A chiral layered Co(II) coordination polymer with helical chains from achiral materials†

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A layered coordination polymer Co(PDC)$(H_2O)_2 \cdot H_2O$ containing two helical chains was synthesized, and the resultant crystals were not racemic as evidenced by the observation of strong signals in vibrational circular dichroism (VCD) spectra.

Helical structures through self-organization are an essence of life and are of interest in supramolecular chemistry because helical structures are reminiscent of DNA molecules. The design and synthesis of chiral inorganic–organic materials have attracted great attention for their potential applications in enantioselective separation and catalysis.[1,2] It is known that the aluminosilicate zeolite β and the titanosilicate ETS-10 are multiphasic with one polymorph crystallized in a chiral space group.[3] The chiral compounds can be synthesized by using chiral reactants, solvents and/or auxiliary agents, by spontaneous resolution, or by the influence of chiral physical environment such as polarized light.[4,5] Recently, chiral templates such as chiral metal complexes have been used to form chiral metal phosphates.[6] The transformation was achieved by chirality direction and chirality transfer. The phenomenon of spontaneous resolution is unusual in coordination chemistry, and the products are normally a racemic mixture of left- and right-handed helical chains, although the each crystal is a single enantiomer.[7]

In this work, we employed an achiral ligand pyridine-2,5-dicarboxylic acid (H_2PDC) and synthesized a 2-D layer coordination polymer Co(PDC)$(H_2O)_2 \cdot H_2O$ containing two helical chains.[8] The synthesis did not involve any chiral reactant or solvent or other auxiliary agent. To our surprise, the resultant crystals were not racemic as evidenced by the observation of strong signals in vibrational circular dichroism (VCD) spectra. VCD spectroscopy is a relatively new but powerful technique to obtain conformational information of chiral molecules.[9]

As a typical preparation procedure, a mixture of H_2PDC (0.5 mmol) and $Co(CH_3COO)_2 \cdot 4H_2O$ (0.5 mmol) was suspended in 8 ml deionized water and sealed in a 20-ml Teflon-lined autoclave. Upon heating at 180 °C for three days, the autoclave was slowly cooled to room temperature. The pink crystals were collected, washed with deionized water and dried in air (0.083 g, yield 60%). The single-crystal data were collected on a Bruker SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). FTIR spectra were obtained on a Nicolet Impact 410 FTIR spectrometer using a KBr pellet. VCD spectra were measured with the Bruker PMA 37 spectrometer. A Perkin-Elmer TGA 7 thermogravimetric analyzer was used to obtain the TG curve in air with a heating rate of 20 °C min^{-1}.

Single-crystal X-ray analysis‡ shows that the compound is a 2-D layer coordination polymer which possesses two types of helical chains. As shown in Fig. 1, Co(II) displays a distorted octahedral coordination environment with one nitrogen atom (N1) and three oxygen atoms (O1, O3, O4) from three H_2PDC ligands, and other two oxygen atoms (O5, O6) from two water molecules, there is one guest water molecule (O7) in the compound. The compound is stable in air and insoluble in water and common organic solvents. [Co(PDC)$(H_2O)_2 \cdot H_2O$]: Anal. Calc. for $C_7H_9NO_7Co$: Co 21.49, C 30.30, H 3.51, N 5.08. Found: Co 21.12 C 30.26, H 3.26, N 5.04%.

The compound crystallizes in the chiral space group $P2_12_12_1$ and there are two types of twofold screw axes along the crystallographic *b* axis. Each carboxylate of the H_2PDC ligands bridges two Co(II) ions in *syn-anti* coordination mode to form infinite right-hand helical –C–O–Co– chains (Fig. 2(a)). The PDC ligands also bridge the cobalt center to form a further tpye of helical –Co–PDC– chains with helical orientation opposite to the former helical chains (Fig. 2(a)). The distance of the repeating parts is about 9.422 Å. The two types of helical chains are interconnected to each other through the cobalt center to produce an interesting

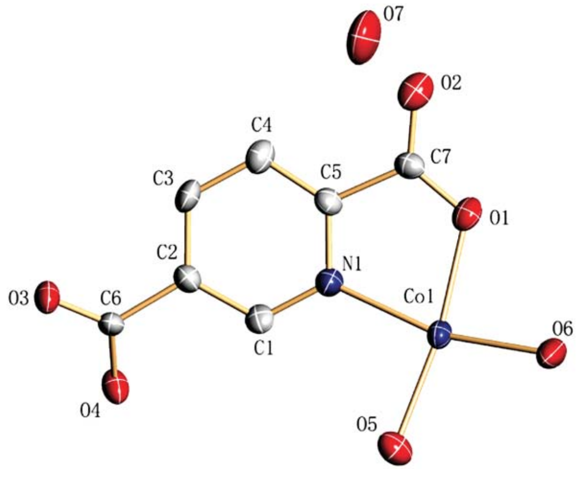

Fig. 1 Thermal ellipsoid plot (50%) showing an asymmetric unit of Co(PDC)$(H_2O)_2 \cdot H_2O$. The N(1)–Co(1) distance is 2.149(4) Å. The Co–O distances are 2.062(3)–2.182(3) Å. The angles around the cobalt atom range from 76.97(14) to 173.71(13)°. The H atoms are omitted for clarity.

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† Electronic supplementary information (ESI) available: χ_m *vs.* *T* and $1/\chi_m$ *vs.* *T* plots of Co(PDC)$(H_2O)_2 \cdot H_2O$. See http://www.rsc.org/suppdata/cc/b4/b417184e/

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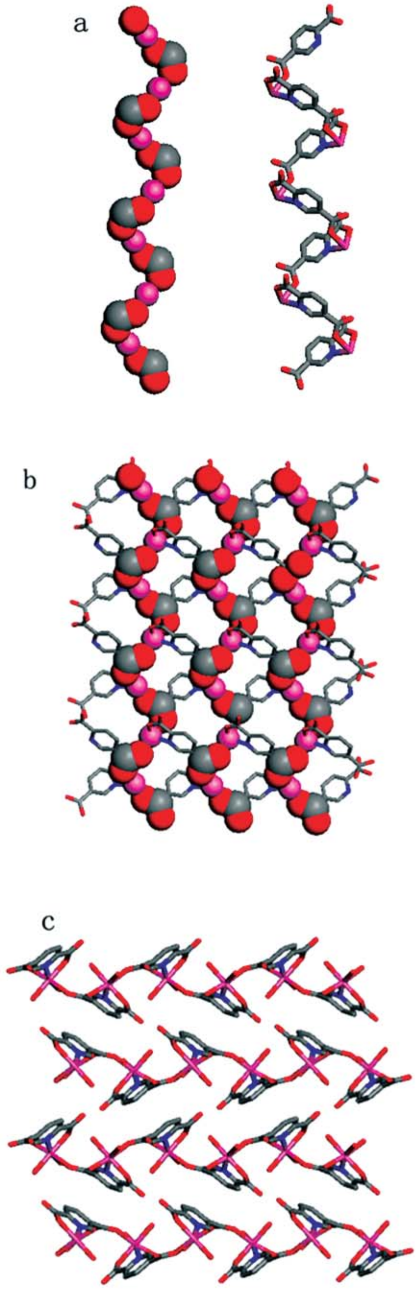

Fig. 2 (a) A space-filling view of the right-handed helical chain of –C–O–Co– and a cylindrical view of the left-handed helical chain of –PDC–Co– along the *b* axis. (b) The 2D structure including two types of helical chains. (c) Packing of the undulating layers along the [100] direction. The H atoms are omitted for clarity. Color code: Co: pink; C: grey; N: blue; O: red.

two-dimensional layered structure (Fig. 2(b)) The two coordinated water molecules and two coordinated carboxylate oxygen atoms form intralayer H-bonds with an O5···O1 distance of 2.691 Å and an O6···O3 distance of 2.693 Å. One coordinated water molecule and the uncoordinated carboxylate oxygen atom of an adjacent layer form an interlayer H-bond with an O5···O2 distance of 2.687 Å. The guest water molecule and one coordinated water form an H-bond with an O7···O6 distance of 2.623 Å. Therefore, the O–H···O hydrogen bonds further extend the 2-D undulating layers in to a 3-D supramolecular framework (Fig. 2(c)).[10]

Thermogravimetric analysis (TGA) showed that compound was stable up to 200 °C. The TG curve showed three weight loss steps. The first weight loss of 7.1% from 100 to 200 °C corresponds to the loss of one guest water molecule. The second weight loss of 17.5% between 200 and 250 °C is attributed to the loss of two water molecules. The third step between 300 and 510 °C corresponds to the loss of all organic ligands and a weight gain of the residue is in accordance with conversion to CoO.

We have obtained VCD spectra in the mid-IR region of the 2-D layer coordination polymer. Fig. 3 shows the VCD and IR spectra of the $Co(PDC)(H_2O)_2 \cdot H_2O$ crystals. The IR spectrum of the compound is assigned as follows: the bands at 1290, 1363, 1394 and 1658 cm^{-1} are attributed to the C=O stretch vibrations; the bands at 1479, 1583 and 1600 cm^{-1} are assigned to the skeleton vibrations of aromatic ring. The experimental VCD bands at 1288–1394 and 1658 cm^{-1} correspond to C=O stretch vibrations, and the bands at 1471–1611 cm^{-1} correspond to the skeleton vibration of aromatic ring. The bond of the C=O group and the aromatic ring construct the two types of helical chains: the right-hand helical –C–O–Co– chains, and the left-hand –PDC–Co– helical chains. There is a good agreement between VCD and IR absorption spectra. The vibrational modes were identified and conformational information also can be observed in the VCD spectra. The strong VCD signals indicate that the crystals of $Co(PDC)(H_2O)_2 \cdot H_2O$ were chiral. The experiment was repeated on the compound obtained from different autoclave experiments six times.

The pyridine-2,5-dicarboxylic acid ligand may play a key role in the two chains. As shown in Fig. 2, the organic ligand acts as the structure directing agent to form the chiral coordination polymer of the right-handed and left-handed helical chains.

In order to understand the reason for the observed enantiomeric excess in the $Co(PDC)(H_2O)_2 \cdot H_2O$ product, we have checked all the reagents and solvents as well as the mother-liquor, and found

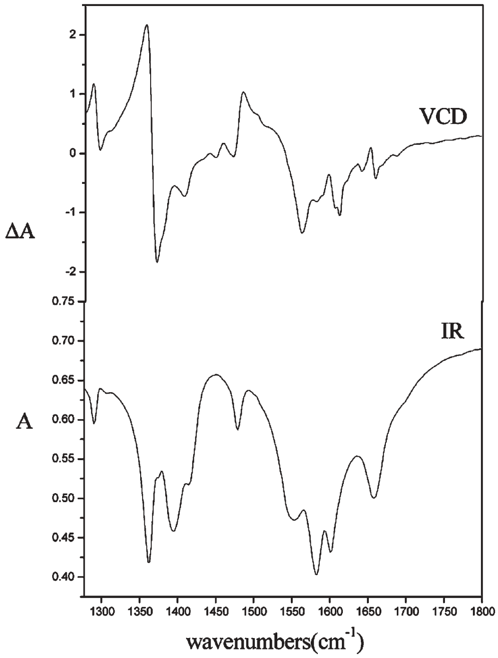

Fig. 3 VCD (top) and IR absorption (bottom) spectra.

that none had optical rotation. There was no VCD signal for the starting materials, H_2PDC and $Co(CH_3COO)_2{\cdot}4H_2O$, or the solids obtained by evaporating the mother-liquor. So far we have made independent preparations using different autoclaves and all yielded crystals with essentially the same VCD signals. We have also checked for and eliminated the possibility of a physical chiral environment effect including light, magnetic field and stirring directions (clockwise or counterclockwise). The enantiomeric excess may be explained by the fact that the initial crystals formed may seed the handedness of the bulk product, and thus the particular handedness of the bulk depends on which random hand is formed by the initial few crystals. Further investigation is in progress to extend the synthesis to other metal and ligand systems and to elucidate the reasons for the observed enantiomeric excess.

The variable-temperature (4–300 K) magnetic susceptibility measurement of the compound is shown in Fig. S1 (ESI†). Between 4 and 300 K, χ_m continuously increases with decreasing temperature. In the $1/\chi_m$ *vs.* T plot, the susceptibility can be fitted to the Curie–Weiss law with $C = 3.045$ cm^3 K mol^{-1}. The Weiss temperature, $\theta = -6.58$ K, indicates that antiferromagnetic interactions exist between metallic Co centers.

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Notes and references

‡ *Crystal data* for $Co(PDC)(H_2O)_2{\cdot}H_2O$: $C_7H_9NO_7Co$, $M = 278.08$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 7.363(2)$, $b = 9.422(3)$, $c = 13.976(4)$ Å, $V = 969.6(5)$ Å^3, $T = 293(2)$ K, $Z = 4$, μ(Mo-Kα) = 1.792 mm^{-1}, Flack parameter = 0.0032, $R = 0.0284$, 2225 reflections measured, 1374 unique ($R_{int} = 0.0288$) which were used in all calculations. The final $wR(F^2)$ was 0.0822 (all data). CCDC 252681. See http://www.rsc.org/suppdata/cc/b4/b417184e/ for crystallographic data in .cif or other electronic format.

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