Single chain magnet behaviour in an enantiopure chiral cobalt(II)–copper(II) one-dimensional compound†

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The self-assembly of an enantiomerically pure, chiral dianionic oxamatocopper(II) complex with cobalt(II) ions leads to neutral oxamato-bridged heterobimetallic chains that combine chirality and slow magnetic relaxation, providing thus the first example of “chiral single chain magnets” (CSCMs).

The design and synthesis of multifunctional magnetic molecular materials (MMMMs) have become an outstanding area of research during the last years and they have opened new possibilities for high-density storage methods and molecular electronics.1–3 Among the class of molecule-based magnetic materials, the so-called single chain magnets (SCMs)4 exhibiting a slow relaxation of the magnetization below a blocking temperature $T_B$ are particularly appealing to get MMMMs. In this contribution, we present a rational approach to obtain chiral magnetic chain compounds that behave as SCMs. The synthetic strategy is based on the use of the sterically hindered, dianionic copper(II) complex with the enantiomerically pure (M)-1,1’-binaphtalene-2,2’-bis(oxamate) [(M)-binaba] ligand (1). Complex 1 can act as bisbidentate metallogand toward solvated cobalt(II) ions through the cis carbonyl oxygen atoms in dimethylformamide (DMF) as solvent. Herein we report the synthesis, crystal structure, chirooptical and magnetic properties of the neutral heterobimetallic chain of formula Cu[(M)-binaba]Co(DMF)$_2$-DMF (2).

The crystal structure5 of 2 has been solved by single-crystal X-ray diffraction using synchrotron radiation at the BM16 beamline in the ESRF. It crystallises in the non-centrosymmetric C221 space group and the absolute configuration could be reliably assigned. Complex 2 consists of enantiomerically pure, oxamato-bridged Cu$^{II}$Co$^{II}$ zigzag chains and crystallization DMF molecules (Fig. 1(a)).

The copper atom has a severely distorted square-planar geometry formed by two amide-nitrogen and two carboxylate-oxygen atoms from two oxamato groups (Cu(1)-O(1) 1.960(2) Å and Cu(1)-O(1) 1.952(2) Å). The large deviations from the CuN$_2$O$_2$ mean plane of 0.384(3) Å for N(1) and 0.340(2) Å for O(1) result in a remarkable tetrahedral distortion of the Cu(1) environment [dihedral angle between the CuN$_2$O$_2$ mean plane and the CuN$_2$O$_2$ mean plane of 0.384(3) Å for N(1) and 0.340(2) Å for O(1)] in a remarkable tetrahedral distortion of the Cu(1) environment [dihedral angle between the CuN$_2$O$_2$ mean plane and the CuN$_2$O$_2$ mean plane of 0.384(3) Å for N(1) and 0.340(2) Å for O(1)] in a remarkable tetrahedral distortion of the Cu(1) environment [dihedral angle between the CuN$_2$O$_2$ mean plane and the CuN$_2$O$_2$ mean plane of 0.384(3) Å for N(1) and 0.340(2) Å for O(1)].

The cobalt atom has a slightly distorted octahedral geometry formed by four cis carbonyl-oxygen atoms from two oxamato groups and two DMF molecules in a cis disposition [Co(1)-O(2) 2.100(2), Co(1)-O(3) 2.119(2) and Co(1)-O(4) 2.091(3) Å]. In contrast to the situation found in the related achiral, oxamato-bridged cobalt(II)-copper(II) zigzag chain MnCu(opba)(dms)$_3$ [opba = o-phenylenebis(oxamate)], only the (A)-isomer is present in 2 due to either spontaneous resolution or conglomerate crystallization. The bond lengths around the cobalt atom are similar to those observed for the high-spin Co$^{III}$ ion in the related achiral, oxamato-bridged cobalt(II)-copper(II) linear chain CoCu(opba)(dms)$_3$. The intrachain Co(1)-Co(1c) separation through the oxamato bridge in 2 is 5.298(1) Å.

The chains of 2 run along a 2$_1$ screw axis which is parallel to the [001] direction, and they are rather well separated from each other (Fig. 1(b)). The bulky binaphthalene groups from the ligands afford an effective shielding between the metal atoms of the neighbouring chains. The shortest interchain Co(1)-Co(1c) and Co(1)-Cu(1c) distances of 2 are 9.3233(14) and 9.1947(11) Å, respectively.

The solid circular dichroism (CD) spectra of 2 confirmed its chirality and enantiomerically pure nature (Fig. 2). They exhibit maximum positive Cotton effects at 210, 265, 380 and 550 nm, whereas maximum negative effects are observed at 335, 480 and 640 nm. They are the result of a chirality induced effect on the two metal centres by the enantiopure...
ligand. The bands in the visible region of the CD spectra of 2 can be attributed to \( d-d \) transitions while those in the UV region can be assigned to metal-to-ligand (ML) charge-transfer transitions while those in the UV region can be assigned to metal-to-ligand (ML) charge-transfer (ML) transitions.

The direct current (dc) magnetic properties of \( \text{CuCo}_8 \) pairs and the metal coordination environments. Hydrogen atoms have been omitted for clarity. The cobalt atoms are depicted as polyhedra.

Hydrogen atoms and crystallization dimethylformamide molecules have been omitted for clarity. The cobalt atoms are depicted as polyhedra.

The lack of a maximum in \( \chi_M \) together with the absence of a \( \lambda \)-peak on the heat capacity measurements on polycrystalline samples of 2 allow to rule out the occurrence of a 3D magnetic order and thus confirm that the chains are magnetically well isolated.

Interestingly, the alternating current (ac) magnetic properties of 2 in the form of the \( \chi'' \) vs. \( T \) plot (\( \chi'' \) being the out-of-phase ac molar magnetic susceptibility per CoCu \( \text{pair} \) and \( T \) the temperature) show evidence of slow magnetic-relaxation effects at very low temperatures which are typical of SCMs (Fig. 3). \( \chi'' \) shows frequency-dependent maxima that vary from 1.8 K at 5700 Hz to 0.6 K at 0.11 Hz. A second non-frequency-dependent peak in the ac susceptibility is also observed at 0.4 K (Fig. 3(b) and S1, ESI†) which may be attributed to a magnetic 3D ordering. The variation of the temperature of the \( \chi'' \) maxima (\( T_{\text{max}} \)) with respect to the frequency of the oscillating ac field (\( v \) for 2, as expressed by the so-called Mydosh parameter \( F \) defined as \( F = \Delta T_{\text{max}}/T_{\text{max}}/\Delta(\log v) \) is characteristic of a SCM behaviour. Thus, the calculated \( F \) value of 0.21 is within the range expected for a SCM (0.1 < \( F < 0.3 \)) supporting a single relaxation process and discarding spin-glass behaviour (\( F < 0.01 \).\( ^{10} \)) The relaxation \( \tau \) for 2 is calculated from the maximum of \( \chi'' \) at a given frequency \( v \) whereby it is assumed that switching of the oscillating ac field matches the relaxation rate of the magnetisation (1/\( \tau = 2\pi\nu \)). The calculated \( \tau \) values at \( T_{\text{max}} \) follow the Arrhenius law characteristic of a thermally activated mechanism: \( \tau = \tau_0 e^{E_a/2k_BT} \) (inset of Fig. 2(b)). The activation energy \( (E_a) \) is 9.2 cm\(^{-1}\) and the pre-exponential factor \( (\tau_0) \) is \( 2.2 \times 10^{-8} \) s. These values are consistent with those previously reported for other oxamate-based SCMs.\(^{4a,b} \)

Fig. 2 CD spectra of 2 in KBr pellets (1 mg in 100 mg of KBr). The inset shows the CD spectra of \( \text{H}_2\text{Et}_2-(M)\)-binaba (…- and 1 (…- in \( \text{CH}_3\text{CN} \) (10\(^{-5} \) mol L\(^{-1} \)).
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Notes and references


5 Crystal data for 2 (ESI): C_{33}H_{33}CoCuN_{5}O_{9}, M_{r} = 766.11, orthorhombic, space group C222, a = 10.566(2), b = 15.364(3), c = 19.755(4) Å, V = 3207.0(11) Å³, T = 293(2) K, λ = 0.7113 Å, Z = 4, D_{x} = 1.587 g cm^{-3}, μ = 1.384 mm^{-1}, Flack parameter = -0.037(17), Measured reflections = 49308, Unique reflections = 3645, Reflections with I > 3σ(I) = 3607 [R(int) = 0.0477]. Refinement of 238 variables with anisotropic thermal parameters for all non-hydrogen atoms gave R1 (all) = 0.0476, R(REF) = 0.0473, wR2 (all) = 0.1304 and wR2 (obs) = 0.1299, with S = 1.061.

6 Strictly speaking, the co-crystallization of (M)-Cu^{II}/(A)-Co^{II} and (M)-Cu^{II}/(A)-Co^{II} crystals would not be a conglomerate because the two compounds are diastereoisomers and not enantiomers.


