-like ligand 4,4′-bipy has been used extensively to ligate metal ions into an open framework with channels [5,11]. And 4,4′-bipy ligands can also lead to the helical structures when linked by appropriate connectors in assembly process. For example, $[Ni(4,4'\text{-bipy})(ArCOO)_2(MeOH)_2]_n$ self-assembles as a helical architecture, in which octahedral metals are connected by linear 4,4′-bipy [9]. However, very few helical structures constructed from sulfonic ligands have been reported, partly due to the weak coordinating ability of sulfonate ligands [12]. Recently, we began to study the reactions of the flexible amino acid ligand taurine (TAU), also named as 2-aminoethanesulfonic acid, and co-ligand 4,4′-bipy with metal ions, with the aim of obtaining information on the coordination ability of sulfonic ligands and for constructing novel coordination architectures. Hydrothermal and solvothermal syntheses have been demonstrated to be an effective and powerful technique for forming extended porous coordination polymer structures [13]. In this work, the solvothermal reaction of Ni $(CH_3COOH)_2$ with 4,4-bipy, TAU and NaOH leads to the formation of a crystalline complex [14], which was analyzed via X-ray crystallography analysis [15].

Molecular structure of $[Ni(TAU)_2(4,4'\text{-bipy})]_n \cdot 2nH_2O$ (**1**) is shown in Fig. 1. Complex **1** crystallizes in the chiral space group P-$3_1$21 with one-half Ni(II) ion, one TAU anion, one-half 4,4′-bipy ligand, and one water guest molecule in the crystallographically asymmetric unit. Each Ni(II) ion is six-coordinate in a distorted octahedral environment defined by two oxygen atoms (O1 and O1A) and two nitrogen atoms (N1 and N1A) from two chelate TAU ligands, as well as two nitrogen atoms from two 4,4′-bpy ligands in *cis* fashion with the N2–Ni1–N2A angle of 88.80(18)°. The Ni–N bond distances are 2.114(3) and 2.109 (3) Å, and the Ni–O bond distance is 2.101(2) Å, close to that of the

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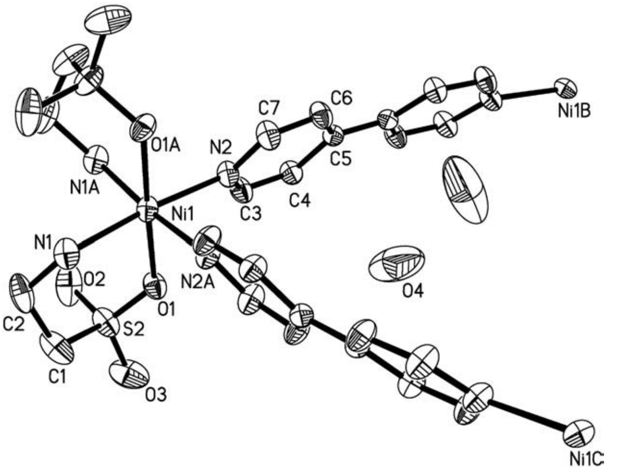

Fig. 1. Molecular structure of $[Ni(TAU)_2(4,4'\text{-bipy})]_n \cdot 2nH_2O$ (**1**), all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–O1 2.101(2); Ni1–N1 2.114(3); Ni1–N2 2.109(3); O1A–Ni1–O1 178.14(15); O1–Ni1–N2A 91.34(11); O1–Ni1–N2 87.33(11); N2A–Ni1–N2 88.80(18); O1–Ni1–N1 89.56(12); N2–Ni1–N1 175.06 (14); O1–Ni1–NA1 91.68(12); N2–Ni1–N1A 87.43(12); N1–Ni1–N1A 96.50(18). Symmetry code: A = −x, −x + y, −z + 1/3.

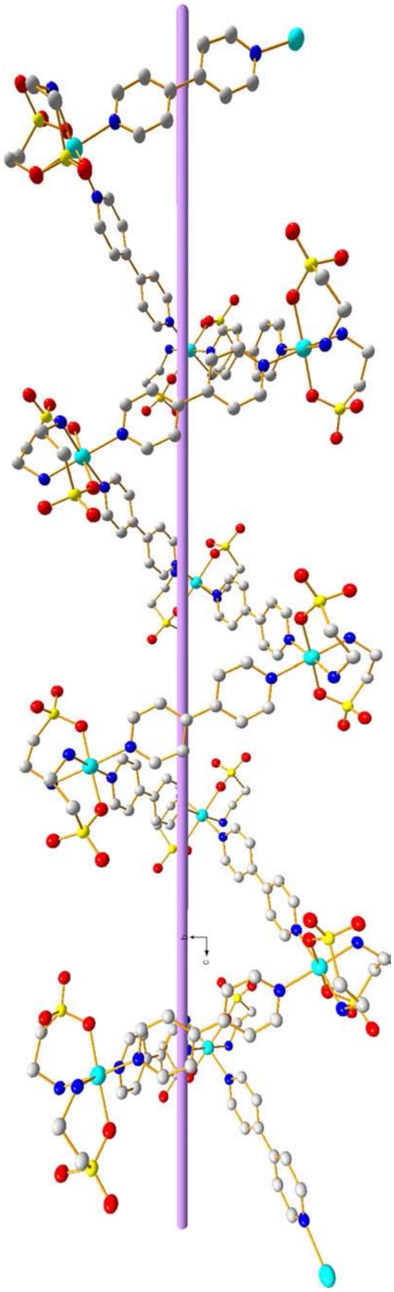

Fig. 2. Right-handed 3_1 helical chain built from alternating $Ni(TAU)_2$ and 4,4-bipy.

literature [16]. The Ni(II) ions are bridged by bidentate 4,4′-bipy ligand with the Ni–Ni distance of 11.288(1) Å (in which two pyridyl rings are twisted from each other with the dihedral of 10.8°) to form an infinite helical chain running along the c-axis (Fig. 2). The right-handed helix is generated around the crystallographic 3_1 axis. Each set of three crystallographically equivalent nickel centers constitutes a single revolution of the helix with a distance of 21.53 Å. The helical chains align in a parallel fashion. Therefore, the bulk crystal is chiral as every helix in an individual crystal is of the homochirality. There is one previous example of 1D Ni(II) zigzag chain polymer $[4,4'\text{-bipy-Ni}(\text{Et-XA})_2 \cdot 0.5\text{EtOH} \cdot \text{CHCl}_3]_n$ (Et-XA = ethylcarbonadithiolate), with 4,4′-bipy bridges having a similar *cis*-conformation, in which solvate molecules sit in open channels which are formed by the packing of the linear polymeric chains of the complex [17]. The similar local coordination geometry of Ni(II) units of two complexes leads to two different 1D structures because of the chiral arrangement of the Ni(II) units in complex **1** comparing with the reported 1D zigzag complex.

Interestingly, the view along the polymer axis (Fig. 3) shows that a trigonal channel with side length approximately 8.4 Å exists within the polymer coil, which is filled with water guest molecules. The PLATON [18] program reveals that the voids in complex **1** occupy 13.4% of the crystal volume (after the removal of the guest water molecules). Each helix further interlinks with six adjacent helices to give a periodically ordered 3D chiral framework, where the interchain C–H···O hydrogen bond contacts between neighboring aromatic C–H groups of 4,4′-bipy and the oxygen atoms of sulfonate groups of TAU are found, and the C–H···O distances and the C–H···O angles are 3.222 (6) Å and 151.5(3)°, respectively (Fig. S1). In trigonal channels, the guest water molecules are interconnected by single hydrogen bonds (Fig. S2a) between two neighboring ones into helical chains (Fig. S2b). The O–H···O distances and the O–H···O angles are 2.810(13) Å and 117.2(5)°, respectively. In addition, all water molecules are hydrogen bonded to the sulfonate oxygen atoms (O2) of TAU in the circumambient helical chain (the O–H···O distances and the O–H···O angles are 2.810(13) Å and 117.2(5)°, respectively). Similar 1D helical water chains have been reported in the cocrystal structure of melamine and trimesic acid, in which a pair of 1:1 left- and right-handed helices exists in the channels [19].

Complex **1** is stable in air at ambient temperature and is almost insoluble in common solvents such as water, alcohol, acetonitrile, chloroform, acetone, and toluene, being consistent with its polymeric nature. Thermal gravimetric analysis (TGA) was carried out in N_2 condition from room temperature to 800 °C for examining the properties of dehydration and stability of **1** (Fig. S3). The first stage of weight loss is 7.05% in the temperature range 50–195 °C, corresponding to the loss of two uncoordinated water molecules per empirical formula (calculated 7.21%). The second weight loss occurs from 265 to 550 °C corresponding to the loss of organic ligands. After decomposition of complex **1** at high temperature, the weight of the residue (15.65%) is responded to NiO (calcd: 14.96%). We explored whether the framework would break down on removal of guest water molecules. Water molecules were removed by heating **1** directly to 200 °C and keeping for 1 h in an oven. And the sample was re-hydrated by standing the heated sample of **1** in air for 24 h. X-ray powder diffraction (XPRD) patterns of hydrated, dehydrated and re-hydrated samples of **1** are nearly identical (Fig. 4), which supports the notion that the crystal lattice remains intact after the guest water molecules have been removed and reintroduced.

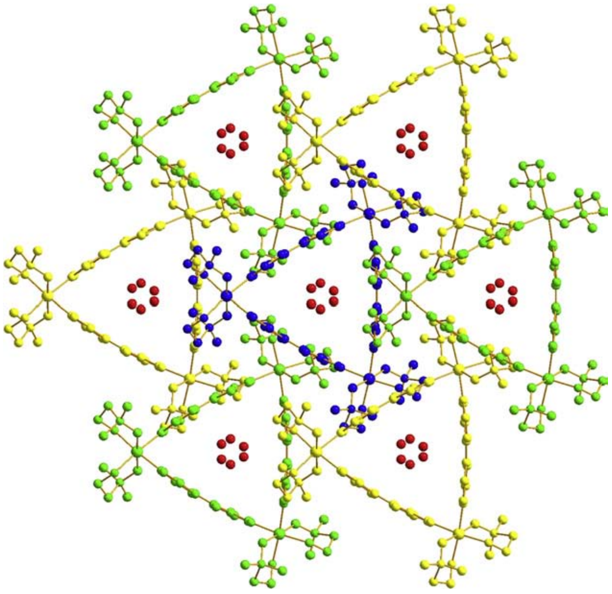

Fig. 3. A schematic view showing the interlinking of adjacent helical chains and the 1D channels existed within the polymer coils.

The magnetic susceptibility was measured in the temperature range 2–300 K on a MPMS-7 SQUID magnetometer, and Fig. 5 shows the plots of χ_m and μ_{eff} *versus* T. At room temperature the effective magnetic moment equals 3.14 B.M. which is characteristic for a pseudo-octahedral high spin Ni(II) complex (2.9–3.4 B.M.) [20]. Upon cooling, the magnetic moment decreases slightly to a value of 2.63 B.M. at 2.0 K, indicating a very weak magnetic interaction between the Ni(II) ions. Considering the 1D infinite chain structure of complex **1**, assuming an isotropic exchange between Ni(II) ions, the magnetic susceptibility per Ni(II) ion can be expressed as [21]:

$$\chi = \frac{Ng^2\beta^2}{kT}\,\frac{2 + 0.0194x + 0.777x^2}{3 + 4.34x + 3.232x^2 + 5.834x^3}$$

with $x = |J|/kT$

where J is the exchange integral between Ni(II) ions bridged by 4,4′-bipy, and the other parameters have their usual meanings. The fitted values are in good agreement with the experimental data and the parameters $J = -0.38\ \mathrm{cm}^{-1}$, $g = 2.21$ and $R = 1.57 \times 10^{-4}$ ($R = \sum(\chi_{obsd} - \chi'_{cacld})^2 / \sum(\chi_{obsd})^2$), which further confirms weak anti-ferromagnetic exchange coupling within the chain. The results are according with those of other reported complexes bridged by 4,4′-bipy ligand [22].

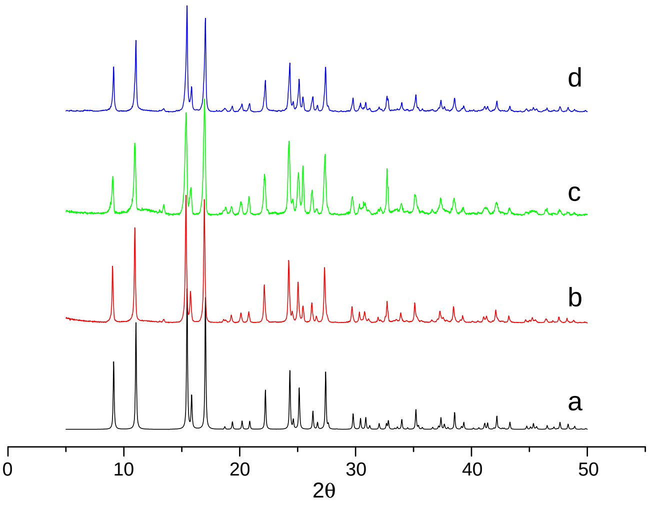

Fig. 4. X-ray powder diffraction patterns of **1**. (a) Simulated line; (b) experimental line of the unheated sample; (c) experimental line of the heated sample; (d) experimental line of the re-hydrated sample.

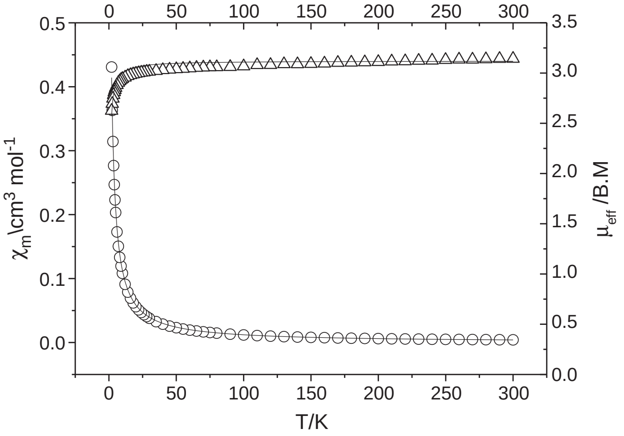

Fig. 5. μ_{eff} (Δ) *versus* T and χ_m (o) *versus* T plot for **1**, the solid lines represent the best fit curve.

In summary, we have demonstrated the self-assembly of homochiral tubes based on helical chains that are built from 4,4′-bipy ligands and linear metal-connecting points. The resulting framework of **1** is robust and can remain intact after guest removal. The structure of **1** effectively combines the presence of polarity and porosity, both of which are of significant relevance to applications in chemistry and materials science.

Acknowledgements

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Appendix A. Supplementary data

Crystallographic data for the structure reported in this article has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 674734. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version doi:10.1016/j.inoche.2010.08.021.

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[14] [14] *Synthesis of* ***1***: A mixture of Ni(CH_3COOH)$_2$ (0.4 mmol, 116 mg), 4,4-bipy (0.4 mmol, 62 mg), taurine (0.6 mmol, 75 mg), NaOH (0.6 mmol, 24 mg), ethanol (15 ml) and distilled water (3 ml) in the molar ratio of 1:1:1.5:1.5:650:417 was sealed in a 25 mL stainless steel reactor with Teflon liner, and heated directly to 110 °C. After keeping at 110 °C for 3 days, it was cooled to room temperature at a rate for 4 °C/h. Blue green block crystals were obtained by filtration, washed with distilled water, filtered and dried in air at room temperature. The yield is 61% based on taurine. Anal. Calc. for $C_{14}H_{24}N_4NiO_8S_2$: C, 33.65; H, 4.81; N, 11.22. Found: C, 33.36; H, 4.98; N, 11.39%. IR spectra (KBr pellet, cm^{-1}): 3564 s; 3303 s; 1612 s; 1259 s; 1173 s; 1123 s; 1036 s; 742 m; 592 m; 529 m.

[15] [15] *Crystal data for* ***1***: $C_{14}H_{24}N_4NiO_8S_2$, Trigonal, space group $P\text{-}3_121$, $M = 499.20$, $a = 11.1597(9)$Å, $b = 11.1597(9)$Å, $c = 14.198(2)$Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 1531.3(3)$ Å^3, $Z = 3$, $D_c = 1.624$ g/cm^3, $F(000) = 780$, and μ(Mo K_α) = 1.205 mm^{-1}, 5697 reflections collected ($2.55 \leq \theta \leq 25.50$), 1897 unique ($R_{int} = 0.0359$), final $R = 0.0352$, $wR2 = 0.0754$ and $S = 1.024$. Crystal structure measurements for complex were performed on a Bruker SMART 1000 CCD diffractometer equipped with graphite monchromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 291±1°K. Data collections and reductions were performed using the SMART and SAINT software. An empirical absorption correction (SADABS) was applied to the raw intensities. The structure was solved by direct methods and refined by full-matrix least squares based on F^2 using the SHELXTL program package. Non-hydrogen atoms were subjected to anisotropic refinement. The H atoms were assigned with common isotropic displacement factors and were included in the final refinement by use of geometrical restraints.

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