A NOVEL HELICAL CHAINLIKE COBALT(II) COORDINATION POLYMER CONTAINING 1D TRIGONAL CHANNELS: SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES

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A novel helical-chain coordination polymer $[Co(tau)_2(4,4'\text{-bipy})]_n \cdot nH_2O$ **1** (tau = taurine, 4,4′-bipy = 4,4′-bipyridine) has been hydrothermally synthesized and characterized by infrared spectroscopy, and thermogravimetric analysis, magnetic measurements, solid-state CD spectra and single crystal X-ray diffraction analysis. The intertwist trigonal-fold helical chains are further connected through hydrogen bonds to give a three-dimensional supramolecular network, in which trigonal microporous channels filled with water guest molecules exist within the polymer coils. Compound **1** shows weak antiferromagnetic interactions among metal ions.

Keywords: Helical chains; 4,4′-bipy; Taurine; Crystal structure determination; Magnetic properties; Bipyridine complexes; Supramolecular chemistry.

The current interest in the crystal engineering of coordination polymer frameworks not only stems from their potential applications as new functional materials, but also because of their intriguing variety of architectures and topologies[1]. Among the numerous metal-organic coordination polymers, the construction of helical coordination polymers has generated a great deal of attention because helical structures are ubiquitous in nature and of fundamental importance in biological systems[2]. So it is a fascinating challenge for chemists to control the formation of helicity at the supramolecular level. In many cases, chiral coordination polymers are prepared with chiral ligands to introduce chirality to the structure or using chiral arrangement of achiral components to form a chiral structure. Nevertheless, it is still a challenge to predict the exact structures and compositions of polymeric compounds assembled in a helical motif, although an increasing

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number of coordination polymers with various helices in the solid state have been reported[3].

The judicious choice of suitable ligand is an important factor that greatly influences the structure of the coordination of the complex formed, and for constructing helical polymers the ligands with a little flexibility and spacial hidrance are very efficient. Despite the simple and common formula, the rigid rod-like ligand 4,4′-bipy has been used extensively to ligate metal ions into the helical structures when linked by appropriate connectors in assembly process[4]. However, very few helical structures constructed from sulfonic ligands have been reported, partly due to the weak coordinating ability of sulfonate ligands. In the previous work of our group, taurine had been paid much attention[5]. To continue our research, Herein, we report an interesting example consisting of three-fold helical chains $[Co(tau)_2(4,4'\text{-bipy})]_n \cdot nH_2O$ **1** obtained by self-assembly of taurine and cobalt(II) ions.

EXPERIMENTAL

Materials and Instruments

All solvents and reagents were of reagent grade, commercially available and used without purification. Elemental analyses for C, H, N and S were performed on a PE 1700 CHN automatic elemental analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken on an Avatar-370 (Nicolet) spectrometer from 4000 to 400 cm^{-1}. Thermogravimetric analyses (TGA) were carried out on a Shimadzu simultaneous TG209 compositional analysis instrument from room temperature to 800 °C under N_2 at a heating rate of 5 °C min^{-1}. The magnetic susceptibility was measured on a MPMS-7 SQUID magnetometer, solid-state CD spectra were recorded by using a JASCO J-810 spectropolarimeter at room temperature. The disks were prepared by mixing and grinding a crystal sample with KCl.

Preparation of $[Co(tau)_2(4,4'\text{-bipy})]_n \cdot nH_2O$

A mixture of $Co(CH_3COO)_2$ (1.0 mmol), 4,4′-bipy (1.0 mmol), taurine (2.0 mmol), KOH (1.5 mmol), ethanol (15.0 ml) and deionized water (1.0 ml) in the molar ratio of 1:1:2:1.5:260:56 was sealed in a 25-ml stainless steel reactor with Teflon liner, and heated directly to 120 °C. After keeping at 120 °C for 4 days, it was cooled to room temperature at a rate for 10 °C h^{-1}. Red prism crystals were obtained by filtration, washed with deionized water, filtered and dried in air at room temperature. The yield wass 70% based on $Co(CH_3COO)_2$. For $C_{14}H_{22}N_4CoO_8S_2$ (497.41) calculated: 33.81% C, 4.46% H, 11.26% N; found: 33.68% C, 4.78% H, 11.32% N.

Crystal Structure Determination

Single-crystal X-ray diffraction analyses of the title compounds were carried out on a Bruker Smart 1000 CCD diffractometer with a graphite-monochromated MoKα radiation (λ = 0.71073 Å) using the ω–θ scan technique at 293 K. Raw frame data were integrated with the

SAINT program[6]. The structures were solved by direct methods with SHELXS97 and refined by full-matrix least-squares on F2 using the SHELXL97 [6]. The empirical absorption correction was applied with the program SADABS. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were set in the calculated positions and refined by a riding mode. The crystallographic details are provided in Table I, while the selected bond distances and angles are listed in Table II, respectively. CCDC 288891 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

TABLE I
Summary of crystal data and refinement for compound **1**

Flack parameter	0.08(5)
Empirical formula	$C_{14}H_{22}CoN_4O_8S_2$
Formula weight, g mol^{-1}	497.41
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system	trigonal
Space group	*P3121*
a, Å	11.2006(8)
b, Å	11.2006(8)
c, Å	14.1148(18)
β, °	90
V, Å^3	1533.5(2)
Z	3
Calculated density, g cm^{-3}	1.616
Absorption coefficient, mm^{-1}	1.093
θ range for data collection, °	3.64 to 27.47
F(000)	771
Range of *hkl*	$-14 \le h \le 14$, $-13 \le k \le 14$, $-17 \le l \le 18$
Reflections measured	11397
Reflections unique	2344
Independent reflection	$R_{int} = 0.0772$
Number of parameters	132
Goodness-of-fit on F^2	1.178
Final *R* indices [$I > 2\sigma(I)$]	$R = 0.0772$, $wR = 0.1525$
R indices (all data)	$R = 0.1231$, $wR = 0.1795$
Maximal and minimal residual density, e Å^{-3}	0.790, –0.504

TABLE II
Selected bond lengths (in Å) and angles (in °) for complex **1**

Co(1)–O(1)	2.097(5)	Co(1)–N(1)	2.140(7)	S(1)–O(3)	1.427(6)
Co(1)–O(1)#1	2.097(5)	Co(1)–N(2)#1	2.154(7)	S(1)–O(2)	1.402(6)
Co(1)–N(1)#1	2.140(7)	Co(1)–N(2)	2.154(7)	S(1)–O(1)	1.450(5)
O(1)–Co(1)–O(1)#1	179.7(4)	N(1)#1–Co(1)–N(1)	88.8(4)	O(1)–Co(1)–N(2)	88.9(2)
O(1)–Co(1)–N(1)#1	93.2(3)	O(1)–Co(1)–N(2)#1	91.3(3)	O(1)#1–Co(1)–N(2)	91.3(3)
O(1)#1–Co(1)–N(1)#1	86.6(2)	O(1)#1–Co(1)–N(2)#1	88.9(2)	N(1)#1–Co(1)–N(2)	87.4(2)
O(1)–Co(1)–N(1)	86.6(2)	N(1)#1–Co(1)–N(2)#1	173.9(3)	N(1)–Co(1)–N(2)	173.9(3)
O(1)#1–Co(1)–N(1)	93.2(3)	N(1)–Co(1)–N(2)#1	87.4(2)	N(2)#1–Co(1)–N(2)	96.8(3)

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

TABLE III
H-bond parameters of the compound **1** (in Å and °)

Donor–H	Acceptor	D–H	H A	D A	∠(DHA)
N(2)–H(9A)	O(3)#1	0.90	2.55	3.349(9)	148.8
N(2)–H(9B)	O(2)#2	0.90	2.54	3.318(13)	144.5

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

RESULTS AND DISCUSSION

Structural Description

The molecule of $[Co(tau)_2(4,4'\text{-bipy})]_n \cdot nH_2O$ **1** is shown in Fig. 1. As depicted, each asymmetric unit contains one Co^{2+} ion, one taurine ligand, one 4,4′-bipy molecule, and one lattice water molecule. The coordination geometry around the Co(II) center is a slightly distorted octahedron, where the equatorial plane comprises two nitrogen atoms (N1 and N1A) belonging to two individual 4,4′-bipy molecules plus two nitrogen atoms (N2 and N2A) from two taurine ligands. Two oxygen atoms (O1 and O1A) of taurine ligands occupy the remaining apical coordination sites. The Co–N bond distances are 2.146(8) and 2.151(8) Å, and the Co–O bond distance is 2.105(6) Å, close to those of the literature[4d,7].

The Co(II) ions are bridged by bidentate 4,4′-bipy ligand with the Co–Co distance of 11.385(6) Å (in which two pyridyl rings are twisted from each

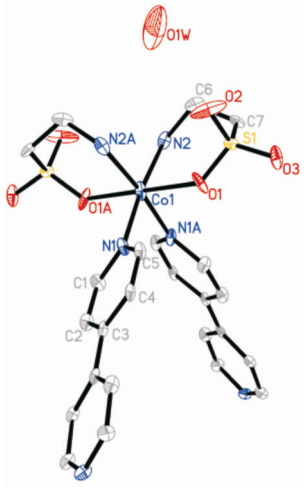

FIG. 1
Building unit of compound **1** with the atomic labeling scheme. Thermal ellipsoids are shown at the 30% probability level. All H atoms are omitted for clarity. Symmetry code for the generated atoms: (A) $-x + y$, $1 - x$, $-1/3 + z$

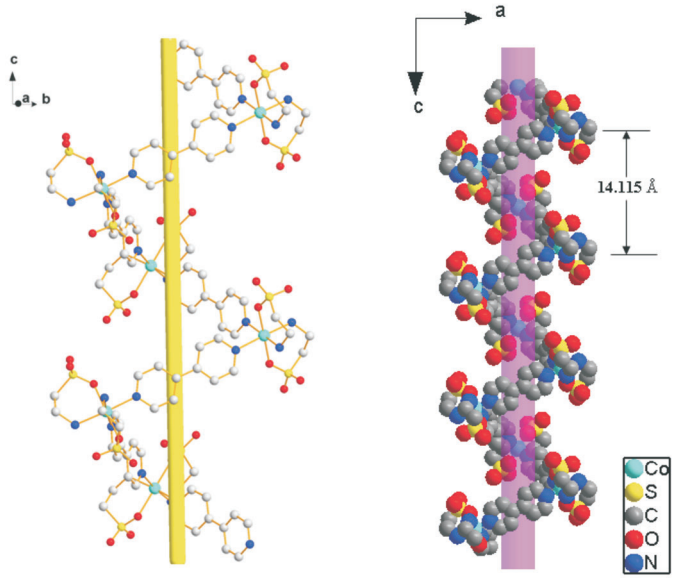

FIG. 2
Right-handed 3_1 helical chain built from alternating $Co(tau)_2$ and 4,4′-bipy

other with the dihedral of 5.6°) to form an infinite helical chain running along the *c*-axis (Fig. 2). The right-handed helix is generated around the crystallographic 31 axis. Each set of three crystallographically equivalent cobalt centers constitutes a single revolution of the helix with a distance of 14.115 Å.

Interestingly, the view along the polymer axis (Fig. 3) shows that a trigonal channel with side length approximately 8.4 Å exists within the

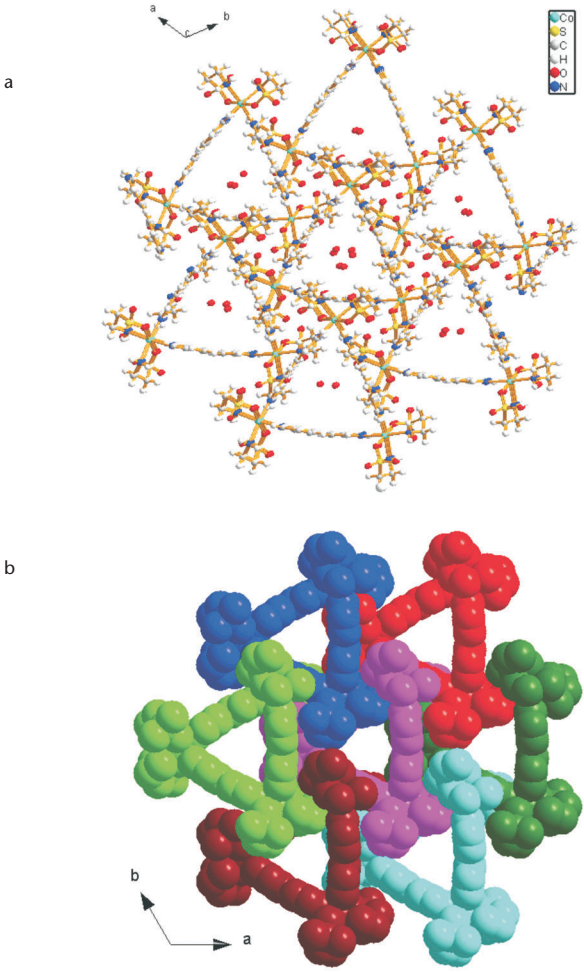

FIG. 3
A schematic view showing the interlinking of adjacent helical chains (a) and the 1D channels existed within the polymer coils (b)

polymer coil. 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 taurine are found, and the C–H···O distances and the C–H···O angles are 3.205(8) Å and 157(6)°. In the title complex, it is supposed that the conformational flexibility of taurine is a key factor in the formation of the striking motif because it can cause the required twist to result in a strong interaction directionality and a six-fold helix symmetry, producing the final helical structure.

Infrared Spectra

By comparing the infrared spectra of free ligand to the complex, we can get some information about the coordination nature of the ligand. The FTIR spectra of **1** (Fig. 4) show a broad band centered around 3400 cm^{-1} attributable to O–H stretching frequency of water and the bands at 3075, 2951 and 3133 cm^{-1} belong to the N–H stretching vibration. Bands assigned to $\nu_{as}(SO_3^-)$ and $\nu_s(SO_3^-)$, which are respectively observed for the free ligand at 1214.2, 1182.6, 1039.6 cm^{-1} shift to 1200.3 1165.5, 1036.3 cm^{-1} in com-

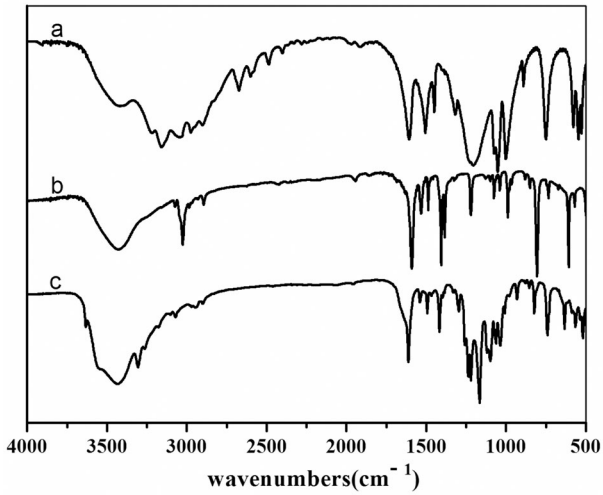

FIG 4
FTIR spectra of taurine (a), 4,4′-bipy (b) and compound **1** (c)

plex **1**. This indicates that the deprotonation of sulfonic groups occurs upon coordination[5d]. Besides, the adsorption peaks of 4,4′-bipy shift from 1592, 1407 and 807 cm^{-1} to 1612, 1417, 823 cm^{-1} in complex **1**, suggesting the existence of coordinate bonds between metal ions and 4,4′-bipy ligands[8].

Thermal Stability

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 was carried out in N_2 condition from room temperature to 800 °C for examining the properties of dehydration and stability of compound **1** (Fig. 5). The TG curve of **1** shows four-stage weight losses. The first stage, which occurs from 20 to 95 °C, is attributed to the release of lattice water molecules. The observed weight loss (3.8%) is in agreement with the calculated value (3.6%). The second weight loss in the temperature range of 300–370 °C corresponds to the removal of one taurine molecule. The observed weight loss of 28.5% is close to the calculated value (25.8%). The third weight loss in the temperature range of 370–430 °C corresponds to the removal of the other taurine molecule. The observed weight loss of

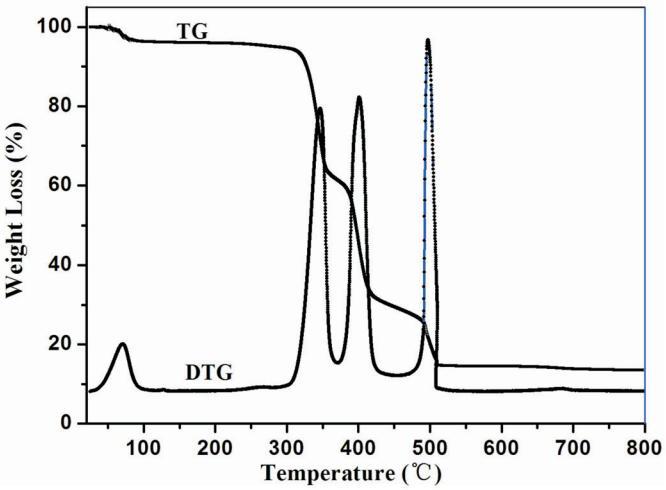

FIG. 5
The TG curves for compound **1**

29.2% is also close to the calculated value (25.8%). The weight loss above 470 °C is due to the decomposition of the 4,4′-bipy ligand. After decomposition of complex **1** at high temperature, the weight of the residue (15.2%) responds to CoO (calculated 15.3%).

Magnetic Property

The temperature-dependent magnetic susceptibility of **1** was collected in the range of 2–300 K on the static magnetic field of 1000 Oe. As shown in Fig. 6, at 300 K, the $\chi_m T$ value of **1** is 2.46 $cm^3\ mol^{-1}$ K, significantly higher than the spin-only value (1.875 $cm^3\ mol^{-1}$ K) of an octahedral high-spin Co(II) ion, indicating the significant spin–orbit coupling interaction of Co(II) ion is involved[9]. Lowering of the temperature caused a gradually decrease of $\chi_m T$, which dropped to 0.56 $cm^3\ mol^{-1}$ K at 2.0 K. The magnetic susceptibility above 20 K obeys Curie–Weiss law very well, giving the Curie constant C of 2.49(1) $cm^3\ mol^{-1}$ K and Weiss constant θ of –6.4(5) K. It was realized that the spin–orbit coupling of the octahedral high-spin Co(II) ions could cause the decrease of $\chi_m T$ value[10], thus this small negative Weiss constant should be ascribed to the spin–orbit coupling of Co(II) ions and the weak antiferromagnetic intra-chain interaction transmitted via 4,4′-bipy.

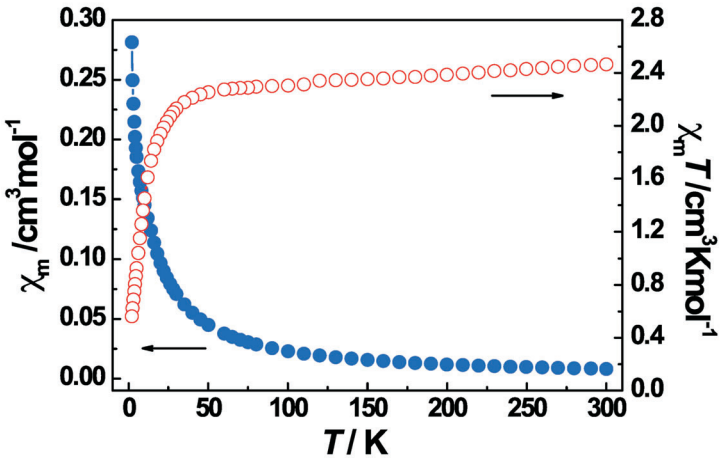

FIG. 6
The temperature-dependent magnetic susceptibility of compound **1** collected on the static field of 1000 Oe

Solid-State CD Spectra

In order to correlate the absolute configurations of the title complex, the solid-state CD spectrum was measured and is shown (Fig. 7). Results of solid-state CD measurements indicate that a single crystal **1** displays dichroic signals. These rotational strengths show that the CD signal is classical negative exciton couplet centered around 304 nm. The intensity of curve is weak. This is primarily due to the very small energy gap between the oppositely signed rotational strengths which leads to a cancellation of most of the CD signal[11].

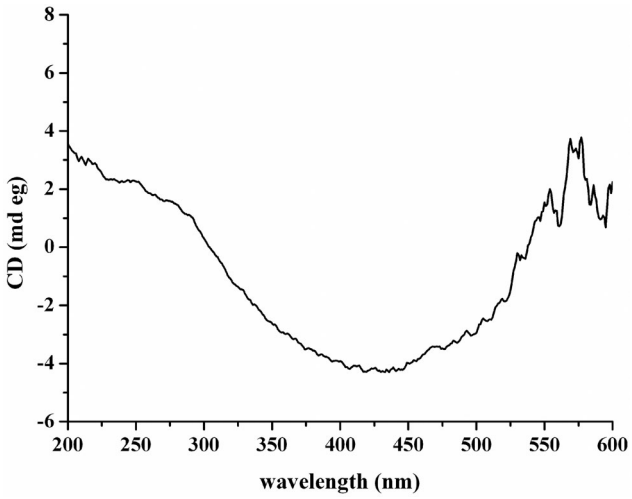

FIG. 7
Solid-state CD spectrum of compound **1** (KCl disk)

CONCLUSIONS

In conclusion, a novel cobalt taurine containing three-fold helical chains, $[Co(tau)_2(4,4'\text{-bipy})]_n \cdot nH_2O$ **1** has been synthesized by hydrothermal technique using taurine and 4,4′-bipy as ligands. The structure of compound **1** comprises triagonal channels that are formed through the intertwist of the three-fold 1D helical chains. It is quite interesting to note that the conformational flexibility of taurine is the key design element that cause the twist required to form the final helical structures.

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