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Unprecedented Interweaving of Hetero-Chiral Single Helical Chains into a 3D Chiral Framework with (10, 3) Topology

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The title compound, [Ni(dcbp)(H₂O)₂](H₂dcbp=2,2'-bipyridine-4,4'-dicarboxy acid), was synthesized under hydrothermal conditions. The structure was determined by single-crystal X-ray diffraction and further characterized by elemental analysis, IR, and TGA. The compound crystallized in an orthorhombic system, P2₁2₁2₁ space group, $a = 6.7665(7)$ Å, $b = 12.9047(14)$ Å, $c = 13.1848(15)$ Å, $\beta = 90^\circ$. In the compound, each Ni(II) atom exhibits a six-coordinated distorted octahedral geometry. Interestingly, carboxylate group from dcbp ligands bridges between adjacent Ni(II) atoms giving rise to unprecedented interweaving of hetero-chiral single helical chains into a 3D chiral (10, 3) framework.

Keywords nickel(II), chiral coordination polymers, hydrothermal synthesis, helical structure

INTRODUCTION

Research activities concerning coordination polymers are expanding rapidly, not only for the pragmatic perspective to obtain new functional materials but also for the fundamental interest to reveal the intriguing structural diversity and assembling processes of these materials.^[1] In this field, a particularly interesting and challenging area is the synthesis of helical coordination polymers and exploration of their potential utilities in asymmetric catalysis and nonlinear optics. On the basis of the pioneering work of Lehn and coworkers,^[2] a variety of appealing helical

coordination polymers have been constructed^[3–6] and well discussed in comprehensive reviews by Okamoto and Albrecht.^[7] Inspired by the aforementioned considerations, we have attempted to extend our work to study the systematic synthesis of novel helical coordination polymers. During our investigations in this area, we have set up an efficient strategy; that is, to employ flexible or V-shaped exo-bidentate bridging ligands.^[8–12] As a member of them, 2,2'-bipyridine-4,4'-dicarboxy acid (H₂dcbp) not only possesses chelating pyridine nitrogen atoms but also contains exodentate carboxyl groups, which could result in the formation of helical structures. To date, its coordination chemistry has been studied and some coordination polymers have been prepared.^[13–15] However, a few of its helical compounds have been obtained.^[13] In order to further research the effect of the ligand on the formation of a helical structure, we enlarged our studies to a wider range of metal ions. Fortunately, we successfully prepared a series coordination polymers by employing the 2,2'-bipyridine-4,4'-dicarboxy acid (H₂dcbp). Herein, we report [Ni(dcbp)(H₂O)₂], which shows an unprecedented interweaving of hetero-chiral single helical chains into a 3D chiral framework.

EXPERIMENTAL

Materials and Physical Measurements

All reagents used in the synthesis were of analytical grade. Elemental analyses for carbon, hydrogen, and nitrogen were performed on a GmbH VariuoEL V3.00 automatic elemental analyzer. The infrared spectra (4000–600 cm⁻¹) were recorded by using KBr pellet on an Avatar 360 FT-IR spectrometer. TGA analyses were recorded with a NETZSCH STA 449C microanalyzer in an atmosphere of nitrogen at a heating rate of 5°C min⁻¹. The crystal determination was performed on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å).

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Synthesis of the Complex $[\text{Ni}(\text{dcbp})(\text{H}_2\text{O})_2]$

A mixture of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.05 mmol, 0.0119 g), H_2dcbp (0.05 mmol, 0.0122 g), and water (10 mL) was sealed in a Teflon reactor. The pH value of the mixture was adjusted to 7 by NaOH solution ($0.1 \text{ mol} \cdot \text{L}^{-1}$) and heated at 170°C for 72 h. Green block crystals were obtained after cooling to room temperature at $33^\circ\text{C} \cdot \text{h}^{-1}$. Yield: 75.8 %. Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{N}_2\text{NiO}_6$, C, 51.62; H, 3.97; N, 10.03. Found: C, 51.58; H, 3.91; N, 9.91. Selected IR data (KBr, cm^{-1}): 3256 m, 1948 w, 1621 s, 1576 s, 1492 s, 1456 s, 1261 w, 1296 w, 1228 m, 1127 w, 1072 w, 1056 w, 1011 w, 935 w, 912 w, 863 m, 828 w, 769 m, 714 m, 693 m, 638 m.

Crystallographic Data Collection and Structures Determination

Single-crystal data were collected at 295(2) K on a CCD Bruker Smart Apex II diffractometer equipped with graphite-monochromated Mo $\text{K}\alpha$ radiation. The structure was solved using direct methods and successive Fourier difference synthesis (SHELXS-97) and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97). The final agreement factor values were $R_1 = 0.0461$, $wR_2 = 0.0842$, $w = 1/[\sigma^2(F_0^2) + (0.0190P)^2 + 2.87P]$ where $P = (F_0^2 + 2F_c^2)/3$. A summary of the crystallographic data is given in Table 1. Selected bond distances and angles are given in Table 2.

TABLE 1
Crystallographic data for **1**

Empirical formula	$\text{C}_{12}\text{H}_{11}\text{N}_2\text{NiO}_6$
Formula weight	337.94
Temperature (K)	296(2)
Wavelength (\AA)	0.71073
Crystal system	Orthorhombic
Space group	$P2(1)2(1)2(1)$
	$a = 6.7665$ (7) \AA
	$b = 12.9047$ (14) \AA
Unit cell dimensions	$c = 3.1848$ (15) \AA
	$\beta = 90^\circ$
Volume, Z	1151.3 (2) \AA^3 , 4
Calculated density (kg/m^3)	1.950
Crystal size (mm^3)	$0.21 \times 0.14 \times 0.09$
θ Range for data collection ($^\circ$)	2.21–25.04
Reflections collected	5844
Independent reflection	2042 ($R_{\text{int}} = 0.0598$)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0461$, $wR_2 = 0.0842$
R indices (all data)	$R_1 = 0.0630$, $wR_2 = 0.0943$

TABLE 2
Selected bond lengths (\AA) and angles ($^\circ$) for **1**

Ni(1)-O(5)#1	2.047 (4)	N(1)-Ni(1)-O(2)	91.3 (2)
Ni(1)-O(1)	2.050 (5)	N(2)-Ni(1)-O(2)	89.0 (2)
Ni(1)-N(1)	2.065 (4)	O(5)#1-Ni(1)-O(6)#2	90.09 (17)
Ni(1)-N(2)	2.068 (5)	N(1)-Ni(1)-O(6)#2	91.60 (19)
Ni(1)-O(2)	2.071 (5)	N(2)-Ni(1)-O(6)#2	92.3 (2)
Ni(1)-O(6)#2	2.121 (4)	C(1)-N(1)-Ni(1)	128.7 (4)
O(5)#1-Ni(1)-O(1)	89.79 (17)	C(5)-N(1)-Ni(1)	114.2 (4)
O(5)#1-Ni(1)-N(1)	169.45 (16)	C(6)-N(2)-Ni(1)	114.8 (4)
O(1)-Ni(1)-N(1)	100.75 (19)	C(10)-N(2)-Ni(1)	127.3 (4)
O(5)#1-Ni(1)-N(2)	89.80 (16)	C(12)-O(5)-Ni(1)#3	132.2 (4)
O(1)-Ni(1)-N(2)	176.1 (2)	C(12)-O(6)-Ni(1)#4	149.7 (4)
N(1)-Ni(1)-N(2)	79.73 (17)	N(1)-C(1)-C(2)	123.2 (5)
O(5)#1-Ni(1)-O(2)	87.15 (19)	N(2)-C(6)-C(7)	121.8 (5)
O(1)-Ni(1)-O(2)	94.8 (2)	N(2)-C(6)-C(5)	114.7 (5)

Symmetry transformations used to generate equivalent atom: #1 $-x, y - 1/2, -z + 1/2$; #2 $-x + 1/2, -y, z + 1/2$; #3 $-x, y + 1/2, -z + 1/2$; #4 $-x + 1/2, -y, z - 1/2$

RESULTS AND DISCUSSION

Crystal Structure Description

Single-crystal structure analyses reveal that the title compound crystallizes in the chiral $P2_12_12_1$ orthorhombic space group. Crystallographic details are shown in Table 1. The coordination environment of the nickel(II) ion is shown in Figure 1. The center nickel atoms are six-coordinated. It is coordinated by chelating bipyridyl nitrogen atoms, two carboxylate oxygen atoms of the two adjacent dcbp ligands, and two coordinated water molecules, all of which give rise to a distorted octahedral geometry. In the compound, Ni(1)-O(5A), Ni(1)-O(1), Ni(1)-N(1), Ni(1)-N(2), Ni(1)-O(2), and Ni(1)-O(6A) bond length is in the range 2.047(4)–2.121(4) \AA ; the axial O(2)-Ni(1)-O(6A) angle is $176.94(18)^\circ$, while the equatorial angles, O(1)-Ni(1)-N(1), O(5A)-Ni(1)-O(1), O(5A)-Ni(1)-N(2), and N(1)-Ni(1)-N(2) are $100.75(19)^\circ$, $89.79(17)^\circ$, $89.80(16)^\circ$, $79.73(17)^\circ$. These are comparable to literature values.^[12]

The coordination polymer takes on a 3D network viewed along the a -axis as shown in Figure 2b. Each dcbp ligand coordinates to three Ni(II) centers: one through chelating bipyridine

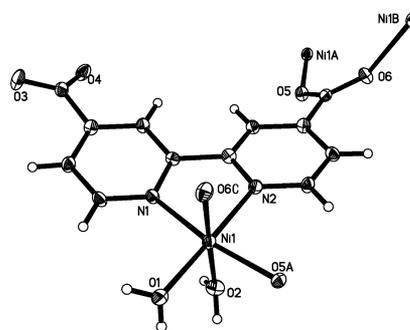


FIG. 1. The coordination environments for Ni(II) atom.

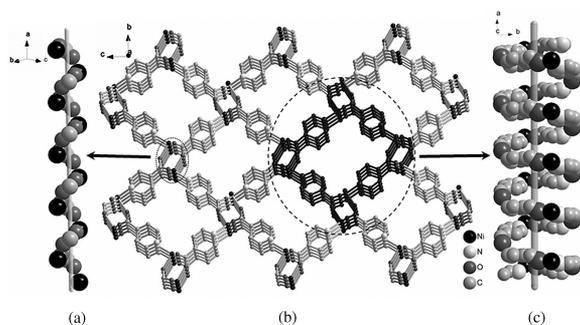


FIG. 2. (a) The small helical chains in the network along a -axis, which is highlighted with dashes in (b); (b) the 3D network viewed along the a -axis (some atoms of the ligands are omitted for clarity); (c) the big left-handed helical chains in the network, which are highlighted with black colors in (b).

nitrogen atoms and two through a bridging carboxyl group. The carboxylate of the deprotonated dcbp ligand interacts with the Ni(II) centers to give rise to Ni–O–C–O–Ni right-handed helical chains, which spiral down the crystallographic 2_1 axis in the a direction, as shown in Figures 2a and 2b. Interestingly, another larger left-handed helical chain is also formed by the dcbp spacers and Ni(II) atom centers, which run along a crystallographic 4_1 axis in the a direction with a pitch of 6.766 Å, as shown in Figures 2b and 2c. The striking feature of the compound is that the interweaving of hetero-chiral helical chains further extended to the 3D chiral framework through sharing Ni(II) atoms, as shown in Figure 2b.

From a topological perspective, the structure of the compound can be simplified to a unique three-connected net with (10, 3) topology. The Ni(II) atom and a part of the dcbp ligand both take on three-connecting nodes. The three shortest circuits for both node types all involve 10 nodes; thus, the net is of (10, 3) topology, as shown in Figure 3. The three-connected net is chiral and has fourfold helices along each of the crystallographic axis. Here, we can see the network for crystal contains these fourfold helices along the c axis, too (as shown in Figure 3).

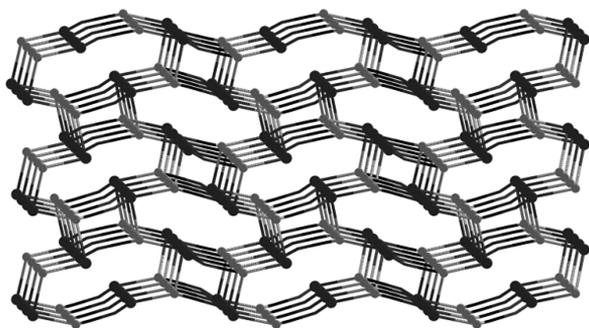


FIG. 3. Schematic illustrating the (10, 3) topology of the 3D network of the title crystal along the c -axis. Deep gray nodes represent the Ni(II) center and light gray nodes a central point in the C12-containing half of the dcbp ligand.

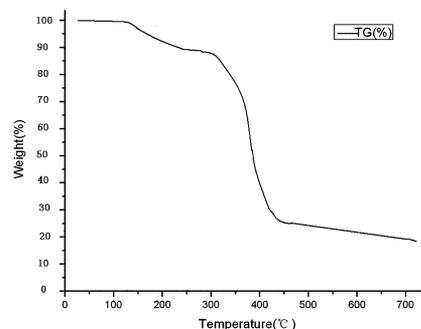


FIG. 4. The TGA curve of the complex.

IR Spectra

The IR spectrum of the compound exhibits a broad peak around 3256 cm^{-1} , which characterizes the ν_{O-H} stretching and indicates the presence of coordinated water molecules. The strong characteristic bands at 1621 and 1456 cm^{-1} are due to the asymmetric and symmetric stretching bands of COO^- groups, herein $\Delta\nu[\nu_{as}(\text{COO}^-)-\nu_s(\text{COO}^-)] \approx 165\text{ cm}^{-1}$, which shows that the dcbp ligand adopts both bidentate and bridging coordination modes. The peak around 1576 cm^{-1} is assigned to the $\nu_{C=C}$ of the bipyridine. Furthermore, the band at 1127 cm^{-1} is attributable to the $\nu_{C=N}$ of bipyridine ring, which reveals the complexation of the N atoms from the bipyridine ring of the ligand.^[16] The analysis of IR spectrum of the complex is in agreement with crystal structure and charge balance consideration.

TGA of the Complex $[\text{Ni}(\text{dcbp})(\text{H}_2\text{O})_2]$

Thermal analysis of the complex was carried out in an atmosphere of nitrogen to establish the content of coordinated water molecules in the complex as shown in Figure 4. The TGA curve of the complex reveals that the first weight loss of 10.58% from 125 to 250°C corresponds to the departure of the coordinated water molecules (calculated value: 10.67%). The second weight loss, which covers a temperature range from 281 to 700°C , may be the decomposition of the organic remains. The remnants are 22.25%, which should be NiO (calcd. 22.14%).

CONCLUSION

In this article, we have reported the synthesis and structure of one three-dimensional chiral coordination polymer $[\text{Ni}(\text{dcbp})(\text{H}_2\text{O})_2]$ network. It contains interweaving of hetero-chiral helical chains constructed from metal centers and dcbp ligands. Therefore, the successful preparation of the compounds provides a valuable approach for the construction of many other coordination polymers containing a helix structure. Further research is ongoing to prepare novel polymeric frameworks in this subfield and explore their valuable properties.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 672158. 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; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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