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COMMUNICATION

A chiral coordination polymer with double coaxially nested helical chains exhibiting spin-canting antiferromagnetism

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A chiral coordination polymer, fabricated by the alternate arrangement of rarely two types of double coaxially nested helical chains, which spiral towards the parallel and inverse directions, exhibits spin-canting antiferromagnetism.

Chiral coordination polymers have been paid remarkable attention in recent years, not only because of their fascinating architectures, but also for the tremendous value in enantioselective separations, nonlinear optics, asymmetric catalysis and magnetism, etc.[1] Many of the synthesized chiral coordination polymers have been found to possess beautiful helical structures, which are usually related to the occurrence of chirality.[2] Up to now, though a large number of helical coordination polymers holding single-, double-, triple-, multiple-stranded helices have been obtained,[3] the nested helical coordination polymers with the same helix axis are not common and only a few cases have been reported,[3d,4] which are constructed by encapsulation of the inner helices into the outer ones. As well, among the present cases, the inner and outer helices spiralling towards opposite directions are rare. Herein, with the chiral D-camphoric acid (D-H_2ca) as a starting material, we have obtained a new coordination polymer $[Ni_3(OH)_2(D\text{-}ca)_2(D\text{-}H_2ca)_3]_n$ (**1**), which is a chiral three-dimensional framework and exhibits spin-canting antiferromagnetism. To the best of our knowledge, Bu' group has made an abundant research in the chirality field and synthesized many beautiful coordination polymers related to camphoric acid.[5] Even so, notably, compound **1** contains two types of double coaxially nested helical chains spiralling towards the parallel and inverse directions, which is seldom reported in helical coordination polymers.[4b] Moreover, it is worth pointing that the coaxially single outer and inner helix of each type are also with opposite handedness.

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† Electronic Supplementary Information (ESI) available: Experimental and crystallographical sections, additional tables (Tables S1—S3), Scheme 1 and graphics (Fig. S1—S10) and for **1**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

A mix of $Ni(NO_3)_2 \cdot 6H_2O$, D-H_2ca, 2,4-diamino-6-chloro-1,3,5-triazine in a molar ratio of 1 : 0.5 : 0.5 and 6 mL H_2O, maintaining temperature at 150 °C for 3 days, green block crystals of **1** were obtained. X-ray single-crystal diffraction reveals that compound **1** crystallizes in orthorhombic, chiral space group $P2_12_12_1$, exhibiting a three-dimensional framework significantly consisting of two types of double nested coaxially helical chains. As illustrated in Fig. 1, the asymmetric unit contains three crystallographically independent nickel atoms, two hydroxyl groups, two completely deprotonated D-ca^{2-} ligands (noted as 1-D-ca^{2-}, 2-D-ca^{2-}, Fig. S1, ESI†) and three D-H_2ca ligands (noted as 3-D-H_2ca, 4-D-H_2ca, 5-D-H_2ca, Fig. S1, ESI†).

Fig.1 insert here

Fig. 1 The asymmetric unit of **1** showing 30 % ellipsoid probability. Color Scheme: Ni green, O orange and C grey. H atoms are omitted for clarity.

All the nickel atoms are assigned as bivalent cations and the u_2-O (O21, O22) atoms as hydroxyl oxygen atoms according to the charge balance and bond-valence sum (BVS) calculations (Table S3, ESI†).[6] Apparently, each Ni atom is featuring six-coordinated $[NiO_6]$ octahedral configuration. The apical positions of Ni1 are occupied by two u_2-OH and the equatorial positions are located by four carboxyl–O atoms from four individual D-ca^{2-} ligands. Both Ni2 and Ni3 are surrounded by one u_2-OH and five carboxyl–O atoms from two D-ca^{2-} and three D-H_2ca ligands, respectively, and located on the either side of Ni1 with distances of Ni1…Ni2 3.4226 Å, Ni1…Ni3 3.4156 Å. The Ni–O distances are in the range of 1.990(5) Å to 2.143(5) Å, comparable to those of normal Ni–carboxyl groups.[7] As a consequence of mixed bridge of four u_2-carboxyl groups and two u_2-OH, a trinuclear nickel unit is formed with the angles of Ni2–O21–Ni1 110.62(19) °, Ni3–O22–Ni1 110.75(19) °, which are related to the antiferromagnetic coupling.[8] Along a-axis direction, a striking phenomenon is observed. The 3-D-H_2ca adopts u_2-η^1:η^0:η^1:η^0 (Scheme 1, ESI†) coordination mode to connect to the bilateral Ni2 and Ni3 ions, as a result, an outer left-handed helix of $\{-3\text{-}D\text{-}H_2ca–Ni_3(OH)_2-\}_n$ is formed with a pitch of 12.4370 Å, equal to the length of crystallographic a-axis (Fig. 2a-b). Simultaneously, an internally nested right-handed helical chain of $\{-1\text{-}D\text{-}ca^{2-}-$

$Ni_3(OH)_2-\}_n$ is encapsulated into the outer one, which is generated by the $syn,syn-u_2-\eta^1:\eta^1$ mode (Scheme 1, ESI†) chelated to Ni1, Ni2 as well as Ni1, Ni3 of each carboxyl group of 1-D-ca^{2-} (Fig. 2c-d). The outer and nested inner single helix surround common 2_1 screw axis but with the opposite handedness (Fig. 2e-f), which is rare in helical coordination polymers. More interestingly, on the other side of shared $Ni_3(OH)_2$ unit, another type of nested double coaxially helical chains is formed by the bridge of $u_2-\eta^1:\eta^0:\eta^1:\eta^0$ 4-D-H$_2$ca and $u_4-\eta^1:\eta^1:\eta^1:\eta^1$ 2-D-ca^{2-}, respectively, holding the antipodal handedness with the former chains (Fig. S2, ESI†). Thus, two types of double coaxially nested helices are generated with parallel and inverse spiral directions and alternately arranged to get 2D sheets, which are further extended to a three-dimensional framework for the remaining coordination site of Ni2 as well as Ni3 taken up by $u_2-\eta^1:\eta^0:\eta^1:\eta^0$ 5-D-H$_2$ca (Fig. 3).

Fig. 2 insert here

Fig. 2 One type of nested coaxially helices of **1** constructed from outer and inner single helix with opposite handedness. Color Scheme: Ni green and O orange. The D-camphoric acid ligands are in green and light blue colors for clarity. H atoms are omitted.

Fig. 3 insert here

Fig. 3 The three-dimensional framework of **1**. Some atoms of D-camphoric acid ligand are omitted for clarity.

From the perspective of structural analysis, D-camphoric acids adopting rational coordination modes, play extremely significant roles in construction of the nested coaxially helical coordination polymer. The bis-monodentate D-H$_2$ca ligands linking to external Ni ions in trinuclear nickel units afford a firm helical shell and enough space for the adjustable insertion of the inner helix; the bis-bidentate D-ca^{2-} ligands chelating to two pairs of Ni ions between adjacent trinuclear nickel units, making the ligands encapsulated in the space, stabilizes the whole helicity.

IR spectrum of **1** provides a further demonstration for the different coordination modes (Fig. S3). The strong peak of 1679 cm^{-1} is resulted from the stretching vibration of C=O in the monodentate carboxyl group of D-H$_2$ca; for the bidentate carboxyl group of D-ca^{2-}, the asymmetric and symmetric stretching vibrations are observed at 1610 cm^{-1} and 1384 cm^{-1} due to resonance; as well, the sharp peak of 3573 cm^{-1} can be attributed to the stretching vibration of u_2-OH. The X-ray power diffraction of **1** was investigated at room temperature. As shown in Fig. S4, the peaks of experimental and simulated patterns agree well with each other, indicating the good phase purity of **1**. The thermogravimetric analysis (TGA) of **1** was carried out in N$_2$ atmosphere at solid state from 25 to 600 °C (Fig. S5, ESI†). Compound **1** is thermally stable up to 250 °C and the two-step weight losses are observed. The first-step weight loss from 250 °C to 326 °C is corresponding to the removal of hydroxyl groups and the D-ca^{2-} ligands (obs. 35.52 %, calcd. 35.65 %). The following weight loss up to 600 °C is consistent with the departure of D-H$_2$ca ligands, resulted in the collapse of the framework (obs. 50.42 %, calcd. 49.76 %). Finally, the remaining residue is nickel. As well, the solid-state circular dichroism spectroscopy of **1** was investigated with a KBr pellet. The CD spectrum (Fig. S6, ESI†) shows a positive Cotton effect with peak at 236 nm, and a negative

Cotton effect around 266 nm and 529 nm, which confirm the presence of chirality in compound **1**.

The temperature-dependent magnetic susceptibility data of compound **1** was measured on crystalline sample under an applied field of 1 KOe in the range of 2–300 K. The χ_mT vs. T plots are depicted in Fig. 4a. The room temperature value of χ_mT is 4.73 cm^3 mol^{-1} K, larger than the expected 3.83 cm^3 mol^{-1} K for three isolated high-spin Ni(II) ions with $S = 1$ and a significant g value of 2.26,[9] indicating the presence of orbital contribution and population of excited-states of Ni(II) ions.[10] Upon cooling, the χ_mT value shows a gradual decrease to reach a rounded minimum of 4.09 cm^3 mol^{-1} K at about 50 K, indicating the antiferromagnetic coupling between nickel ions. When the cooling continues, the χ_mT value follows by a quick increase to a maximum of 5.35 cm^3 mol^{-1} K at about 2 K, featuring ferromagnetic performance. Such spontaneous magnetization at low temperature can be ascribed to spin-canting behaviour,[11] which is further demonstrated by the field dependence of χ_mT (Fig. 4a, insert).[10,12] The Curie-Weiss law is used to fit the χ_m^{-1} vs. T above 80 K (Fig. S7, ESI†), resulting in the value of Curie constant $C = 0.30$ cm^3 K mol^{-1} and Weiss temperature $\theta = -0.062$ K, which further confirm the weak antiferromagnetic interactions. Assuming the trinuclear Ni(II) unit as linear and centrosymmetric (O21–Ni1–O22 179.9(2) °, Ni2–O21–Ni1 110.62(19) °, Ni3–O22–Ni1 110.75(19) °, Ni1…Ni2 3.4226 Å, Ni1…Ni3 3.4156 Å), an attempt was made to fit the magnetic data of compound **1** according to a simple $S = 1$ linear trimer model with the Hamiltonian $H = -2J(S_1S_2 + S_2S_3)$, where S_2 represents the spin state of the central Ni(II) ion:[13]

$$\chi_m = \frac{Ng^2\beta^2}{kT} \times \frac{28e^{4x}+10e^{-2x}+2e^{-6x}+10e^{2x}+2}{7e^{4x}+8e^{-2x}+3e^{-6x}+5e^{2x}+e^{-4x}+3} \quad (1)$$

Notably, N is Avogadro's number, β is the Bohr magneton, and $x = J / k$ T. The good fitting to χ_m vs. T curve in the range of 25–300 K gives $g = 2.40$, $J = -0.156$ cm^{-1} with the agreement factor $R = 1.19 \times 10^{-6}$ (Fig. S8, ESI†). The g value is reasonable for octahedral Ni(II) ions[14] and the negative J value is consistent with the weak antiferromagnetic interactions, which may transfer by the $syn-syn^{14b,15}$ carboxyl groups of D-ca^{2-} and the Ni–u_2-OH–Ni bridge with the angles at about 110 ° in trinuclear nickel units.[8]

(a)

Fig.4a insert here

(b)

Fig. 4b insert here

Fig. 4 (a) The χ_mT vs. T plot of **1** in the range of 2-300 K at 1 KOe; insert: χ_mT vs. T plots at different external fields; (b) the field-dependent magnetization of **1**; insert: the magnetic hysteresis loop of **1**.

The field dependence of the isothermal magnetization M(H) was measured as shown in Fig. 4b. The curves display an increasing trend with the increase of field and the final value at 2 K is 6.34 $N\beta$ when the field reaches 5 T, without reaching the saturation value of 6.78 $N\beta$ (M_s, $g = 2.26$) expected for three isolated Ni(II) ions. As well, a hysteresis loop at 2 K was observed a remnant magnetization (M_r) of 0.0074 $N\beta$ and a coercive field (H_c) of 16 Oe (Fig. 4b, insert), indicative the existence of weak ferromagnetic state. The canting angle can be estimated to 0.063 ° according to the equation $\sin(\alpha) = M_r/M_s$.[16] It is well known that spin canting is usually caused by

single-ion magnetic anisotropy or antisymmetric exchange interaction.[10,17] For compound **1**, no inversion center is present between Ni(II) ions and adjacent trinuclear nickel units, which may result in the spin-canting behavior.

To fully understand the magnetic behavior of **1** at low temperature, the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves under 100 Oe and 200 Oe were investigated (Fig. S9, ESI†). No divergence is observed in ZFC and FC curves at the same field. Additionally, the temperature dependence of ac susceptibilities in the range of 500–5000 Hz (Fig. S10, ESI†) show the similar characteristics. No peaks above 2 K and no frequency dependence are shown in the χ' *vs.* *T* as well as the χ'' *vs.* *T* curves.

Conclusions

In summary, we have reported a chiral 3D coordination polymer fabricated by trinuclear nickel units and camphoric acid, where two types of double coaxially nested helical chains are alternately arranged and spiral towards the parallel and inverse directions. The compound also exhibits spin-canting antiferromagnetism. Further work about charity and helix is underway.

Acknowledgements

Notes and references

‡ Synthesis of compound **1**: A mixture of Ni(NO₃)₂·6H₂O (1 mmol, 0.290 g), D-H₂ca (0.5 mmol, 0.100 g), 2,4-diamino-6-chloro-1,3,5-triazine (0.5 mmol, 0.073 g) and H₂O (6 mL) was placed in a 25 mL Teflon-lined stainless steel vessel, heated to 150 °C for 3 days, then cooled to room temperature. Green block crystals of **1** were obtained, washed by distilled water (Yield: 0.053 g, 43.9 % based on D-H₂ca). Elemental analysis (%): calcd for C 49.82, H 6.53; found: C 49.78, H 6.58. FT-IR (KBr pellet, cm⁻¹): 3573w, 3415w, 2969m, 2883w, 1679s, 1610s, 1462m, 1418s, 1384s, 1360s, 1176w, 1127w, 787w.

§ Crystal data for **1**: C₅₀H₇₈Ni₃O₂₂, M_r = 1207.25, Orthorhombic, $P2_12_12_1$, a = 12.4370(6) Å, b = 14.0606(7) Å, c = 32.3952(16) Å, α = β = γ = 90 °, V = 5665.0(5) Å³, Z = 4, D_c = 1.415 g cm⁻³, μ = 1.063 mm⁻¹, $F(000)$ = 2552, R_1 = 0.0618, wR_2 = 0.1562, Flack parameter = 0.05(3). CCDC number is 1404806.

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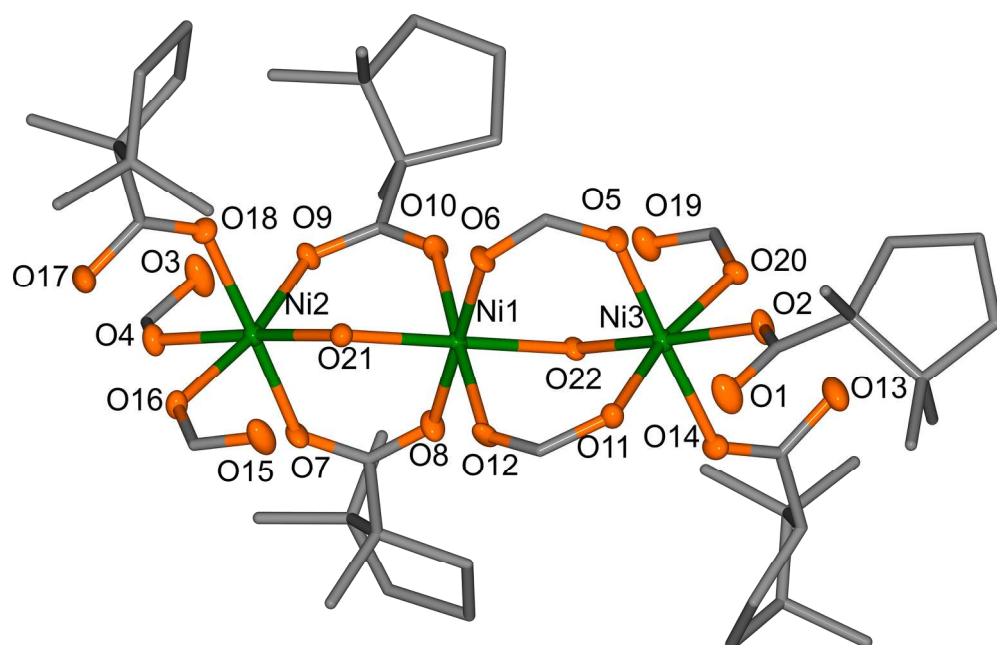
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Fig. 1 The asymmetric unit of 1 showing 30 % ellipsoid probability. Color Scheme: Ni green, O orange and C grey. H atoms are omitted for clarity.
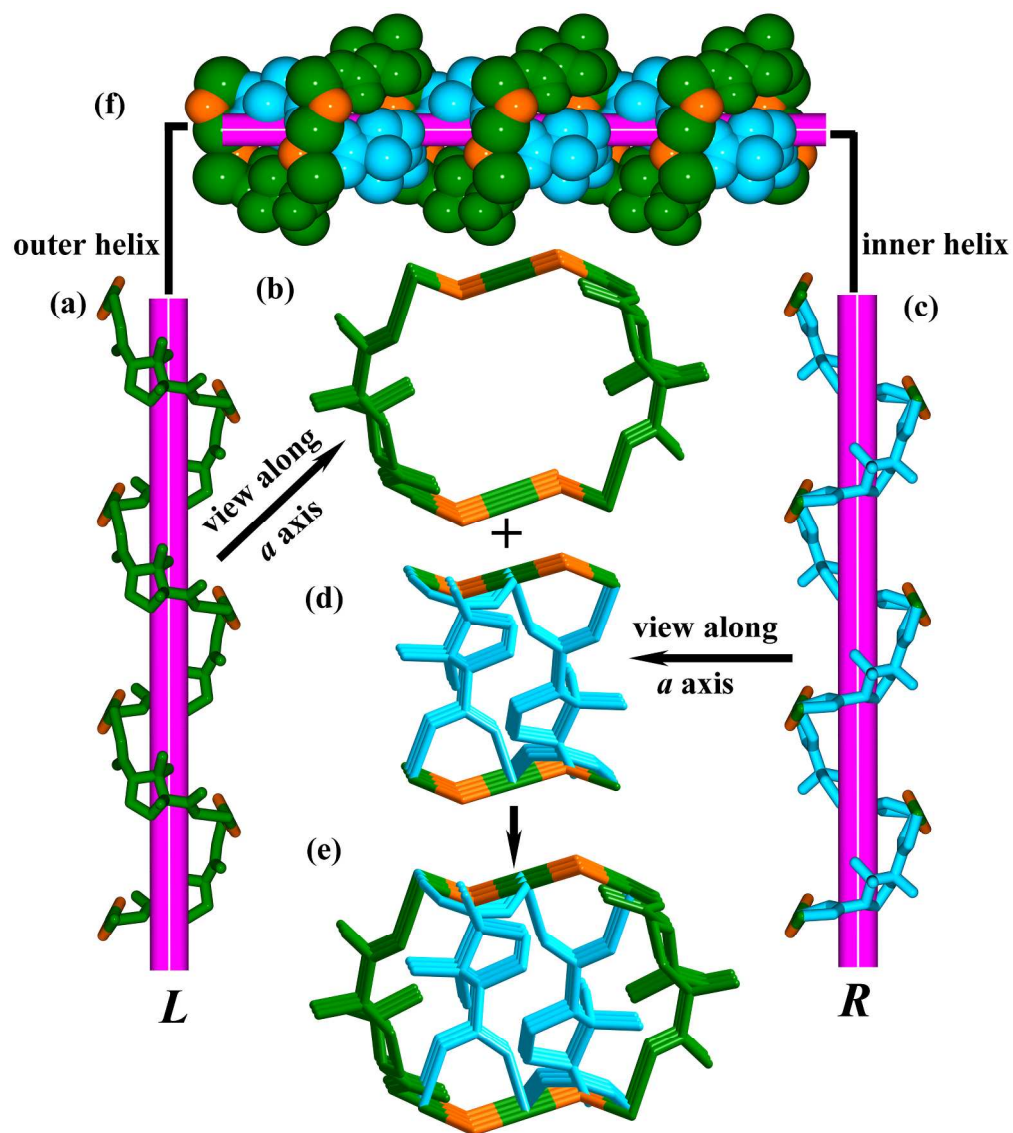
Fig. 2 One type of nested coaxially helices of 1 constructed from outer and inner single helix with opposite handedness. Color Scheme: Ni green and O orange. The D-camphoric acid ligands are in green and light blue colors for clarity. H atoms are omitted.
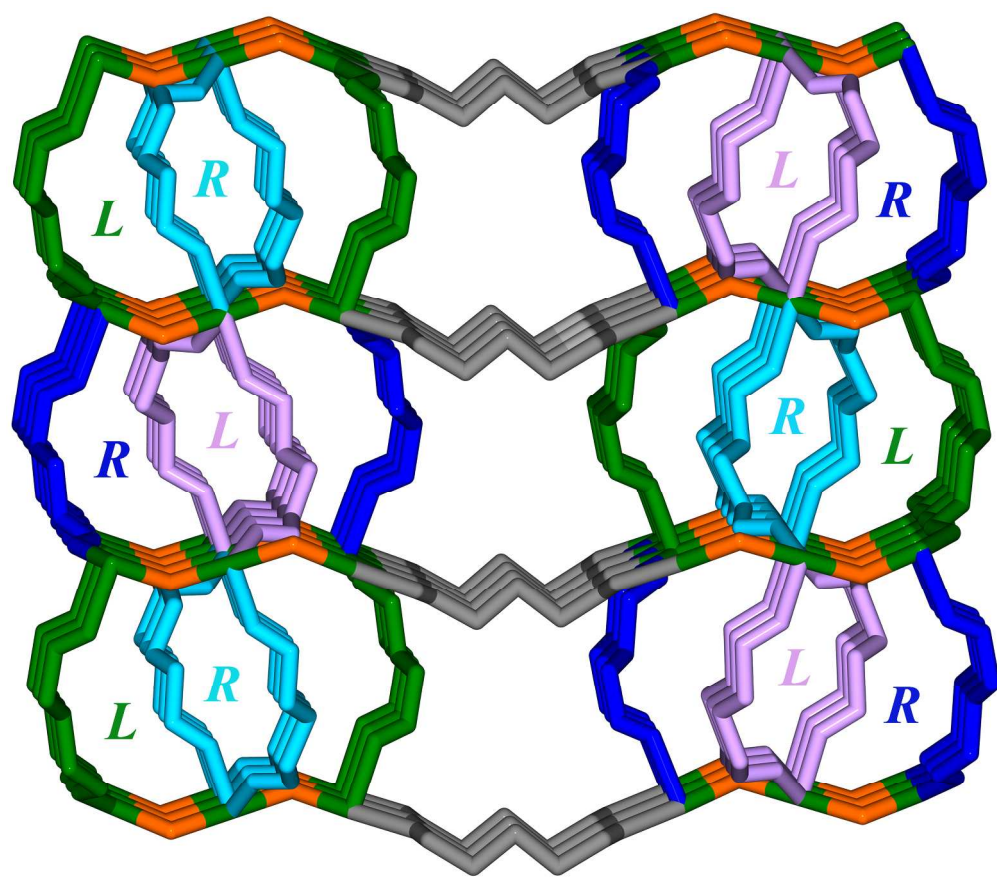
Fig. 3 The three-dimensional framework of 1. Some atoms of D-camphoric acid ligand are omitted for clarity.
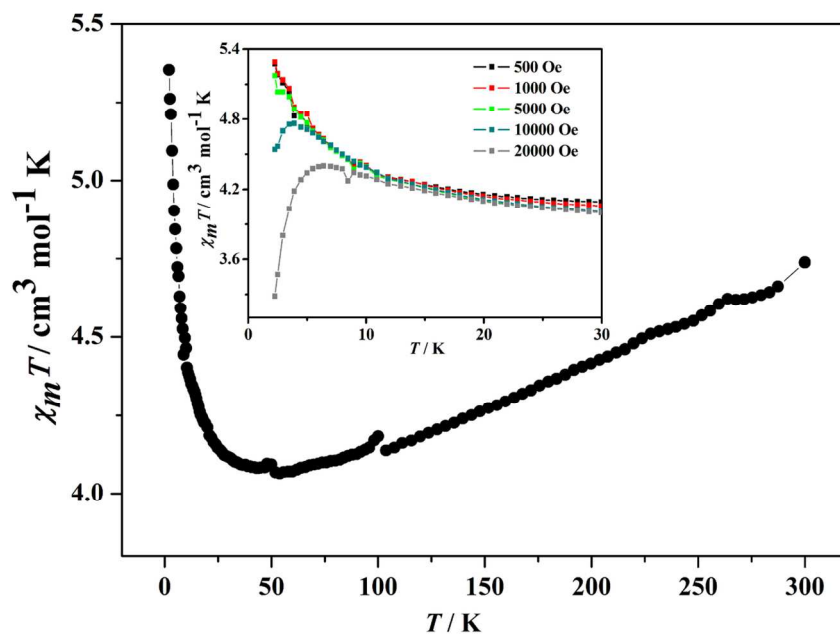
Fig. 4 (a) The χmT vs. T plot of 1 in the range of 2-300 K at 1 KOe; insert: χmT vs. T plots at different external fields;
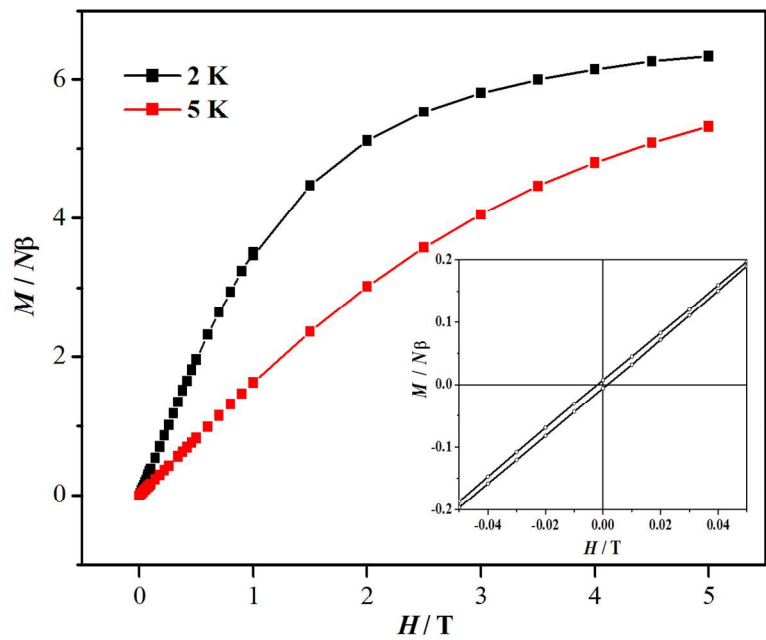126x98mm (300 x 300 DPI)

Fig. 4 (b) the field-dependent magnetization of 1; insert: the magnetic hysteresis loop of 1.

Graphical Abstract

A chiral coordination polymer is reported, which contains rarely two types of double coaxially nested helical chains, exhibiting spin-canting antiferromagnetism.