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A novel chiral framework constructed through three-fold interpenetration of (4,4) nets of Ni(II)–muconate–4,4′-bipyridine

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Abstract

The assembly of Ni(II) ions with linear spacers *trans*,*trans*-muconic acid (H_2L) and 4,4′-bipyridine (4,4′-bpy) has afforded a compound, $[Ni(L)(4,4'\text{-bpy})(H_2O)_2]_n$ (**1**). Single crystal X-ray diffraction analysis reveals that both 4,4′-bpy and deprotonated H_2L act as linear bridges to bind square-planar Ni(II) nodes. Achiral ligands 4,4′-bpy induced in a chiral configuration link metal nodes into chiral chains, which are further bound into homochiral sheets by rigid L. Finally, a novel 3D chiral framework forms through three-fold slantwise interpenetration of those chiral (4, 4) nets. The magnetic studies in the range 2–300 K show that magnetic behavior of **1** possesses a large zero-field splitting of Ni(II) ions and an anti-ferromagnetic interaction between metal centers.

Keywords: Interpenetration framework; Magnetism; Muconate; Chirality

Synthesis of chiral interpenetrating or porous structures through spontaneous resolution upon crystallization without any chiral auxiliary is a challenge and more meaningful for polyfunctional materials [1–4]. Although full understanding of the spontaneous resolution is not yet complete, two factors would be crucial: chiral units and homochiral interactions between them [5]. Ligands of C_{2h}-symmetry [6–10] are potential sources of chiral units for spontaneous resolution on condition that they are induced into a chiral configuration by coordination bonds or hydrogen bonds [11–13]. Recently, long rigid multifunctional ligands are widely used to construct interpenetrating or porous metal-organic frameworks with aesthetic topology structures [14,15]. Therefore, the long rigid ligands with C_{2h}-symmetry, such as *trans*,*trans*-muconic acid (H_2L) [16–19] (Scheme 1) and 4,4′-bipyridine (4,4′-bpy), are especially attractive in the construction of chiral supramolecular species of interpenetrated architectures. Herein, we report the self-assembly of *trans*,*trans*-muconic acid, 4,4′-bpy, and nickel(II) ions under hydrothermal conditions. The resultant assembly of formula $[Ni(L)(4,4'\text{-bpy})(H_2O)_2]_n$ (**1**) is a novel three mutually slantwise interpenetrated (4, 4) nets with chirality. Meanwhile, we also report the results of thermo-stability and the magnetism studies.

The hydrothermal treatment of a mixture of $Ni(CH_3COO)_2 \cdot 4H_2O$, H_2L, and 4,4′-bpy at a mole ratio of 2:1:1 at 170 °C gave rise to green crystals $[Ni(L)(4,4'\text{-bpy})(H_2O)_2]_n$ (**1**), which was determined by IR, elemental analysis, and single crystal X-ray diffraction analysis [20,21].

Compound **1** crystallizes in a trigonal space group $P3_121$. The Ni(II) center in **1** has a distorted octahedral coordination environment (shown in Fig. 1), ligated by two O atoms from two deprotonated H_2L and two N atoms from two 4,4′-bpy in the equatorial plan (Ni–O, 2.039 Å; Ni–N, 2.067 and 2.094 Å), and by two oxygen atoms from water molecules at the axial sites (Ni–O, 2.110 Å).

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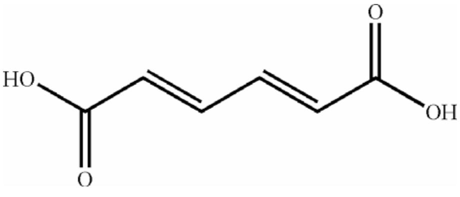

Scheme 1.

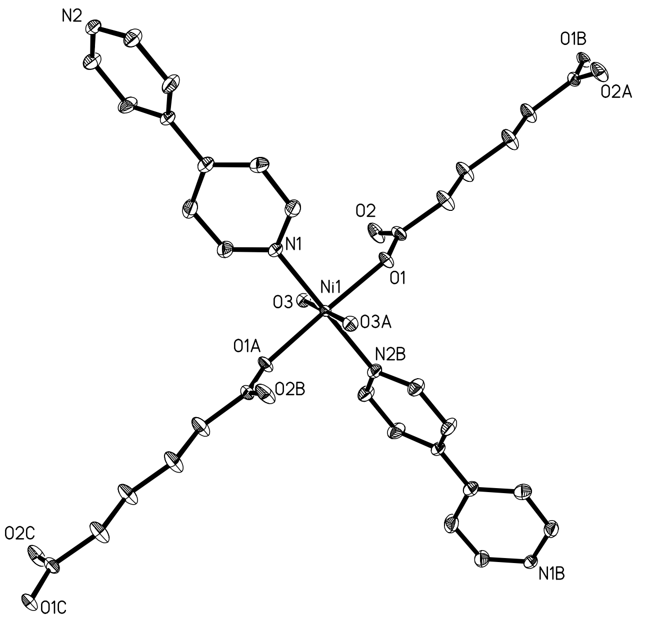

Fig. 1. Coordination environment of Ni(II) ion in compound **1**.

Notably, the foundational structural moieties in compound **1** are the square meshes with the metal centers acting as four-connecting nodes and both of L and 4,4′-bpy ligands acting as linear bridges between the metal atoms. The square meshes with each theoretic dimensions of 11.220 × 12.254 Å then extend into two-dimensional coordination sheets suitable for interpenetration. Due to the large cavity, each square mesh of a sheet is interlocked with two adjacent square meshes of the other two sheets in a slantwise manner as illustrated in Scheme 2. As a result, a beautiful three-dimensional framework forms through the three-fold interpenetration of those identical but independent two-dimensional (4,4) topology structures (shown in Fig. 2). In addition, the interpenetration mode is stabilized through hydrogen bonding between the coordinated water molecules of a sheet and the uncoordinated O atoms of L from the adjacent interlocking sheets with the O···O distance being about 2.838 Å.

Scheme 2.

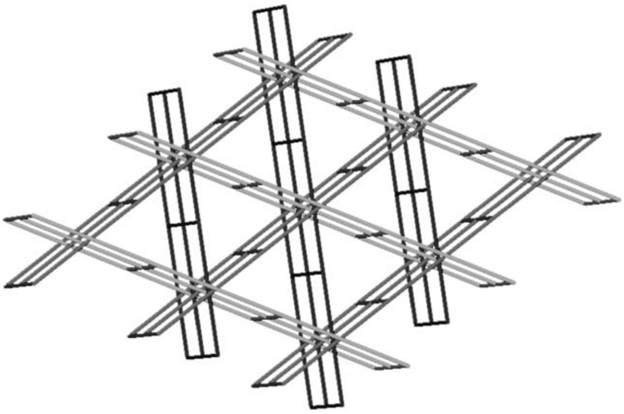

Fig. 2. A representation of the modes of inclined interpenetration by complementary (4,4) networks for **1**.

Another stimulating result is the introduction of chirality into compound **1** by spontaneous resolution upon crystallization. In compound **1**, the two pyridine rings of 4,4′-bpy are out of planar with the dihedral angle of 29.6°. The twisted configuration, perhaps, is induced and stabilized by weak C–H···π interactions (The ortho hydrogen of 4,4′-bpy in a sheet directs to the pyridine plane of neighboring sheet with the distance of C···aromatic centroid 3.459 Å and the angle of C–H···aromatic centroid 132.27°). Thus, the originally introduced achiral 4,4′-bpy ligands are in a chiral configuration in **1**, which lead to the formation of chiral Ni(II)-4,4′-bpy chains. With the further bonding of rigid ligands L with metal nodes, the chirality in chain units is extended into 2D homochiral sheets, and then the three-dimensional chiral framework in a space group $P3_121$ is generated through three-fold slantwise interpenetration of the chiral (4,4) nets.

Thermogravimetric analysis (TGA) of the polycrystalline sample of **1** under a nitrogen atmosphere reveals two steps of weight losses. The first weight loss of 10.03% occurs in the temperature range from 98 to 160 °C, which may be attributed to the loss of all the coordinate water molecules (9.2%). The dehydrated framework is still stable up to 340 °C. The second weight loss of 66.3% occurs above 340 °C, in agreement with the decomposition of ligands L and 4,4′-bpy (cal. 67.6%). The relic being 18.5% may be attributed to NiO (cal. 19.1%).

The temperature (T) dependence of the magnetic susceptibility (χ_M) of title compound was measured in the range 2–300 K under fixed field of 10 kG. Fig. 3 shows the corresponding χ_M vs. T and μ_{eff} vs. T plot. For compound **1**, μ_{eff} decreases very slowly from 3.16 μ_B at 300 K to 2.90 μ_B at 10 K and then decreases rapidly to 1.96 μ_B at 2 K. The μ_{eff} of 3.16 μ_B per Ni^{II} at room temperature is larger than that of calculated for the spin only case (2.83 μ_B), revealing a

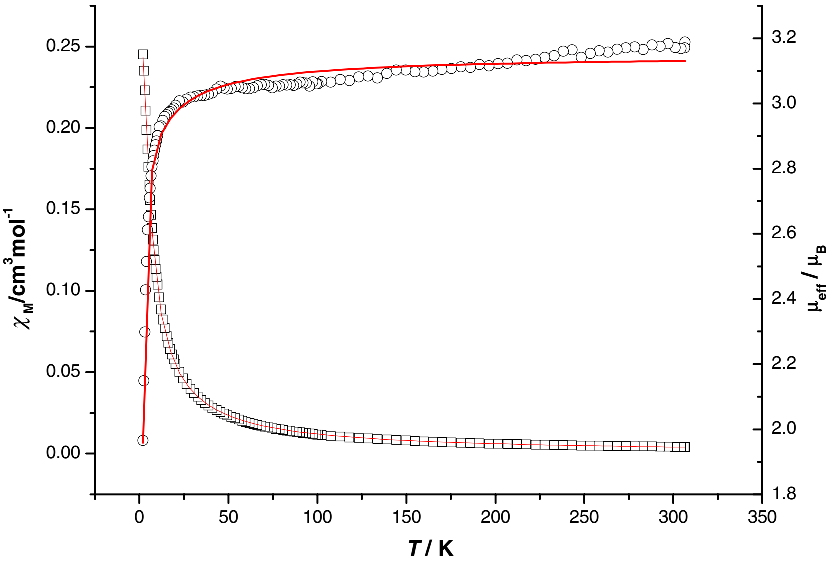

Fig. 3. χ_M (□) and μ_{eff} (○) vs. T with the theoretical fit (–) for **1**.

significant orbital contribution, which always causes zero-field splitting. The magnetic behavior of title compound can be explained by large zero-field splitting as well as an anti-ferromagnetic interaction under the molecular field approximation. The best fit of Eq. (1) to the data is achieved with $g = 2.21$, $D/k = 4.99$, $\theta = -1.57$ and $R = 7.50 \times 10^{-7}$ $[R = \sum(\chi_{\text{obsd}} - \chi_{\text{cacld}})^2 / \sum \chi^2_{\text{obsd}}]$.

$$\chi_M = \frac{2Ng^2\beta^2}{3k(T-\theta)}\left[\frac{2kT/D - 2kT\exp(-D/kT)/D + \exp(-D/kT)}{1+2\exp(-D/kT)}\right] \tag{1}$$

The result indicates that the bridge conjugated ligands L and 4,4′-bpy are unfavorable for the electronic interactions needed for efficient superexchange between paramagnetic metal centers.

Acknowledgements

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Appendix A. Supplementary data

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 292009. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) or also available from the author Maochun Hong on request. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.01.002.

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[20] Synthesis of compound **1**: Mixture of $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.2 mmol, 0.025 g), *trans*, *trans*-muconic acid (0.1 mmol, 0.014 g), 4,4′-bipyridine (0.1 mmol, 0.016 g) and deionized water (10 mL) was adjusted to a pH value of about 6 by adding 0.1 M sodium hydroxide solution. The reaction solution was sealed in an autoclave Teflon-line stainless vessel and heated at 170 °C for 3 days. Then green crystals of

1 suitable for X-ray analysis were obtained, yield 72%. Elemental analysis results of the crystals are consistent with the stoichiometry of title compound. Calc. for $C_{16}H_{16}N_2NiO_6$ (%): C, 49.23; H, 4.13; O, 24.61; N, 7.18; Found: C, 49.26; H, 4.11; O, 24.56; N, 7.14. FT/IR data (cm^{-1}): 3329s, 3082m, 1613s, 1538s, 1491w, 1417m, 1372s, 1285m, 1218vs, 1189m, 1069vs, 1008vs, 874vs, 817vs, 763w, 724s, 671m, 638s, 571w, 503s.

[21] *Crystal data for compound* **1**: $C_8H_8NNi_{0.50}O_3$: $M_r = 195.51$, trigonal, space group $P3_121$, $a = b = 11.2198(5)$ Å, $c = 12.2544(10)$ Å, $V = 1335.96(14)$ Å^3, $Z = 6$, $\mu = 1.122$ mm^{-1}, $\rho_c = 0.458$ g/cm^3, $F_{000} = 606$. Data were collected over the 2θ range 3.36–27.46° at 173(2) K on a Siemens SMART-CCD Diffractometer equipped with a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 6750 reflections were obtained and 2039 unique reflections ($R_{int} = 0.0243$) were collected in by ω-2θ scan mode of which 1931 reflections with $I > 2\sigma(I)$ were used in the succeeding refinement. The final $R = 0.0250$, $wR = 0.0621$, $(\Delta\rho)_{max} = 0.354$ e/Å^3, $(\Delta/\sigma)_{max} = 0.001$ and $S = 1.074$.