

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

Emilio Pardo,<sup>\*a</sup> Cyrille Train,<sup>a</sup> Rodrigue Lescouëzec,<sup>a</sup> Yves Journaux,<sup>\*a</sup> Jorge Pasán,<sup>b</sup> Catalina Ruiz-Pérez,<sup>b</sup> Fernando S. Delgado,<sup>c</sup> Rafael Ruiz-García,<sup>d</sup> Francesc Lloret<sup>d</sup> and Carley Paulsen<sup>e</sup>

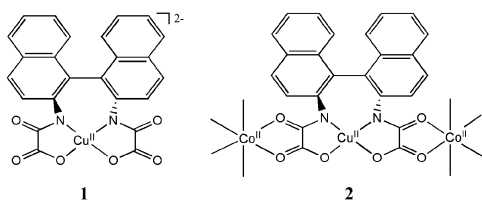
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**The self-assembly of an enantiomerically pure, chiral dianionic oxamato-copper(II) complex with cobalt(II) ions leads to neutral oxamato-bridged heterobimetallic chains that combine chirality and slow magnetic relaxation, providing thus the first 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.<sup>1–3</sup> Among the class of molecule-based magnetic materials, the so-called single chain magnets (SCMs)<sup>4</sup> 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'-binaphthalene-2,2'-bis(oxamate) [(*M*)-binaba] ligand (**1**). Complex **1** can act as bisbidentate metalloligand toward solvated cobalt(II) ions through the *cis* carbonyl oxygen atoms in dimethylformamide (DMF) as solvent. Herein we report the



synthesis, crystal structure, chiroptical and magnetic properties of the neutral heterobimetallic chain of formula  $\text{Cu}[(M)\text{-binaba}]\text{Co}(\text{DMF})_2\text{-DMF}$  (**2**).

The crystal structure<sup>5</sup> 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  $C222_1$  space group and the absolute configuration could be reliably assigned. Complex **2** consists of enantiomerically pure, oxamato-bridged  $\text{Cu}^{\text{II}}\text{Co}^{\text{II}}$  zigzag chains and crystallization DMF molecules (Fig. 1(a)).

The copper atom has a severely distorted square-planar geometry formed by two amidate-nitrogen and two carboxylate-oxygen atoms from the two oxamato groups [Cu(1)–N(1) 1.952(2) Å and Cu(1)–O(1) 1.960(2) Å]. The large deviations from the  $\text{CuN}_2\text{O}_2$  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 N1–Cu1–O1 and N1a–Cu1–O1a planes of 148.31(9)°], with only one of the two possible enantiomers (*M*) being present.

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  $\text{MnCu}(\text{opba})(\text{dmsO})_3$  [opba = *o*-phenylenebis(oxamate)],<sup>7a</sup> only the ( $\Lambda$ )-isomer is present in **2** due to either spontaneous resolution or conglomerate crystallization.<sup>6</sup> The bond lengths around the cobalt atom are similar to those observed for the high-spin  $\text{Co}^{\text{II}}$  ion in the related achiral, oxamato-bridged cobalt(II)–copper(II) linear chain  $\text{CoCu}(\text{opba})(\text{dmsO})_3$ .<sup>7b</sup> The intrachain Co(1)··Cu(1) 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

<sup>a</sup> Institut Parisien de Chimie Moléculaire, UPMC Univ Paris 06, UMR 7071, F-75005 Paris, France.

E-mail: Yves.Journaux@upmc.fr; Fax: 33144273841; Tel: 33144275562

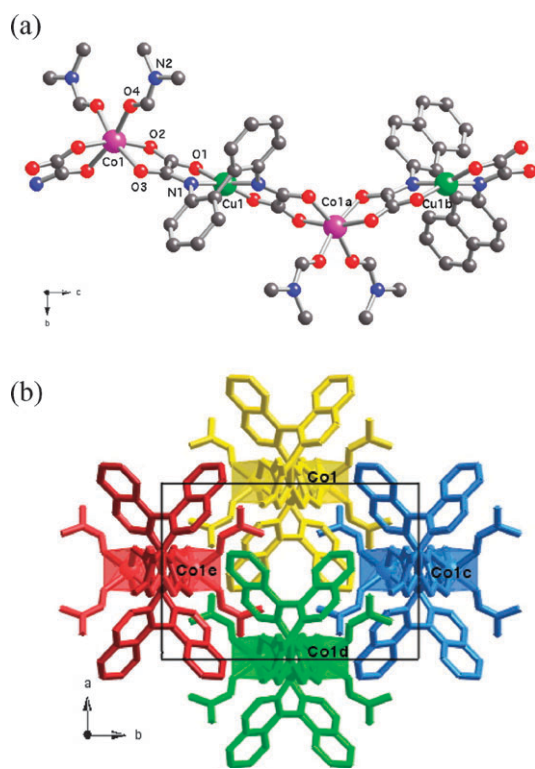
<sup>b</sup> Laboratorio de Rayos X y Materiales Moleculares, Departamento de Física Fundamental I, Universidad de La Laguna, 38201 Tenerife, Spain

<sup>c</sup> BM16, European Synchrotron Radiation Facility (ESRF), 38043 Grenoble CEDEX 9, France

<sup>d</sup> Departament de Química Inorgànica, Instituto de Ciencia Molecular (ICMOL), Universitat de València, 46100 Paterna, València, Spain

<sup>e</sup> Centre National de la Recherche Scientifique, Institut Néel, BP166, 38042 GRENOBLE Cédex 9, France

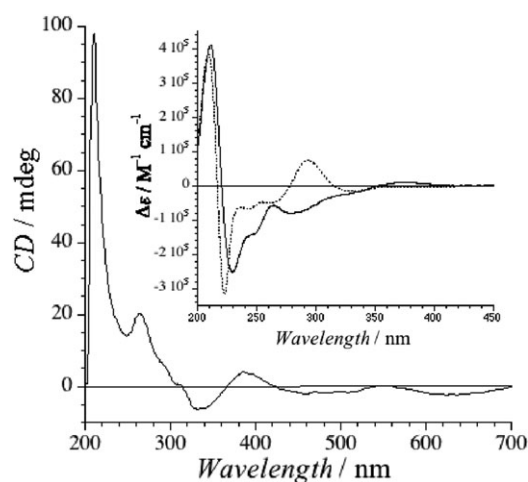
† Electronic supplementary information (ESI) available: Preparation and physical characterization data of the ligand and the complexes **1** and **2**, and crystallographic refinement details for **2**. CCDC 720897. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b920231e



**Fig. 1** (a) View of a fragment of the chain of **2** with atom labelling for the metal coordination environments. Hydrogen atoms have been omitted for clarity. (b) Crystal packing of the chains of **2** along the *c* axis [symmetry codes: (a) = *x*, *-y*, *-z*; (b) = *-x*, *y*, *-z* + 1/2; (c) = *-x* + 1/2, *-y*, *z*; (d) = 1 + *x*, *y*, *z*; (e) = *-x* + 1/2, *-y* + 1, *z*]. Hydrogen atoms and crystallization dimethylformamide molecules have been omitted for clarity. The cobalt atoms are depicted as polyhedra.

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 and intraligand (IL) transitions, by comparison with the solution CD spectra of the proligand H<sub>2</sub>Et<sub>2</sub>-(*M*)-binaba and the copper(II) precursor **1** (inset of Fig. 2).

The direct current (dc) magnetic properties of **2** in the form of the  $\chi_M T$  vs. *T* plot ( $\chi_M$  being the molar magnetic susceptibility per CuCo<sup>8</sup> pair and *T* the temperature) show a minimum around 65 K which is typical of ferrimagnetic bimetallic chain compounds (Fig. 3(a)).<sup>4a,b</sup> Least-squares fitting of the experimental data through the branch chain model developed by Kahn *et al.*<sup>9</sup> (ESI†) in the temperature range 40–300 K gave  $J = -28.9 \text{ cm}^{-1}$ ,  $J' = 153.0 \text{ cm}^{-1}$ ,  $\kappa = 0.82$ ,  $\Delta = 663.0 \text{ cm}^{-1}$ ,  $g_{\text{Cu}} = 2.05$  and  $g_{\text{Co}} = 2.44$  (solid and dashed lines in the inset of Fig. 3(a)), where *J* and *J'* are the intrachain magnetic coupling and effective spin–orbit coupling parameters,  $g_{\text{Cu}}$  and  $g_{\text{Co}}$  are the Zeeman factors of the metal ions, and  $\Delta$  and  $\kappa$  are the axial orbital splitting and orbital reduction parameters of the Co<sup>II</sup> ion. The antiferromagnetic coupling between Cu<sup>II</sup> and Co<sup>II</sup> ions through the oxamato bridge in **2** ( $-J = 28.9 \text{ cm}^{-1}$ ) is somewhat smaller than that found in a related series of oxamato-bridged cobalt(II)–copper(II) chains ( $-J = 35.0\text{--}45.8 \text{ cm}^{-1}$ ).<sup>4a,b</sup> The tetrahedral distortion from the ideal square-planar surrounding for the Cu<sup>II</sup> ions in **2** can

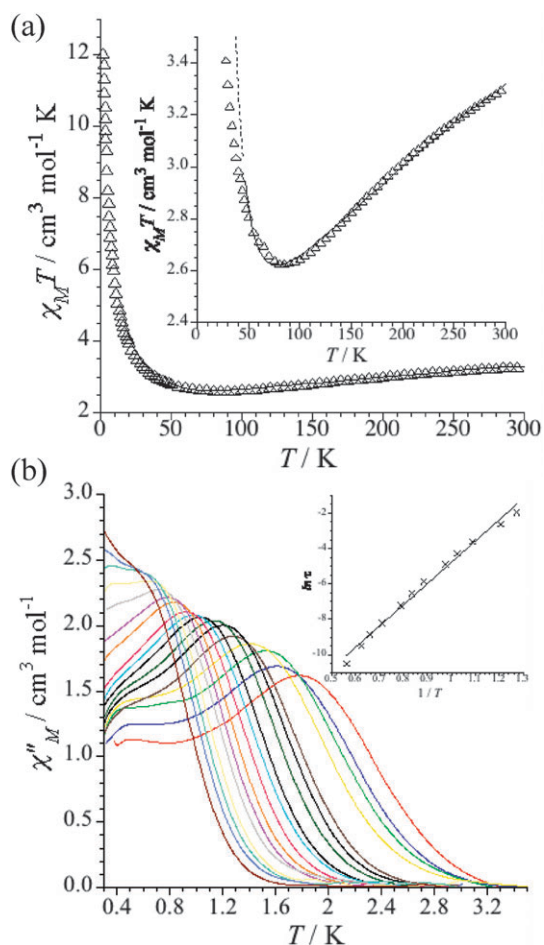


**Fig. 2** CD spectra of **2** in KBr pellets (1 mg in 100 mg of KBr). The inset shows the CD spectra of H<sub>2</sub>Et<sub>2</sub>-(*M*)-binaba (···) and **1** (—) in CH<sub>3</sub>CN (10<sup>-5</sup> mol L<sup>-1</sup>).

explain these differences. The effective spin–orbit coupling ( $J'$ ) can be related with the spin–orbit coupling parameter ( $\lambda$ ) through the expression  $J' = -(3/2)\kappa\lambda$ . This gives a value of  $\lambda$  of  $-124.4 \text{ cm}^{-1}$  ( $\lambda = -180 \text{ cm}^{-1}$  for the free ion). The value of  $\Delta$  for the high-spin Co<sup>II</sup> ions in **2** is similar to those reported for the aforementioned series of oxamato-bridged cobalt(II)–copper(II) chains ( $\Delta = 538\text{--}719 \text{ cm}^{-1}$ ).<sup>4a,b</sup>

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  $\chi_M''$  vs. *T* plot ( $\chi_M''$  being the out-of-phase ac molar magnetic susceptibility per CoCu pair) show evidence of slow magnetic-relaxation effects at very low temperatures which are typical of SCMs (Fig. 3).  $\chi_M''$  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  $\chi_M''$  maxima ( $T_{\text{max}}$ ) with respect to the frequency of the oscillating field ( $\nu$ ) for **2**, as expressed by the so-called Mydosh parameter<sup>10</sup> ( $F$ ) defined as  $F = (\Delta T_{\text{max}}/T_{\text{max}})/\Delta(\log \nu)$ , 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 ( $F < 0.01$ ).<sup>10</sup> The relaxation time  $\tau$  for **2** is calculated from the maximum of  $\chi_M''$  at a given frequency  $\nu$ , 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:  $\tau = \tau_0 \exp(E_a/k_B T)$  (inset of Fig. 2(b)). The activation energy ( $E_a$ ) is  $9.2 \text{ cm}^{-1}$  and the pre-exponential factor ( $\tau_0$ ) is  $2.2 \times 10^{-8} \text{ s}$ . These values are consistent with those previously reported for other oxamate-based SCMs.<sup>4a,b</sup>



**Fig. 3** (a) Temperature dependence of  $\chi_M T$  of **2** ( $\Delta$ ) in an applied magnetic field of 1 T ( $T \geq 50$  K) and 250 G ( $T < 50$  K). The inset shows the minimum of  $\chi_M T$ . The solid lines are the best-fit curves (see text). (b) Temperature dependence of  $\chi_M''$  of **2** in zero applied static field and under 1 G oscillating field where the frequencies are 0.021, 0.057, 0.11, 0.21, 0.57, 1.11, 2.1, 5.7, 11.1, 21, 57, 111, 211, 570, 1110, 2110 and 5700 Hz. The inset shows the Arrhenius plot.

In conclusion, a new enantiopure heterobimetallic chain has been successfully synthesised by using the chiral mononuclear copper(II)-(*M*)-binaba complex as bisbidentate ligand toward cobalt(II) ions. By following this ‘complex-as-ligand’ strategy, the chiral information contained in the configuration of the (*M*)-binaba organic ligand (*chiragen*-type ligand) can be transferred to the stereochemistries of both the Cu<sup>II</sup> and Co<sup>II</sup> centres in a controlled manner and, consequently, a pre-determination of the absolute configuration of the final Co<sup>II</sup>Cu<sup>II</sup> chain can be reached.<sup>1e</sup> In addition, a slow relaxation of the magnetisation typical of SCMs was observed in the enantiopure magnetic chain compound, constituting thus the first example of a new class of MMMs, referred to as chiral single chain magnets (CSCMs). The large magnetic moment due to the SCM behavior of the one-dimensional array of magnetic ions which are also the chiral centers ensure a strong coupling effect between the two physical properties, opening thus excellent perspectives to study the magnetochiral dichroism effect in enantiopure 1D compound with a higher  $T_b$ .<sup>2</sup>

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- Crystal data for **2** (ESI†): C<sub>33</sub>H<sub>33</sub>CoCuN<sub>5</sub>O<sub>9</sub>,  $M_r = 766.11$ , orthorhombic, space group C221,  $a = 10.566(2)$ ,  $b = 15.364(3)$ ,  $c = 19.755(4)$  Å,  $V = 3207.0(11)$  Å<sup>3</sup>,  $T = 293(2)$  K,  $\lambda = 0.7513$  Å,  $Z = 4$ ,  $D_c = 1.587$  g cm<sup>-3</sup>,  $\mu = 1.384$  mm<sup>-1</sup>, Flack parameter =  $-0.037(17)$ , Measured reflections = 49 308, Unique reflections = 3645, Reflections with  $I > 2\sigma(I) = 3607$  [ $R(\text{int}) = 0.0477$ ]. Refinement of 238 variables with anisotropic thermal parameters for all non-hydrogen atoms gave  $R1$  (all) = 0.0476,  $R(\text{obs}) = 0.0473$ ,  $wR2$  (all) = 0.1304 and  $wR2$  (obs) = 0.1299, with  $S = 1.061$ .
- Strictly speaking, the co-crystallization of (*M*)-Cu<sup>II</sup>( $\Delta$ )-Co<sup>II</sup> and (*M*)-Cu<sup>II</sup>( $\Delta$ )-Co<sup>II</sup> crystals would not be a conglomerate because the two compounds are diastereoisomers and not enantiomers.
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