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New 3D and Chiral 1D $Cu^{II}Cr^{III}$ Coordination Polymers Exhibiting Ferromagnetism

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The reaction of $K_3[Cr(CN)_6]$ and the copper(II) bis-diamino complex of the ligand 1,3-diaminopropane (tn) led to the new cyanide-bridged 3D polymer $\{[(Cu(tn)_2)_3(Cr(CN)_6)][Cr(CN)_6]\}_\infty$ (**1**). Crystallographic data for **1:** trigonal space group $R\bar{3}$, $a = b = 15.4908(11)$, $c = 16.7699(13)$ Å, $Z = 3$, $V = 3485.0(4)$ Å^3. By the same reaction using *trans*-cyclohexane-(1R,2R)-diamine [1R,2Rchxn] or *trans*-cyclohexane-(1S,2S)-diamine [1S,2Schxn] as ligands, the chiral 1D polymers $\{[Cu(1R,2Rchxn)_2]_3[Cr(CN)_6]_2 \cdot 4.75H_2O\}_\infty$ (**2**) and $\{[Cu(1S,2Schxn)_2]_3[Cr(CN)_6]_2 \cdot 4.25H_2O\}_\infty$ (**3**), respectively, were obtained. **2** and **3** are isostructural and crystallize in the triclinic space group $P1$, with $a = 8.5421(6)$, $b = 12.6379(9)$, $c = 16.1571(11)$ Å, $\alpha = 104.594(5)°$, $\beta = 98.425(6)°$, $\gamma = 97.440(5)°$, $Z = 1$, $V = 1644.3(2)$ Å^3 for **2**, and $a = 8.5435(8)$, $b = 12.6309(12)$, $c = 16.1711(17)$ Å, $\alpha = 104.632°$, $\beta = 98.429(8)°$, $\gamma = 97.375(8)°$, $Z = 1$, and $V = 1645.1(3)$ Å^3 for **3**. The complexes have been characterized by X-ray crystallography, IR, and magnetic susceptibility measurements. The chirality of **2** and **3** has been confirmed by circular dichroism measurements in the solid state. From the magnetic point of view, **1** shows 3D ferromagnetic ordering at ca. 4K, and **2** shows a weak intrachain ferromagnetic exchange, as a result of magnetic orbital orthogonality between Cr(III) and Cu(II) in the chain, with very long Cu−N(cyano) distances (2.665(5) and 2.671(5) Å) due to the long Jahn−Teller axis of the copper(II) ions.

Introduction

The design and synthesis of well-characterized molecular-based magnets remains a challenge. They have been developed in an interdisciplinary research area in the past two decades. On the basis of past achievements, current interest is targeted on multifunctional magnets with other physical and/or chemical properties such as optical properties, electric conductivity, chirality, porosity, and so forth.[1−8] Here, we targeted the preparation of a complete ferromagnet, that is a magnet exhibiting a 3D ferromagnetic interaction through a 3D isotropic network structure, similar to the CrNi structure described by Kitagawa et al.[9] Such magnets having a 3D structure and a ferromagnetic network are rare among general metal oxides and molecule-based magnets; antiferromagnetic interactions usually operate between such magnetic centers. Innovative molecular design and synthetic strategies are necessary for the creation of a complete ferromagnet. A promising strategy for producing molecular-based magnets is to create a bimetallic network by assembling two kinds of paramagnetic metal ions. Cyano complexes were among the first coordination compounds ever prepared, and they are still popular in coordination and organometallic chemistry.

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Metal cyanide extended networks, analogues of Prussian blue, are of great interest to the molecule-based magnetism community[10–12] because of the nature of the magnetic exchange, which can be anticipated in advance from basic orbital interaction arguments. The predictable structure-directing quality of the cyanide bridge can facilitate supramolecular and network design.[5] Prussian blue analogues, derived from hexacyanometallate anions and hexasolvated metal complexes, exhibit novel magnetic and electronic properties, and some of them present magnetic ordering at a critical temperature (T_c) as high as 376 K.[7,13,14] A wide range of magnetic phenomena have been observed in metal cyanides, including high-spin clusters,[15–17] metamagnetism,[5,18,19] room temperature magnetic ordering,[6,13] spin-glass behavior,[20,21] and photomagnetism.[22,23] However, the difficulty of obtaining single crystals suitable for X-ray structure determination precludes a thorough magnetostructural correlation of these 3D systems of high symmetry.[24]

Using the $[Cr(CN)_6]^{3-}$ anion, three new bimetallic complexes have been prepared: the 3D framework $\{[(Cu(tn)_2)_3(Cr(CN)_6)][Cr(CN)_6]\}_\infty$ (**1**) (tn = 1,3-diaminopropane) and the chiral 1D polymeric complexes $\{[Cu(1R,2Rchxn)_2]_3[Cr(CN)_6]_2\cdot 4.75H_2O\}_\infty$ (**2**) (1R,2Rchxn = *trans*-cyclohexane-(1R,2R)-diamine) and $\{[Cu(1S,2Schxn)_2]_3[Cr(CN)_6]_2\cdot 4.25H_2O\}_\infty$ (**3**) (1S,2Schxn = *trans*-cyclohexane-(1S,2S)-diamine). Here, we report on the crystal structures and magnetic susceptibility studies of these compounds. The chiral nature of **2** and **3** has been confirmed by solid-state circular dichroism (CD) measurements.

Experimental Section

Physical Measurements. Elemental analyses of carbon, hydrogen, and nitrogen were performed by the Microanalysis Service of the Laboratory of Pharmaceutical and Organical Propedeutical Chemistry at the University of Geneva (Geneva, Switzerland). Infrared spectra were measured using KBr pellets in the interval of 4000−400 cm^{-1} and were recorded on a PerkinElmer 1720X FTIR spectrometer. Circular dichroism (CD) spectra were measured as KBr pellets on a J-500C spectropolarimeter in the range of 800−300 nm at 298K. Magnetic measurements were carried out in the Servei de Magnetoquímica (Universitat de Barcelona) on polycrystalline samples (20−30 mg) with a Quantum Design SQUID MPMS-XL susceptometer working in the 2−300 K range. The magnetic field was 0.05 T. The diamagnetic corrections were evaluated from Pascal's constants.

Synthesis. All reagents were purchased from chemical sources and used without further purification. All of the operations for the synthesis were carried out in the dark to avoid the decomposition of $[Cr(CN)_6]^{3-}$.

$\{[(Cu(tn)_2)_3(Cr(CN)_6)][Cr(CN)_6]\}_\infty$ (**1**). Under aerobic conditions, 1,3-diaminopropane (0.084 mL, 1.0 mmol) was slowly added with stirring to a concentrated aqueous solution of $CuCl_2\cdot 2H_2O$ (0.171 g, 1.0 mmol), leading to the immediate appearance of a pale-green precipitate. A concentrated aqueous solution of NaOH (2.0 mmol) was added dropwise to obtain a clear solution. This was then heated at ca. 70 °C for 10 min and subsequently filtered. An aqueous solution of $K_3[Cr(CN)_6]$ (0.195 g, 0.6 mmol) was then added dropwise to the hot filtrate. The reaction mixture was stirred for 30 min, and then $NaClO_4$ (0.12 g, 1 mmol) was added to aid crystallization. After stirring for a few minutes, the mixture was filtered, and after 4−5 days dark blue-green platelike crystals appeared. Elemental anal. Found C, 34.02; H, 5.98; N, 31.62%; $C_{30}H_{60}N_{24}Cr_2Cu_3$: requires C, 34.27; H, 5.75 N, 31.97%. IR (KBr): ν(NH) 3324 and 3295 (vs), ν(CH) 2947 (s) and 2881 (s), ν(CN) 2152, 2135 and 2124 (vs), $\delta(NH_2)$ 1619(m) and 1593 (m), $\delta(CH_2)$ 1471 (s), 1440 (s), ν(Cr−C) 581 (m), δ(Cr−CN) 464(s).

$\{[Cu(1R,2Rchxn)_2]_3[Cr(CN)_6]_2\cdot 4.75H_2O\}_\infty$ (**2**). To a stirred aqueous solution (3 mL) of $Cu(NO_3)_2\cdot H_2O$ (145 mg, 0.6 mmol) was added dropwise a methanol solution (3 mL) of *trans*-cyclohexane-(1R,2R)-diamine (136 mg, 1.2 mmol). The mixture was stirred for 10 min, and the violet precipitate obtained was filtered-off, washed with methanol, and dried in air. This solid was dissolved in 10 mL of a methanol−water (1:1) mixture and was then added slowly to an aqueous solution of $K_3[Cr(CN)_6]$ (66 mg, 0.15 mmol). By slow diffusion of the two solutions, purple block-shaped crystals of **2** were obtained after several days. Elemental anal. Found C, 41.32; H, 6.56; N, 24.22%; Calcd. for $C_{48}H_{84}N_{24}Cr_2Cu_3\cdot 4.75H_2O$: C, 41.85; H, 6.84; N, 24.40%. IR (KBr) ν(OH) 3447(s), ν(NH) 3326 (s), 3264 (vs), ν(CH) 2932 (s), 2854 (m), ν(CN) 2126 (vs), $\delta(NH_2)$ 1591 (s), $\delta(CH_2)$ 1452 (s), ν(Cr−C) 678 (s), δ(Cr−CN) 562 (s).

$\{[Cu(1S,2Schxn)_2]_3[Cr(CN)_6]_2\cdot 4.25H_2O\}_\infty$ (**3**). **3** was repared starting from *trans*-cyclohexane-(1S,2S)-diamine as described above for **2**. Elemental anal. Found C, 41.55; H, 6.77; N, 24.33%; Calcd. for $C_{48}H_{84}N_{24}Cr_2Cu_3\cdot 4.25H_2O$: C, 42.11; H, 6.81; N, 24.55%. IR (KBr) ν(OH) 3418(vs), ν(NH) 3272 (vs), 3138 (s), ν(CH) 2939 (s), 2855 (s), ν(CN) 2127 (vs), $\delta(NH_2)$ 1589 (vs), $\delta(CH_2)$ 1384 (s), ν(Cr−C) 708 (m), δ(Cr−CN) 564 (s), 495 (s).

X-ray Structural Determination. A dark blue-green crystal of **1** (0.5 × 0.5 × 0.5 mm^3) and dark-violet crystals of **2** (0.4 × 0.25 × 0.38 mm^3) and **3** (0.4 × 0.3 × 0.3 mm^3) were mounted on a Stoe Mark-I Image Plate for **1** and a Mark-II Image Plate diffractometer system for **2** and **3**, both equipped with a graphite-monochromator. Data collections were performed using Mo Kα radiation (λ = 0.71073 Å) at 173 K. The structures ware solved by direct methods using the program *SHELXS-97*[25] and refined by full matrix least-squares on F^2 with *SHELXL-97*.[25] All non-hydrogen atoms were refined anisotropically. Semi-empirical absorption corrections were applied for **1**−**3** using MULscanABS in *PLA-*

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Table 1. Crystal and Structure Refinement Data for **1**, **2**, and **3**

	1	**2**	**3**
formula	$C_{30}H_{60}N_{24}Cr_2Cu_3$	$C_{48}H_{93.5}N_{24}Cr_2Cu_3O_{4.75}$	$C_{48}H_{92.5}N_{24}Cr_2Cu_3O_{4.25}$
fw	1051.64	1377.59	1369.08
λ(Å)	0.71073	0.71073	0.71073
T(K)	173(2)	173(2)	173(2)
cryst syst	trigonal	triclinic	triclinic
space group	$R\bar{3}$	P1	P1
a(Å)	15.4908(11)	8.5421(6)	8.5435(8)
b(Å)	15.4908(11)	12.6379(9)	12.6309(12)
c(Å)	16.7699(13)	16.1571(11)	16.1711(17)
α(°)	90.00	104.594(5)	104.632(8)
β(°)	120.00	98.425(6)	98.429(8)
γ(°)	90.00	97.440(5)	97.375(8)
V(Å^3)	3485.0(4)	1644.3(2)	1645.1(3)
Z	3	1	1
ρ_{calcd}(mg/m^3)	1.503	1.391	1.382
μ(mm^{-1})	1.855	1.334	1.332
reflns measured	8944	22711	8017
indep. reflns/R$_{\text{int}}$	1511/0.0244	11 837/0.0437	7760/0.0362
obsd.reflns: $I > 2\sigma(I)$	1344	10507	6466
no. of params	92	751	756
R1^a [$I > 2\sigma(I)$]	0.0252	0.0395	0.0343
wR2^b [$I > 2\sigma(I)$]	0.0699	0.0981	0.0648
S	1.094	1.008	0.946
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (eÅ^{-3})	1.546/−0.206	0.552/−0.681	0.370/−0.237
Flack x factor		0.006(11)	0.027(16)

[a] $R1 = \Sigma||;F_o| - |F_c||;/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

TON.[26] Four fully occupied and one partially occupied (occupancy 0.75 for **2** and 0.25 for **3**) water molecules of crystallization were located in both crystal structures, giving a total of 4.75H_2O for **2** and 4.25H_2O for **3**. Some of the NH_2 and water hydrogen atoms in the complexes could be located from difference Fourier syntheses and were freely refined (N−H) or with distance restraints (O−H). The remainder of the hydrogen atoms were included in calculated positions and treated as riding atoms using *SHELXL-97* default parameters. The absolute configurations of **2** and **3** were determined by Flack's method.[27] Further details of the data collection and refinement are given in Table 1.

Results and Discussion

Crystal Structures. The crystal structure analysis of **1** $\{[(Cu(tn)_2)_3(Cr(CN)_6)][Cr(CN)_6]\}_\infty$ shows that it is a 3D metal-organic framework. The asymmetric unit consists of a centrosymmetric $[Cu(tn)]^{2+}$ cation and two independent $[Cr(CN)_6]^{3-}$ anions, both situated on 3-fold rotation axes (part a of Figure 1). All of the cyanide groups of the $[Cr(CN)_6]^{3-}$ anion involving atom Cr1 are coordinated to adjacent copper atoms. The second $[Cr(CN)_6]^{3-}$ anion, involving atom Cr2, is situated on a 3-fold rotation axis and is not involved in coordination to the copper(II) cation. Each chromium anion has a perfect octahedral geometry (Cr1−C4 = 2.067(2) Å and Cr2−C5 = 2.085(2) Å). The Cu1 ion is coordinate to four amino nitrogen atoms (N1, N2, and the symmetry-related atoms) of the ligand tn and to two cyanide nitrogen atoms (N3 and the symmetry related atom N3′).

In the lattice, a 3D framework is constructed on the basis of a Cr_4Cu_4 octanuclear cyclic unit (part b of Figure 1). This is formed by the μ_6-$[Cr(CN)_6]^{3-}$ array and the $[Cu(tn)]^{2+}$ cations through Cr1−CN−Cu1−NC−Cr1 linkages.

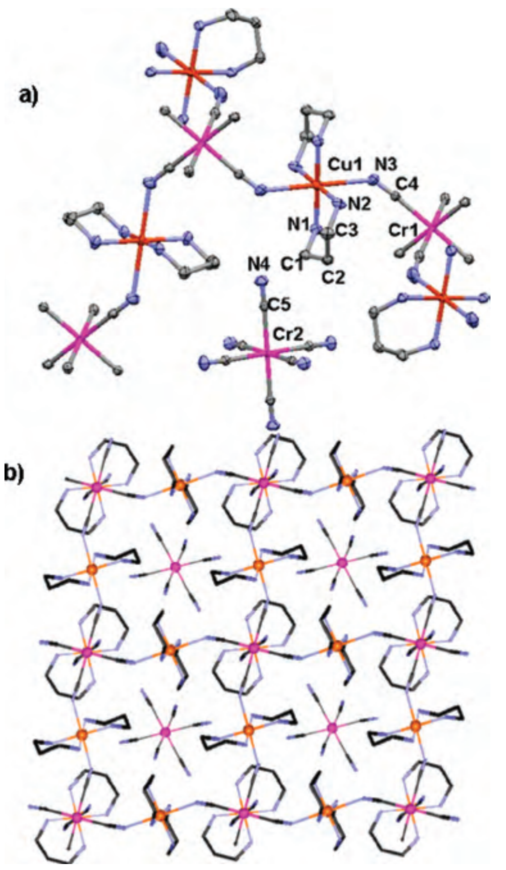

Figure 1. (a) Partial view of the molecular structure of $\{[(Cu(tn)_2)_3(Cr(CN)_6)][Cr(CN)_6]\}_\infty$ (**1**), showing the numbering scheme and displacement ellipsoids at the 50% probability level. (b) View of the octanuclear Cr_4Cu_4 cyclic units.

The non-coordinated $[Cr(CN)_6]^{3-}$ anion, involving atom Cr2, is situated in the center of the cyclic unit and equilibrates the charges (Figure 2). Atom Cu1 is situated on an inversion center and has an elongated octahedral geometry. The Cu1−N1(eq) and Cu1−N2(eq) bond distances are 2.038(2) and 2.045(2) Å, respectively, whereas the Cu−N3(ax)

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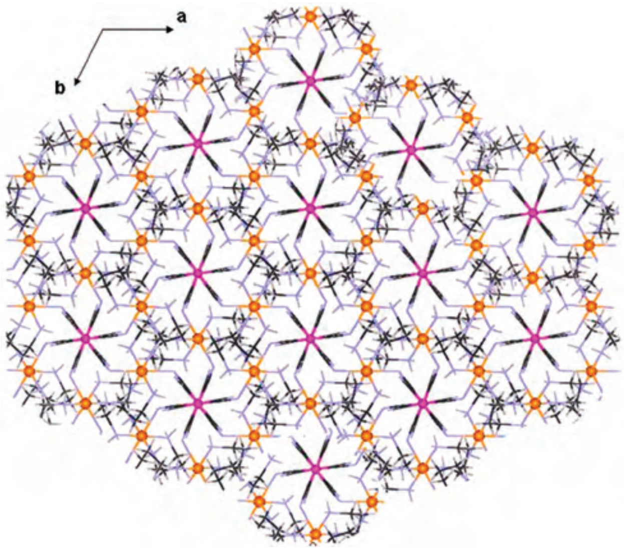

Figure 2. View of the 3D network structure of $\{[(Cu(tn)_2)_3(Cr(CN)_6][Cr(CN)_6]\}_\infty$ (**1**) along the 3-fold *c* axis.

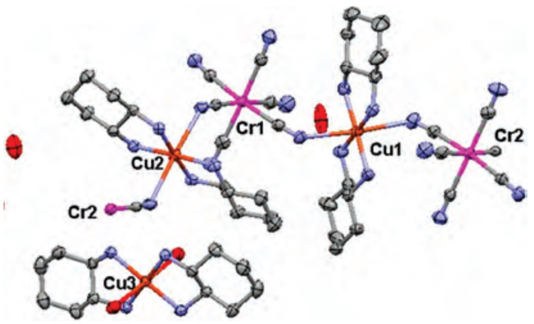

Figure 3. View of the asymmetric unit of $\{[Cu(1R,2Rchxn)_2]_3[Cr(CN)_6]_2 \cdot nH_2O\}_\infty$ (**2**), showing the numbering scheme and displacement ellipsoids at the 50% probability level.

distance is 2.503(3) Å. The Cu1−N1−C1 and Cu1−N2−C3 bond angles are 116.4(1) and 119.6(2)°, respectively, and bond angle Cu1−N3−C4 is 135.3(2)°.

$\{[Cu(1R,2Rchxn)_2]_3[Cr(CN)_6]_2 \cdot 4.75H_2O\}_\infty$ (**2**) and $\{[Cu(1S,2Schxn)_2]_3[Cr(CN)_6]_2 \cdot 4.25H_2O\}_\infty$ (**3**) crystallize in the non-centrosymmetric triclinic space group P1. They are isostructural to the $[Fe(CN)_6]^{3-}$ analogues.[28] The asymmetric unit of **2** is shown in Figure 3. The 1D zigzag chains consists of two independent negatively charged units consisting of a $[Cu(1R,2R\ chxn)_2]^{2+}$ cation linked to a $[Cr(CN)_6]^{3-}$ anion. The overall negative charge of −2 is compensated for by an isolated $[Cu(1R,2Rchxn)_2]^{2+}$ cation. The axial positions on the copper atoms, Cu1 and Cu2, are occupied by cyano groups. These Cu−N distances are very long compared to those in the equatorial plane: Cu1−N(ax) 2.665(5) and 2.671(5) Å, compared to Cu1−N(eq) 1.997(4)−2.021(5) Å, and Cu2−N(ax) 2.595(4) and 2.603(4) Å, compared to Cu2−N(eq) 2.003(3)−2.025(4) Å. Thus, the Cu−N(ax) bond distances can be considered as a Jahn−Teller distortion.[29] The Cu−N−C bond angles are nonlinear, with values ranging between 126.3(4) and 131.3(3)°. This phenomenon has been observed previously in similar compounds.[28,30–37]

Each chromium anion, with four terminal and two bridging CN ligands, has a slightly deformed octahedral coordination geometry (Cr−C bond lengths vary from 2.061(5) to 2.093(4) Å). Copper atom Cu3 of the isolated *trans*-$[Cu(1R,2R\text{-}chxn)_2(2H_2O)_2]^{2+}$ cation has a distorted octahedral geometry (Cu3−N(eq), 2.016(4)−2.038(4)Å; Cu3−O1(ax), 2.433(4) Å; Cu−O2(ax), 2.462(4) Å). Two water molecules of crystallization (O3 and O4) hydrogen bond to both the terminal and the bridging CN groups of the Cr1 unit and to the NH_2 groups of the Cu1 moiety.

Circular Dichroism Measurements. Solid-state diffuse reflectance CD spectra of **2** and **3** are shown in Figure 4. For **2**, the *R*,*R* isomer exhibits a maximum positive Cotton effect at 510 nm, as was observed for the aqueous solution of the precursor. The *S*,*S* isomer has, as expected, a negative Cotton effect at the same wavelength. The chirality and enantiomeric nature of **2** and **3** were controlled in view of a future study of magnetochiral dichroism.

Magnetic Properties. Magnetic data for **1** were measured at 0.05 T. At room temperature, $\chi_m T$ (for each Cu_3Cr_2 unit) is near 5 $cm^3\ mol^{-1}$ K, which corresponds to two chromium(III) and three copper(II) uncoupled ions (spin-only value, i.e. with $g = 2.00$, would give $\chi_m T = 4.875\ cm^3\ mol^{-1}$ K). From room temperature to 75 K, $\chi_m T$ is practically constant. It then increases rapidly to a value of 14 $cm^3\ mol^{-1}$ K at 3.5 K and decreases to 8 $cm^3\ mol^{-1}$ K at 2 K (limit of the measurement) (Figure 5). It is important to note that there is a clear variation of the $\chi_m T$ curves at low temperature on varying the magnetic field: 20, 100, 500, and 1000 G; the lower the magnetic field, the higher the magnetization (Figure 5 inset). At 20 G, there is a maximum at 4 K of ca. 400 $cm^3\ mol^{-1}$ K. This feature can indicate ferromagnetic ordering at low temperature.

The ferromagnetic ordering in **1** is corroborated by the following data: (i) the shape of the $M/N\mu_B$ curve (Figure 6). There is a rapid increase from 0 to 200 G and then it increases more slowly to a maximum value of 8 $N\mu_B$ at 5 T without reaching saturation. However, the hysteresis is extremely small at the minimum temperature (2 K) of the SQUID [Figure 6 inset], (ii) the zero-field cooled/field cooled magnetization (at 50 G) exhibits an abrupt change at ca. 4 K and both curves diverge in the ferromagnetic phase (Figure 7), (iii) the most important and clear proof is the presence of the out-of-phase ac measurement (χ'') frequency independent (Figure 7 inset). According to the ZFC/FC and the

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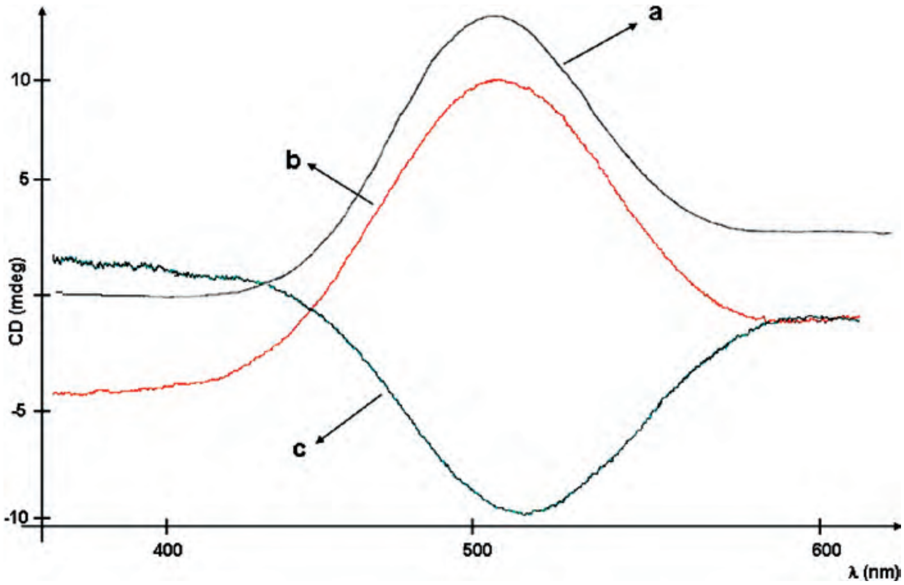

Figure 4. CD spectra of (a) an aqueous solution of the bis-chelated precursor [Cu(*trans*-(1*R*,2*R*)-chxn)$_2$(H$_2$O)$_2$](NO$_3$)$_2$, (b) {[Cu(1R,2Rchxn)$_2$]$_3$-[Cr(CN)$_6$]$_2$˙nH$_2$O}∞ (**2**) in KBr pellet, (c) [Cu(1S,2Schxn)$_2$]$_3$[Cr(CN)$_6$]$_2$˙nH$_2$O}∞ (**3**) in KBr pellet.

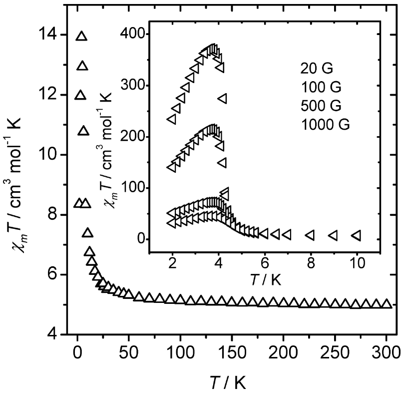

Figure 5. Thermal variation $\chi_m T$ for **1**. Inset: plot of $\chi_m T$ vs T varying the applied field (20, 100, 500, and 1000 G).

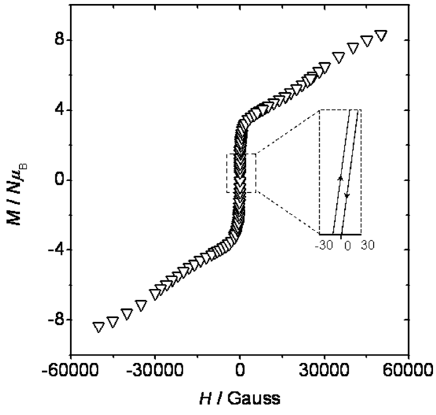

Figure 6. Plot of the $M/N\mu_B$ vs H for **1**. Inset: View of the very small hysteresis loop.

maximum in the ac measurements, the T_c (critical temperature of the phase change) is very close to 4 K.

As a consequence, this material is a molecule-based magnet. Although it is not possible to calculate the J value between chromium(III) and copper(II) in this 3d system, the topology of the magnetic orbitals allow us to propose that the magnetic exchange is ferromagnetic in character. Indeed, the copper(II) and chromium(III) magnetic orbitals are, per se, orthogonal. As a consequence, the magnetic ordering, even if at very low temperature, is not due to a canting of an uncompensated antiferromagnetic system but is due to a ferromagnetic ordering. This feature is evidenced from the study of the magnetic coupling of **2** and, furthermore, with previous literature data. Similar behavior has been reported for a 2D copper(II)−chromium(III) cyanide-bridged magnet $T_c = 9.5$ K.[38]

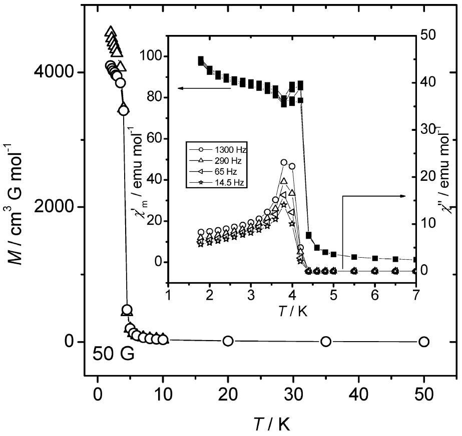

Figure 7. ZFC/FC at 50 G for **1**. Inset: Thermal variation χ' and χ'' for **1**. The frequencies used were 1300, 290, 65, and 14.5 Hz (solid lines are only present as a visual guide).

The magnetic behavior of **2** in the form of $\chi_M T$ versus T plot is shown in part a of Figure 8. The global feature is characteristic of a weak ferromagnetic interaction. The $\chi_M T$ value per [Cu$_3$Cr$_2$] unit at 300 K is 5.20 cm^3 mol^{-1} K, which practically corresponds to three isolated copper(II) ions ($S_1 = {}^1/_2$) and two chromium(III) ions ($S_2 = {}^3/_2$) ($\chi_M T = 4.875$ cm^3 mol^{-1} K in the spin-only approach). $\chi_M T$ increases smoothly from room temperature to ca. 50 K and then

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(38) Thétiot, F.; Triki, S.; Pala, J.-S.; Gómez-García, C. J.; Golnen, S. *Chem. Commun.* **2002**, 1078.

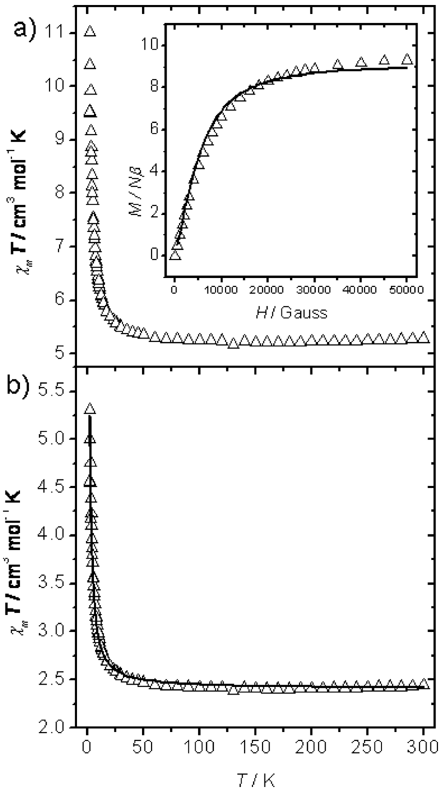

Figure 8. (a) Thermal variation of $\chi_M T$ for **2** per [Cu_3Cr_2] unit. Inset: plot of the reduced magnetization ($M/N\mu_B$) vs H at 2 K, (b) Fit of the thermal variation of $\chi_M T$ for **2** after subtraction of $\chi_M T = 0.41$ cm^3 mol^{-1} K (text). **Note**: The fit was made with a [Cu_4Cr_4] ring, but the plot is given for only one $Cu^{II}-Cr^{III}$ entity; (b) A view of the octanuclear Cu_4Cr_4 cyclic units of the 3D network of **1**, with the isolated $[Cr(CN)_6]^{3-}$ ion in the center.

increases rapidly at lower temperatures, reaching a maximum value of 11.1 cm^3 mol^{-1}K at 2 K. This is consistent with the behavior expected for ferromagnetic intramolecular interactions between the copper(II) and chromium(III) ions. The field dependence of the magnetization (0−5 T) measured at 2 K is shown in part a of Figure 8 (inset) in the form of $M/N\mu_B$ (per Cu_3Cr_2 fragment) versus H. The magnetization tends to 9.18 $N\mu_B$, which is close to the expected value for three copper(II) ions and two chromium(III) system ($S_T = {}^9/_2$). The shape of the curve matches rather well with the Brillouin function for an $S = {}^9/_2$ ground state, assuming $g_{\text{average}} = 2.1$. This feature indicates that **2** does not present magnetic ordering, such as occurs in **1**.

To calculate the J parameter, it is necessary to consider the overall structure and the possible pathways in the 1D $Cu^{II}-Cr^{III}$ chain. The overall structure consists of a mixture of 1D $Cu^{II}-Cr^{III}$ chains separated by isolated [Cu(1*R*,2*R*chxn)$_2$]$^{2+}$ cations. The interpretation of the magnetic data can be made assuming that: (i) the isolated [Cu(diamine)$_2$]$^{2+}$ entity follows the Curie law (except at very low temperatures), (ii) a standard value of g_{Cu} of 2.1 for the Cu^{2+} ion in this isolated [Cu(diamine)$_2$]$^{2+}$ entity. With this g value, $\chi_M T$ = constant = 0.41 cm^3 mol^{-1} K. Thus, for the treatment of the magnetic data, we can subtract 0.41 from the values obtained for the magnetic measurements given in part b of Figure 8. After subtraction, the final magnetic entity will depend only on the $Cu^{II}-Cr^{III}$ chain, corresponding to the 1D system. The modified plot of $\chi_M T$ versus T is indicated in part b of Figure 8. It is very important to underline here that this plot is given for only one $Cu^{II}-Cr^{III}$ entity, given that now we assume that we are dealing with a heteronuclear [Cu−Cr] 1D system. On the basis of these considerations, the experimental magnetic data can be fitted using the following isotropic Heisenberg Hamiltonian:

$$H = -\Sigma J(S_{Cu(i)} S_{Cr(i+1)})$$

There is no exact mathematical formula for fitting such an alternating chain ($S = {}^3/_2 - {}^1/_2$). However, assuming that all of the J values for Cr−CN−Cu are the same, which is in agreement with the structural data, calculations were carried out with the *CLUMAG* program,[39] using the irreducible tensor operator formalism (ITO), employing a closed rings of eight atoms: Cu4Cr4. The experimental data for **2** were then fitted in the range 300−2 K, with allowance for variation in all of the parameters. The best least-squares fit, shown in part b of Figure 8 (per one CuCr unit, above), gives J = 1.64 ± 0.3 cm^{-1}, $g_{av} = 2.03$, and $R = 2.80 \times 10^{-4}$, where $R = \Sigma[(\chi_M T)_{exp} - (\chi_M T)_{calcd}]^2/\Sigma[(\chi_M T)_{exp}]$. The assumption of equal g values for copper(II) and chromium(III) is an approximation because g_{Cu} must be >2.00 and g_{Cr} must be <2.00.

The value of the exchange parameter $J = +1.64$ cm^{-1} for **2** is placed in the lowest limit of the magnetic data found in the literature for analogous complexes: The coupling is always ferromagnetic, ranging from +1.31 cm^{-1}[40] to +45 cm^{-1},[41] depending on the Cu−N distance and on the position of the NC group with respect to the magnetic orbital of the copper(II) ion. The Cu−N distance in the complex with J = +45 cm^{-1} is 1.971 Å,[41] whereas in **2** the same distance varies between 2.595(4) to 2.671(5) Å: For the complex with $J = +1.31$ cm^{-1},[40] no structural data are available. However, for two other analogous compounds, reported by Kou et al.,[37] values of $J = +2.4$ and +12 cm^{-1} with Cu−N distances of 2.505 and 2.378 Å, respectively, have been reported. The magnetic behavior of Prussian Blue analogues is well-known, and the general trends of their magnetic properties are well established. In particular, the ferromagnetic interaction between iron(III) or chromium(III) and copper(II) ions can be rationalized in terms of the strict orthogonality of the magnetic orbitals of these ions. According to the crystal structure and ligand-field theory, a copper(II) ion in an elongated octahedral surrounding has one unpaired electron in a $d_{x^2-y^2}$ orbital (x and y axes are taken along the donor atoms), which interacts with the molecular orbitals of the cyano bridge having the same symmetry, producing a magnetic orbital with σ character. A chromium(III) ion in an octahedral environment has three unpaired electrons in the t_{2g} orbitals, which interact with other molecular orbitals of the cyano bridge, having appropriate symmetry that produces a magnetic orbital with π character. Consequently strict orthogo-

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nality is obeyed, and the interaction between copper(II) and chromium(III) should be ferromagnetic. The strict orthogonality is through the long Cu−N distances (2.595(4)−2.671(5) Å), resulting from the Jahn−Teller distortion on each copper ion. Hence, this long distance explains the weak magnitude of the ferromagnetic coupling.

Conclusions

Three new bimetallic complexes, $\{[(Cu(tn)_2)_3(Cr(CN)_6)][Cr(CN)_6]\}_\infty$ (**1**), with a 3D structure based on a Cr_4Cu_4 octanuclear cyclic unit, $\{[Cu(1R,2Rchxn)_2]_3[Cr(CN)_6]_2 \cdot nH_2O\}_\infty$ (**2**), and $\{[Cu(1S,2schxn)_2]_3[Cr(CN)_6]_2 \cdot nH_2O\}_\infty$ (**3**), with chiral 1D zigzag chains, were successfully synthesized and fully characterized. **1** exhibits 3D magnetic ordering over the crystal lattice, with T_c close to ca. 4 K. **2** shows weak ferromagnetic coupling, which is due to the orthogonality of the corresponding magnetic orbitals. Its weak character is due to the long Jahn−Teller axis of the copper(II) ions [2.595(4)−2.671(5) Å].

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Supporting Information Available: Crystallographic data for **1**, **2**, and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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