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# Design of chiral magnets: cyanide-bridged bimetallic assemblies based on cyclohexane-1,2-diamine

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## Abstract

Four magnetic compounds based on chiral ligands *trans*-(1*S*,2*S*)-chxn and *trans*-(1*R*,2*R*)-chxn (chxn: cyclohexane-1,2-diamine), [Ni(*trans*-(1*S*,2*S*)-chxn)<sub>2</sub>]<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O (**1**), [Ni(*trans*-(1*R*,2*R*)-chxn)<sub>2</sub>]<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O (**2**), [Cu(*trans*-(1*S*,2*S*)-chxn)<sub>2</sub>]<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>·4.5H<sub>2</sub>O (**3**) and [Cu(*trans*-(1*R*,2*R*)-chxn)<sub>2</sub>]<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>·4.5H<sub>2</sub>O (**4**), are reported. The four compounds are chiral, as confirmed by X-ray analyses and circular dichroism measurements. From the magnetic point of view, **1** and **2** behave as ferromagnets, whereas **3** and **4** show a paramagnetic behavior.

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**Keywords:** Chiral ligands; Cyanide complexes; Molecular magnets

## 1. Introduction

Lately many efforts are being devoted to the preparation of molecule-based magnets with high Curie temperatures. Among the many existing strategies to attain this, the synthesis of the so-called Prussian-blue analogues is one of the most successful and, therefore, widespread. Particularly, the assembly of polyaminoalkane metal complexes and hexacyanometalates has given rise to a large family of compounds showing different connectivities, dimensionalities and magnetic properties [1], partially determined by the nature and size of the polyamine ligand. Since the ligand can also be chosen in order to introduce a second physical property in the system, this is a rather straightforward approach for obtaining multifunctional materials. The use of a chiral ligand, for instance, makes it possible to prepare one-network chiral ferri- [2] and ferromagnets [3]. Since the discovery of a small magnetochiral dichroism (MChD) in a chiral paramagnetic material by Rikken and Raupach [4] in 1997, compounds combining chirality

and magnetic ordering are a common target for observing larger magnetochiral effects.

In this respect, our work with the two chiral forms of the cyclohexane-1,2-diamine (chxn) ligand, *trans*-cyclohexane-(1*S*,2*S*)-diamine and *trans*-cyclohexane-(1*R*,2*R*)-diamine, has taken us to the synthesis of four chiral cyanide-bridged bimetallic species of M<sup>II</sup>/M<sup>III</sup> 3/2 type. Compounds **1** and **2** (M<sup>II</sup> = Ni<sup>II</sup>; M<sup>III</sup> = Fe<sup>III</sup>) behave as ferromagnets, whereas compounds **3** and **4** (M<sup>II</sup> = Cu<sup>II</sup>; M<sup>III</sup> = Fe<sup>III</sup>) show no magnetic ordering. Their chiral nature has been confirmed by circular dichroism (CD) measurements of the two enantiomeric pairs.

## 2. Experimental

### 2.1. Synthesis

#### 2.1.1. [Ni(*trans*-(1*S*,2*S*)-chxn)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O

A solution of *trans*-cyclohexane-(1*S*,2*S*)-diamine (1 g, 8.77 mmol) in water (10 ml) was added dropwise to a stirred solution of [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (1.07 g, 2.92 mmol) in the same amount of water. A violet precipitate of [Ni(*trans*-(1*S*,2*S*)-chxn)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O appeared im-

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mediately. It was filtered-off, washed with water and air-dried. Anal. Calc. for  $C_{18}H_{44}Cl_2N_6NiO_9$ : C, 34.97; H, 7.17; N, 13.59. Found: C, 34.85; H, 8.04; N, 13.80%.

### 2.1.2. $[Ni(trans-(1S,2S)-chxn)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$ (**1**)

To a solution of  $[Ni(trans-(1S,2S)-chxn)_3](ClO_4)_2 \cdot H_2O$  (100 mg, 0.17 mmol) in a water–acetonitrile mixture (1/1, 40 ml) were added 0.1 equiv. of  $[Ni(H_2O)_6](ClO_4)_2$  with continuous stirring, followed by the dropwise addition of an aqueous (20 ml) solution of  $K_3[Fe(CN)_6]$  (56 mg, 0.17 mmol). The resulting solution was kept away from light. Dark brown crystals formed after a few days. Single crystals were grown by slow diffusion of the precursors in the water–acetonitrile mixture. Anal. Calc. for  $C_{48}H_{88}Fe_2N_{24}Ni_3O_2$ : C, 43.64; H, 6.71; N, 25.44. Found: C, 43.56; H, 6.49; N, 25.26% [3].

### 2.1.3. $[Ni(trans-(1R,2R)-chxn)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$ (**2**)

Prepared starting from *trans*-cyclohexane-(1*R*,2*R*)-diamine as described above for **1**. Anal. Calc. for  $C_{48}H_{88}Fe_2N_{24}Ni_3O_2$ : C, 43.64; H, 6.71; N, 25.44. Found: C, 43.46; H, 6.63; N, 25.34% [3].

### 2.1.4. $[Cu(trans-(1S,2S)-chxn)_2(H_2O)](NO_3)_2$

A solution of *trans*-cyclohexane-(1*S*,2*S*)-diamine (228 mg, 2 mmol) in methanol (5 ml) was added dropwise to a stirred solution of  $Cu(NO_3)_2 \cdot 3H_2O$  (242 mg, 1 mmol) in the same amount of methanol. A violet precipitate appeared immediately. It was filtered-off, washed with methanol and air-dried. Anal. Calc. for  $C_{12}H_{30}N_6CuO_7$ : C, 33.21; H, 6.97; N, 19.37. Found: C, 32.96; H, 6.74; N, 19.12%.

### 2.1.5. $[Cu(trans-(1S,2S)-chxn)_2]_3[Fe(CN)_6]_2 \cdot 4H_2O$ (**3**)

This compound was obtained by slow diffusion of  $[Cu(trans-(1S,2S)-chxn)_2(H_2O)](NO_3)_2$  (125 mg, 0.3 mmol) and  $K_3[Fe(CN)_6]$  (66 mg, 0.2 mmol) in water. After a few days, dark brown crystals formed. Anal. Calc. for  $C_{48}H_{93}Fe_2N_{24}Cu_3O_{4.5}$ : C, 41.75; H, 6.79; N, 24.35. Found: C, 41.58; H, 6.76; N, 24.50%.

### 2.1.6. $[Cu(trans-(1R,2R)-chxn)_2]_3[Fe(CN)_6]_2 \cdot 4H_2O$ (**4**)

Prepared starting from *trans*-cyclohexane-(1*R*,2*R*)-diamine as described above for **3**. Anal. Calc. for  $C_{48}H_{93}Fe_2N_{24}Cu_3O_{4.5}$ : C, 41.75; H, 6.79; N, 24.35. Found: C, 41.22; H, 6.78; N, 24.62%.

## 2.2. X-ray measurements

X-ray diffraction data of compound **1** were collected on a Stoe Image Plate Diffraction System [5] by the  $\phi$ -

scan method ( $3.27^\circ < 2\theta < 52.1^\circ$ ),  $\lambda(Mo K\alpha) = 0.71073 \text{ \AA}$ ,  $T = 153(2) \text{ K}$ . Of 12 498 measured reflections, 10 383 were independent ( $R_{int} = 0.0616$ ) and used to refine 707 parameters (three restraints). The structure was solved by Patterson and Fourier methods using the software SHELXS-97 [6] and refined by full-matrix least-squares procedures on  $F^2$  (SHELXL-97) [7]. Hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The water H atoms could not be located. The non-H atoms were refined anisotropically. Max./min. residual peaks in the final difference map were  $0.409/-0.382 \text{ e \AA}^{-3}$ . The absolute structure parameter was  $-0.02(2)$ .

X-ray diffraction data of compound **2** were collected on a Stoe Image Plate Diffraction System [5] by the  $\phi$ -scan method ( $3.27^\circ < 2\theta < 52.1^\circ$ ),  $\lambda(Mo K\alpha) = 0.71073 \text{ \AA}$ ,  $T = 153(2) \text{ K}$ . Of 9016 measured reflections, 7878 were independent ( $R_{int} = 0.1191$ ) and used to refine 455 parameters (three restraints). An empirical absorption correction was applied using DIFABS routine in PLATON [8] ( $\mu = 1.371 \text{ mm}^{-1}$ , min./max. transmission: 0.269 and 0.720). The structure was solved by Patterson and Fourier methods using the software SHELXS-97 [6] and refined by full-matrix least-squares procedures on  $F^2$  (SHELXL-97) [7]. Hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The water H atoms could not be located. The carbon atoms were refined isotropically due to a number of them being non-positive definitive on anisotropic refinement. For three  $NH_2$  nitrogen atoms (N6, N8 and N12) their anisotropic displacement parameters were made equal to that of atom N1. The remainder of the non-H atoms was refined anisotropically. The crystal was a twin with approximately 20% overlap of reflections. For structure solution and refinement, the major component of the twin was obtained using the TWIN integration method [5]. Max./min. residual peaks in the final difference map were  $0.582/-0.737 \text{ e \AA}^{-3}$ . The absolute crystal structure was determined by Flack's method [9] (Flack number = 0.00(4)).

X-ray diffraction data of compound **3** were collected with a Nonius KappaCCD diffractometer using a graphite monochromated  $Mo K\alpha$  radiation source ( $\lambda = 0.71073 \text{ \AA}$ ). DENZO and SCALEPACK [10] programs were used for cell refinements and data reduction. The structure was solved by direct methods using SIR-97 [11] program with the WinGX [12] graphical user interface. The structure refinement was carried out with SHELX-97 [6,7]. A multiscan absorption correction based on equivalent reflections was applied to the data using the program SORTAV [13] ( $T_{max}/T_{min} = 0.660/0.575$ ). H atoms on O and N atoms were found in different maps and were refined positionally with geometric restraints ( $O-H = 0.82 \text{ \AA}$ ,  $N-H = 0.89 \text{ \AA}$  and  $H \cdots H = 1.35 \text{ \AA}$ ) and with  $U_{iso}(H) = 1.2U_{eq}(N,O)$ . The

remaining H atoms were placed in calculated positions and refined with a riding model, with C–H = 0.97 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The occupancy of three water molecules were refined, adopting values close to 0.5 and, in the next refinement, they were fixed to these values and refined isotropically. All other non-hydrogen atoms were refined anisotropically. Seven low-angle reflections were omitted from the final cycles of refinement because their observed intensities were much lower than the calculated values as a result of being partially obscured by the beam stop.

Crystallographic data of **1**, **2** and **3** are summarized in Table 1.

### 3. Results and discussion

#### 3.1. Structural analysis

Compounds **1** and **2** are isostructural. Although similar two-dimensional bimetallic compounds with (12,3) topology are known [14], **1** presents a novel (12,4) topology made up of alternating *trans*-[Ni(*trans*-(1*S*,2*S*)-chxn)<sub>2</sub>]<sup>2+</sup> cations and [Fe(CN)<sub>6</sub>]<sup>3-</sup> anions (Fig. 1(a)) [3]. Iron atoms (Fe2) belonging to [Fe(CN)<sub>6</sub>]<sup>3-</sup> anions bind to four adjacent *trans*-[Ni(*trans*-(1*S*,2*S*)-chxn)<sub>2</sub>] moieties in a η<sup>4</sup>-mode. Two of these nickel ions (Ni2) are placed roughly at the center of the short sides

of the grid. The other nickel units (Ni1 and Ni3), and so iron atoms (Fe1) belonging to η<sup>2</sup>-[Fe(CN)<sub>6</sub>]<sup>3-</sup> anions, are located at the long sides. Two water molecules hydrogen-bond to these latter anions and occupy the free space within the rhomboidal grids. A projection of the crystal structure onto the *bc*-plane (Fig. 1(b)) shows bulky cyclohexane rings arranging at both sides of the layer, leading to a large interplane distance of 12.639 Å.

A view of compound **3** along *a*-axis (Fig. 2) shows the existence of Cu1–NC–Fe1–CN–Cu2 zig-zag chains composed of alternating *trans*-[Cu(*trans*-(1*S*,2*S*)-chxn)<sub>2</sub>]<sup>2+</sup> cations and [Fe(CN)<sub>6</sub>]<sup>3-</sup> anions. The axial positions of copper atoms (Cu1 and Cu2) are occupied by CN-groups, with very long Cu–N distances compared to those of equatorial bisdiamine ligands (Cu1–N(ax): 2.656(3) and 2.687(3) Å; Cu1–N(eq): 1.999(3)–2.020(2) Å; Cu2–N(ax): 2.649(3) and 2.777(3) Å; Cu2–N(eq): 1.994(3)–2.017(2) Å). Cu–N–C angles deviate considerably from linearity, with values ranging between 132.0° and 122.2°. This is a common feature of copper-containing compounds [15]. Isolated from the chain, axially distorted octahedral *trans*-[Cu(*trans*-(1*S*,2*S*)-chxn)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> cations compensate the charge of the polymer (Cu3–N: 2.007(3)–2.026(3) Å; Cu3–O1: 2.500(3) Å; Cu3–O2: 2.474(3) Å). Two water molecules (O3 and O4) hydrogen-bond to both terminal and bridging CN-groups of the Fe1 unit and to an NH<sub>2</sub>-group of the Cu2 moiety. The remaining water molecules (O1 and O2) hydrogen-bond to terminal CN-groups of adjacent chains, giving rise to a two-dimensional structure.

Table 1  
Summary of crystallographic data for **1**, **2** and **3**

	<b>1</b>	<b>2</b>	<b>3</b>
Chemical formula	C <sub>48</sub> H <sub>88</sub> Fe <sub>2</sub> N <sub>24</sub> ·Ni <sub>3</sub> O <sub>2</sub>	C <sub>48</sub> H <sub>88</sub> Fe <sub>2</sub> N <sub>24</sub> ·Ni <sub>3</sub> O <sub>2</sub>	C <sub>48</sub> H <sub>93</sub> Fe <sub>2</sub> N <sub>24</sub> ·Cu <sub>3</sub> O <sub>4.5</sub>
Formula weight	1321.25	1321.25	1380.78
<i>T</i> (K)	153(2)	153(2)	293(2)
Space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1
<i>Z</i>	1	1	1
Unit cell dimensions			
<i>a</i> (Å)	9.0917(8)	9.0858(10)	8.44470(10)
<i>b</i> (Å)	12.6682(12)	12.6638(15)	12.72030(10)
<i>c</i> (Å)	14.9606(14)	14.9822(16)	16.12770(10)
α (°)	99.107(11)	98.900(10)	105.4881(3)
β (°)	93.897(11)	93.950(10)	98.5223(3)
γ (°)	109.239(11)	109.450(10)	96.6158(3)
<i>V</i> (Å <sup>3</sup> )	1593.0(3)	1592.4(3)	1629.16(3)
ρ <sub>calc</sub> (Mg m <sup>-3</sup> )	1.377	1.378	1.407
μ (Mo Kα) (mm <sup>-1</sup> )	1.371	1.371	1.458
λ (Å)	0.71073	0.71073	0.71073
<i>R</i> ( <i>F</i> <sub>o</sub> ) <sup>a</sup>	0.0329, 0.0517	0.0604, 0.1377	0.0318, 0.0739
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> ) <sup>b</sup> , <i>I</i> > 2σ( <i>I</i> )			
All data	0.0779, 0.0583	0.1090, 0.1507	0.0465, 0.0789

<sup>a</sup>  $R(F_o) = \sum(|F_o| - |F_c|) / \sum|F_o|$ .

<sup>b</sup>  $R_w(F_o) = \sum(w|F_o|^2 - |F_c|^2 / \sum w|F_o|^4)^{1/2}$ .

#### 3.2. Magnetic properties

Both enantiomers **1** and **2** show the same magnetic behavior as the racemic mixture [3,16]. The magnetic susceptibility, measured on polycrystalline samples between 2 and 300 K, follows a Curie–Weiss law above 50 K with a Weiss constant  $\theta$  of 24.4 K pointing to the presence of ferromagnetic interactions between neighboring Fe(III) and Ni(II) ions. Below 15 K,  $\chi_m$  increases sharply and saturates to a value of 28.3 emu mol<sup>-1</sup> (Fig. 3), which suggests the onset of a long-range ferromagnetic ordering. This behavior is confirmed by specific heat measurements (Fig. 3, inset). A lambda peak appears at the critical temperature  $T_c = 13.8$  K. At 2 K, the compounds exhibit a magnetic hysteresis with a coercive field of 0.17 T and a remnant magnetization of 6.6 μ<sub>B</sub>. This behavior is typical of hard magnets. When the temperature is increased, the coercive field decreases (Fig. 4). The first magnetization curve saturates rapidly to a value of 7.7 μ<sub>B</sub> at 5 T. This value is very close to 8 μ<sub>B</sub>, which is the expected for a ferromagnetic alignment of interacting spins in Ni<sub>3</sub>Fe<sub>2</sub> unit ( $S_{\text{Ni}} = 1$ ,  $S_{\text{Fe}} = 1/2$ ).

Compounds **3** and **4** also show identical magnetic behavior. Magnetic susceptibility was measured on

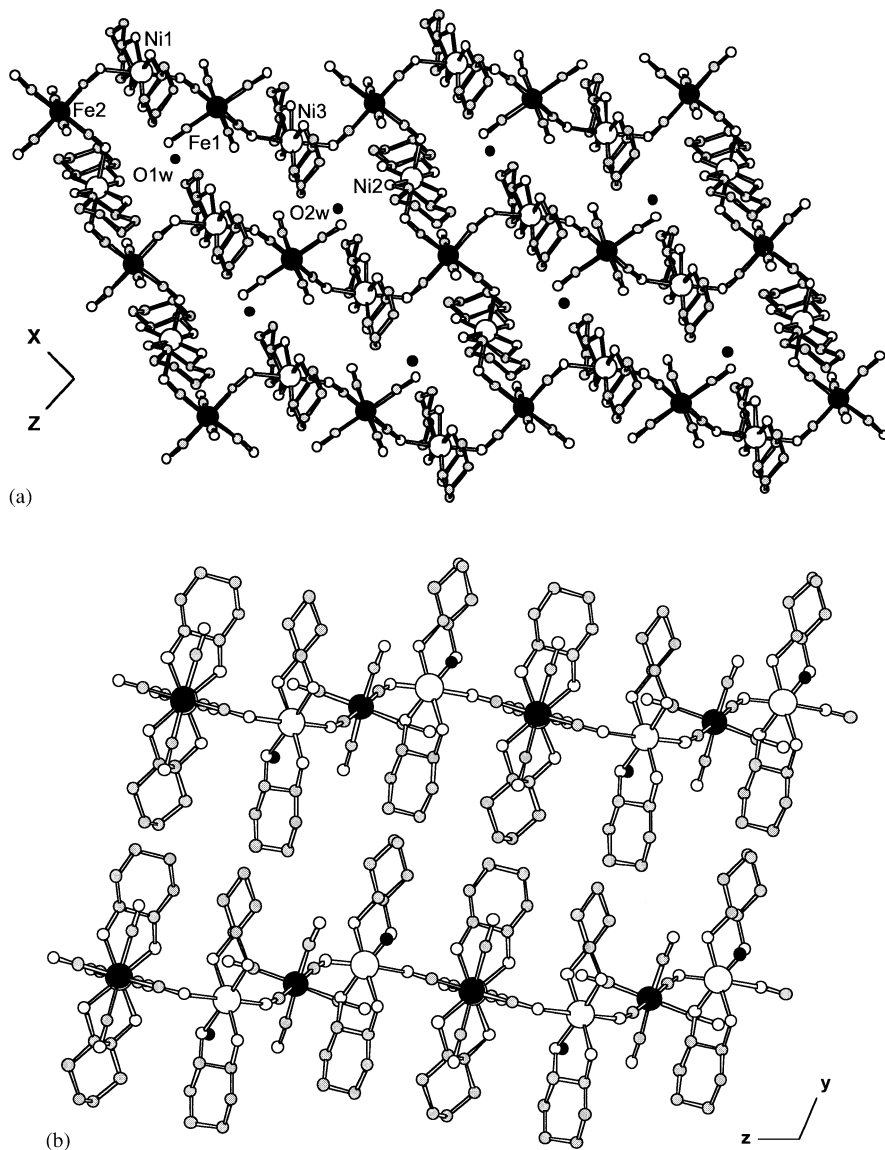


Fig. 1. (a) View of the crystal structure of **1** in *ac*-plane showing the numbering scheme for significant atoms. (b) View of the crystal structure along *a*-axis.

polycrystalline samples between 2 and 300 K. The thermal variation of the  $\chi_m T$  product for **3** is shown in Fig. 5. At 300 K,  $\chi_m T$  equals  $2.48 \text{ emu K mol}^{-1}$ . This value is somewhat higher than that expected for uncorrelated spins ( $S_{\text{Cu}} = 1$ ,  $S_{\text{Fe}} = 1/2$ ;  $0.375 \text{ emu K mol}^{-1}$  per  $S = 1/2$ , considering  $g = 2$ ) due to spin-orbit coupling effects causing the  $g$  value of Fe(III) ions to be greater than 2. Moreover, the orbital contribution to the magnetic moment is responsible for the smooth decrease in  $\chi_m T$  on cooling. At about 10 K,  $\chi_m T$  presents a decrease which may be attributed to weak magnetic interactions between adjacent metal centers and/or to zero-field splitting of Fe(III). The isothermal magnetization curve performed at 2 K shows a paramagnetic behavior. It reaches a value of  $4.69 \mu_B$  at 5 T, which is

very close to the one expected ( $\geq 5 \mu_B$ ) for the sum of the constituent spins.

### 3.3. Circular dichroism measurements

CD spectra were recorded in order to confirm the chirality and the enantiomeric nature of compounds **1** and **2**, on one hand, and **3** and **4**, on the other hand (Fig. 6). Compound **1** (*S,S* isomer) exhibits maximum positive Cotton effects at 450 and 725 nm, whereas a maximum negative effect is observed at 585 nm. Compound **2** (*R,R* isomer) presents Cotton effects of the opposite sign at the same wavelengths [3]. Compound **3** (*S,S* isomer), in turn, shows positive maxima at 530 and 690 nm and a negative maximum at 350 nm.

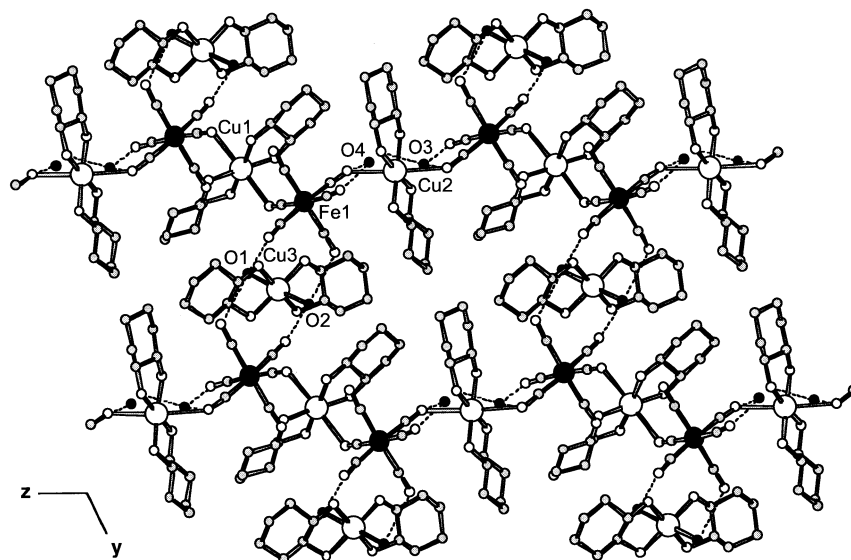


Fig. 2. Projection of the crystal structure of **3** onto *bc*-plane showing the numbering scheme for significant atoms. Dotted lines convey hydrogen bonds.

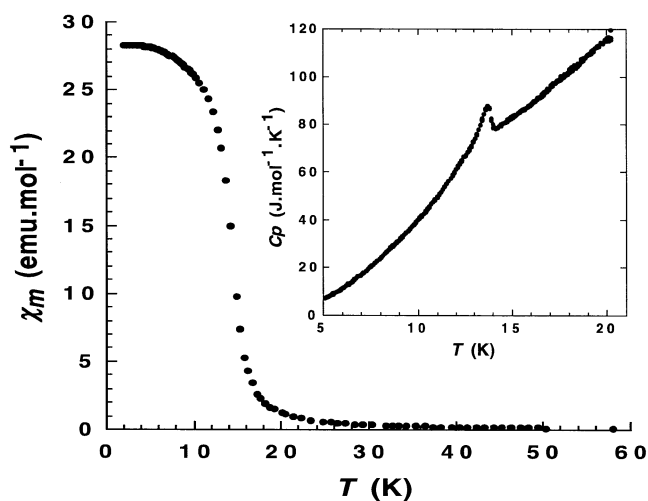


Fig. 3. Thermal variation of  $\chi_m$  for **1** under a field of 1000 G. Inset: specific heat plot.

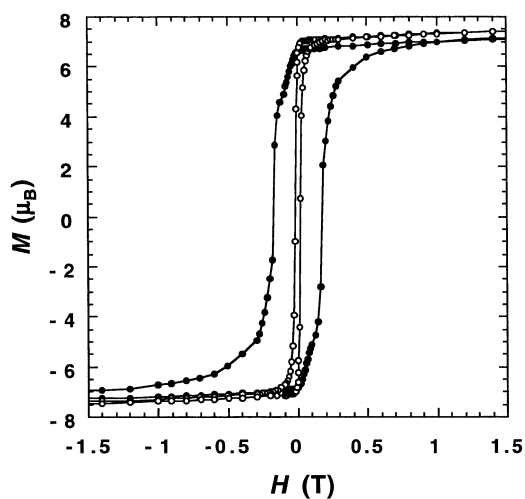


Fig. 4. Hysteresis curve of **1** performed at 2 K (solid circles) and 5 K (empty circles).

Compound **4** (*R,R* isomer), as expected, exhibits Cotton effects of the opposite sign at the same wavelengths. The signals observed in the visible region of CD spectra can be attributed to d–d transitions, while dichroic signals at lower wavelengths can be assigned to charge-transfer transitions.

#### 4. Conclusions

Two approaches to the synthesis of chiral magnets exist. They require the use of chiral precursors, which can be either chiral complexes [17] or chiral ligands. Here, we have reported the results obtained by using the

bulky ligand *trans*-chxn as a piece to build multifunctional systems that combine chirality and cooperative magnetism. Following this strategy in the synthesis of two-dimensional cyanide-bridged bimetallic assemblies both ensures the chirality of the final coordination polymers and favors their ferromagnetic ordering. This has been confirmed to be so in Ni<sup>II</sup>/Fe<sup>III</sup> synthesized compounds. However, Cu<sup>II</sup>/Fe<sup>III</sup> compounds have turned out to be paramagnetic. The Jahn-Teller effect causes axial distances of octahedral Cu(II) cations to be extremely long, avoiding magnetic interaction between metal centers. Further investigation of these and alike systems, including neutron diffraction and MChD measurements, is in progress.

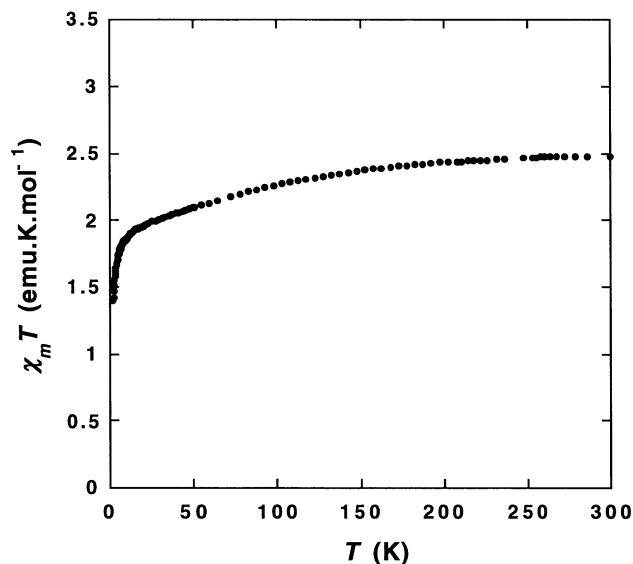


Fig. 5. Thermal variation of  $\chi_m T$  for **3** under a field of 1000 G.

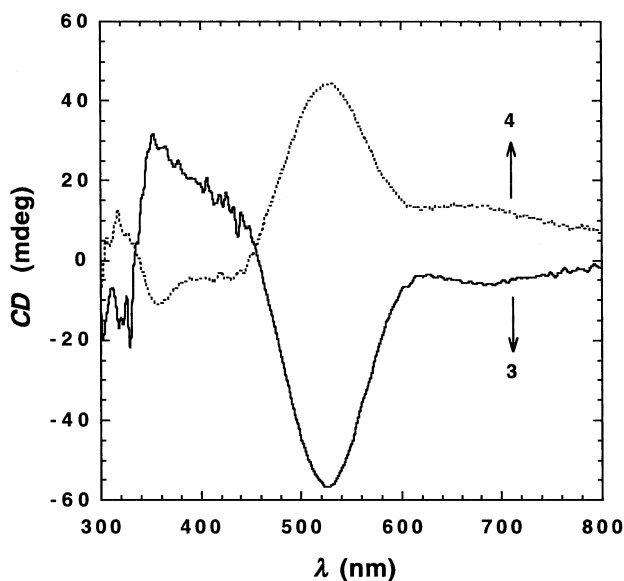


Fig. 6. CD spectra of **3** (*S,S* isomer, continuous line) and **4** (*R,R* isomer, dashed line) in KBr pellets.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 179498, 179499 and 201531 for **1**, **2** and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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