Stoichiometric Control of the Magnetic Properties in Copper(II) Cyano-Bridged Bimetallic Complexes

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Control of the Cu^{2+} ion coordination environment affords a 1D, magnetically diluted compound, $[Cu(cis\text{-chxn})_2]_3[Fe(CN)_6]_2\cdot 7H_2O$ (**1**) and the 2D ferromagnetic material $[Cu(cis\text{-chxn})]_3[Fe(CN)_6]_2\cdot 6H_2O$ (**2**) with a critical temperature, T_c, of 3.5 K.

Introduction

The search for bimetallic cyanide systems based on Prussian blue has given rise to a rich and well-documented family of molecule-based magnets. Most of these systems are obtained from the assembly of unsaturated cations of the $[M^{II}(L)_n]^{2+}$ type (where M = Ni[1−9] or Cu;[1,9−18] L = polydentate ligand) and hexacyanometallate anions: $[M^{II}(CN)_6]^{4-}$ or $[M^{III}(CN)_6]^{3-}$ (where M^{II} = Fe^{II}; M^{III} = Fe^{III}, Mn^{III}, Co^{III}, or Cr^{III}). The choice of the polydentate ligand, the metal ion and its number of free coordination sites in the cationic unit endow us with potential control over the dimensionality and magnetic properties of these systems. Ni^{2+} ions invariably present six-coordination, whereas d^9 Cu^{2+} ions are stereochemically more versatile and can be either tetra-, penta- or hexacoordinate. Therefore, the use of $[Cu(L)_n]^{2+}$ building blocks should enable the preparation of new compounds with novel structures and perhaps improved magnetic properties. However, not very many examples of these have been reported to date. Only two of such copper-containing compounds, $[Cu(EtOH)_2][Cu(en)]_2[Cr(CN)_6]_2$ (en = 1,2-diaminoethane)[15] and $[Cu(tn)]_3[Cr(CN)_6]_2\cdot 3H_2O$ (tn = 1,3-diaminopropane),[18] have been structurally characterised and exhibit spontaneous magnetisation, with critical temperatures, T_c, of 57 K and 9.5 K, respectively. To the best of our knowledge, no $Cu^{II}-Fe^{III}$ cyanide-bridged compounds showing magnetic ordering have been reported so far, as most of the $Cu^{II}-Fe$ bimetallic systems are indeed formed by diamagnetic hexacyanoferrate(II) units. By stoichiometric control of the copper-coordination environment, allowing either axial or equatorial coordination of the hexacyanometallate anions, the compounds $[Cu(cis\text{-chxn})_2]_3[Fe(CN)_6]_2\cdot 7H_2O$ (**1**) and $[Cu(cis\text{-chxn})]_3[Fe(CN)_6]_2\cdot 6H_2O$ (**2**) (where *cis*-chxn = *cis*-cyclohexane-1,2-diamine), respectively, were obtained. Herein we report their syntheses, structural characterizations and magnetic properties.

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Results and Discussion

Compound **1** crystallises in the centrosymmetric $P\bar{1}$ space group. A view of the crystal structure along the *a* axis (see Figure 1) shows the existence of Cu(1)−NC−Fe(1)−CN−Cu(2) zigzag chains running along the [011] direction and composed of alternating *trans*-$[Cu(cis\text{-chxn})_2]^{2+}$ cations and $[Fe(CN)_6]^{3-}$ anions. The latter exhibit an octahedral environment and bind axially to the copper ions in a μ^2-mode. The Cu(1) and Cu(2) atoms of the cationic unit show centrosymmetric, elongated, octahedral geometries due to Jahn−Teller effects, with long axial Cu−N distances as compared to those of equatorial ligands [Cu(1)−N(ax): 2.818(3) Å; Cu(1)−N(eq): 1.995(3) Å and 2.027(2) Å; Cu(2)−N(ax): 2.676(3) Å; Cu(2)−N(eq): 1.996(3) Å and 2.017(2) Å]. Cu−N−C angles within the chain deviate greatly form linearity, with values ranging between 120.8° and 109.4°. Similar values have been reported for other copper-containing compounds.[4,12−14,17,18] Isolated from the chain, square planar $[Cu(cis\text{-chxn})_2]^{2+}$ cations compensate the charge of the polymer. The shortest Cu(3)−N[Fe(1)] distances is 3.123(3) Å. Seven water molecules of crystallisation are present in the structure per formula unit. Four of them [O(1) and O(2)] are hydrogen-bonded to each other and to terminal cyanide groups belonging to adjacent chains, leading to a two-dimensional network.

The thermal variation of the $\chi_m T$ product for **1** is shown in Figure 2. At room temperature $\chi_m T$ equals 2.42 emu·K·mol^{-1}. This value differs from the spin-only value

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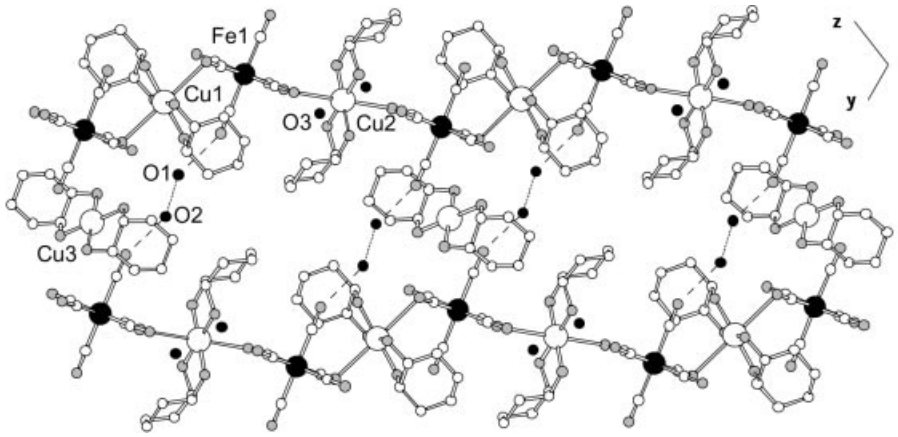

Figure 1. View of the crystal molecular structure of **1** along the *a* axis; dashed and dotted lines refer to hydrogen bonds

of 1.875 emu·K·mol^{-1} calculated for uncorrelated spins, owing to the orbital contribution in low-spin Fe^{III} complexes. Spin-orbit coupling accounts for the smooth decrease in $\chi_m T$ observed on cooling. Below 4 K, $\chi_m T$ decreases on lowering the temperature, indicating the existence of weak intermolecular magnetic interactions.

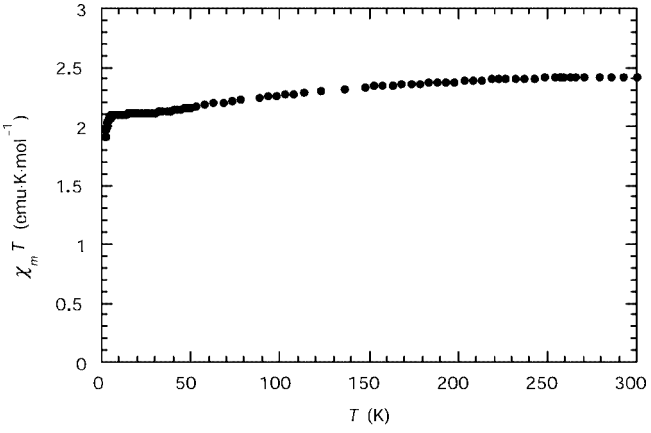

Figure 2. Temperature dependence of the χT product for **1**

Compound **2** also crystallises in the $P\bar{1}$ space group. It presents a structure similar to that reported previously for compound [Cu(tn)]$_2$[Fe(CN)$_6$]·KCl·5H$_2$O[18] (see Figure 3). The binding of [Cu(*cis*-chxn)]$^{2+}$ cations and [Fe(CN)$_6$]$^{3-}$ anions yields a two-dimensional [Cu(*cis*-chxn)]$_2$[Fe(CN)$_6$] monocationic assembly made up of defective cubane units. The structure can also be viewed as a hexagonal close packing of copper ions, in which the iron atoms occupy the octahedral sites ($CdCl_2$-type layered structure). Thus, every [Fe(CN)$_6$]$^{3-}$ moiety links to six copper atoms in a μ^6-mode, whereas each copper ion presents a square-based pyramidal geometry and links to three iron units. Two cyanide ligands and a bidentate *cis*-chxn ligand bind to the equatorial positions of the square-based pyramids and the apical sites are occupied by the third bridging CN$^-$ anion (see Table 1). One *cis*-chxn ligand is disordered over two positions in the coordination sphere of the Cu(3) metal centre. Cu−N−C angles are close to linear; the values range between 163.9° and 177.3°. Fe(2) ions occupy an inversion centre in the structure. A view along the *b* axis (see Figure 3) shows all iron atoms lying in the same *ab* plane and all copper atoms, as well as bulky cyclohexane rings, lying on both sides of this central plane. A very long interlayer Cu···Cu separation of 12.290 Å results. It should be noted that the presence of isolated [Fe(CN)$_6$]$^{3-}$ anions between the layers ensures electroneutrality and yields an overall two-component material.

The value of the $\chi_m T$ product of **2** at room temperature (2.32 emu·K·mol^{-1}) is slightly higher than the spin-only value and accounts for the orbital contribution of the low-spin iron(III) ions. A continuous decrease of $\chi_m T$ is observed on cooling (see Figure 4), as expected from the spin-orbit coupling of the iron sites. Below 15 K, $\chi_m T$ increases sharply, pointing to the onset of long-range ferromagnetic order. The first magnetisation curve performed at 2 K reaches a value of 4.69 μ_B at 5 T, close to the one expected for complete saturation. AC susceptibility measurements performed between 2 and 5 K show the appearance of an out-of-phase signal below the critical temperature, T_c = 3.5 K (Figure 4, inset). The frequency dependence of this signal appears to be a common feature in bimetallic magnets based on chxn ligands.[7,8] Finally, the magnetic order was confirmed by specific-heat measurements. The typical metamagnetic behaviour reported for several bimetallic cyanide systems was not observed in our case, a result that is attributed to the large interplanar distance induced by the presence of the bulky chxn ligands.[1,8]

Conclusion

Simple molecular orbital considerations predict the observation of ferromagnetic interactions between hexacyanoferrate(III) anions (t_{2g}^5 electronic configuration) and copper(II) ions (t_{2g}^6 e_g^3) in octahedral geometry. Surprisingly, this type of interaction has rarely been observed in such bimetallic systems and there is no previously reported example of a Cu^{II}−Fe^{III} cyano-bridged magnet, despite the fact that several two-dimensional structures have been de-

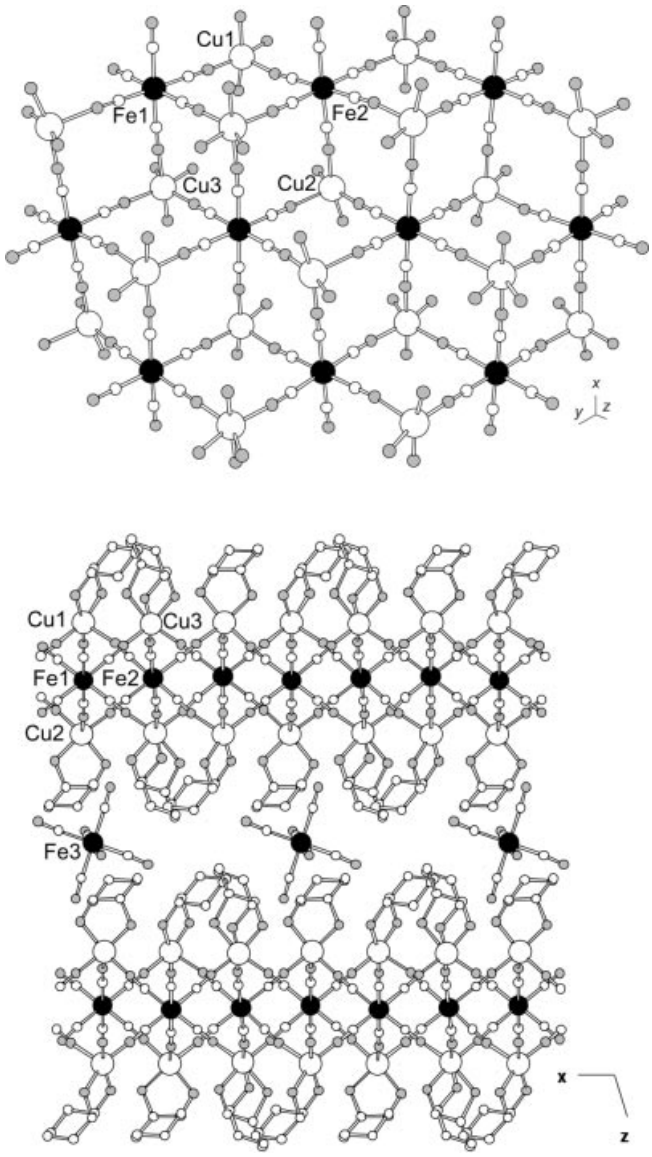

Figure 3. Crystal structure of **2**: (top) projection of the 2D monocationic network showing the defective cubane units (cyclohexane rings have been omitted for clarity); (bottom) view along the *b* axis of the interlayer arrangement and the isolated hexacyanoferrate(III) anions

scribed. It can be anticipated that the use of $[Cu(L)_2]^{2+}$ precursors (where L = diamine) in the synthesis of Cu_3Fe_2 bimetallic complexes compels axial coordination of the cyanide ligands. In fact, the soft, stronger diamine ligands are expected to occupy the equatorial positions of the Cu^{2+} coordination sphere. Due to the Jahn−Teller effect, long intrachain Cu···N(Fe) distances result and a magnetic behaviour of quasi-isolated spins is observed. As shown here, compound **1**, obtained from the $[Cu(cis\text{-chxn})_2]^{2+}$ precursor (either prepared in situ or isolated), follows exactly the same behaviour. These occurrences are overcome by the use of $[Cu(cis\text{-chxn})]^{2+}$ building blocks, enabling cyanide-bridging ligands to bind to the equatorial positions in the Cu^{II} coordination environment. Shorter Cu···N(Fe) distances and higher dimensionality are achieved in this coordination

Table 1. Cu−N distances (Å) for compound **2**

Bond	Distance (Å)
Cu(1)−N(1)	2.012(3)
Cu(1)−N(2)	2.024(2)
Cu(1)−N(3)	1.977(2)
Cu(1)−N(4)	1.987(2)
Cu(1)−N(5)	2.209(3)
Cu(2)−N(6)	2.017(2)
Cu(2)−N(7)	2.004(3)
Cu(2)−N(8)	2.235(3)
Cu(2)−N(9)	1.981(2)
Cu(2)−N(10)	1.971(3)
Cu(3)−N(11)	2.021(4)
Cu(3)−N(11′)	2.031(7)
Cu(3)−N(12)	2.007(3)
Cu(3)−N(13)	2.111(3)
Cu(3)−N(14)	1.967(2)
Cu(3)−N(15)	2.024(3)

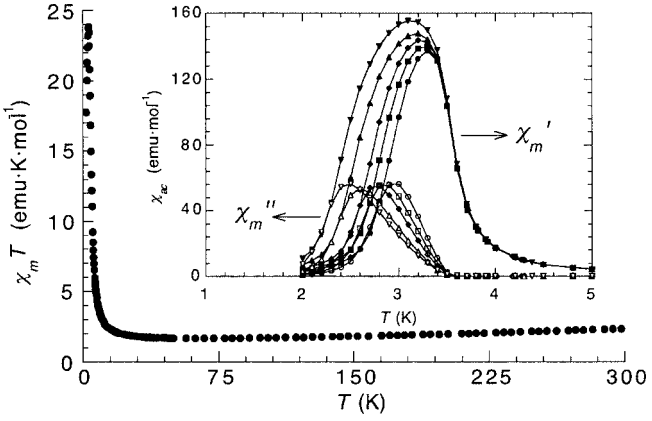

Figure 4. Temperature dependence of the *dc* $\chi_m T$ product for **2**; inset: real (filled symbols) and imaginary (open symbols) components of the *ac* magnetic susceptibility for **2** at frequencies of 997 (circles), 332 (squares), 110 (rhombuses), 10 (up triangles) and 1 Hz (dow

mode. It is also interesting to compare the quasi-linear Cu···Fe bridges of **2** with the extremely bent angles observed in **1**. This is expected to enhance the ferromagnetic components of the magnetic interactions for the former compound. All these features allow the observation of long-range magnetic ordering, despite the poor energy match between the orbitals of the different metal centres. Indeed, compound **2** is the only $Cu^{II}-Fe^{III}$ cyano-bridged ferromagnet reported to date. In addition, it exhibits a two-component structure comprising ferromagnetic layers and paramagnetic ferricyanide anions located in between. Experiments in progress (Mössbauer and single-crystal EPR) may provide information about the magnetic environment of the different sites present in the structure.

Experimental Section

General Remarks: Compounds $Cu(NO_3)_2{\cdot}3H_2O$ (Panreac), $K_3[Fe(CN)_6]$ (Fluka) and *cis*-chxn (Fluka) were of reagent grade and used without further purification.

[Cu(*cis*-chxn)$_2$(NO$_3$)$_2$]: This precursor was prepared by a method similar to that reported previously for the *trans*-chxn analogue.[19] A solution of *cis*-chxn (228 mg, 2 mmol) in methanol (5 mL) was added dropwise to a stirred solution of Cu(NO$_3$)$_2$·3H$_2$O (242 mg, 1 mmol) in the same amount of methanol. The violet precipitate was filtered off, washed with methanol and air-dried. $C_{12}H_{28}CuN_6O_6$ (415.94): calcd. C 34.65, H 6.79, N 20.2; found C 34.60, H 7.08, N 20.91. IR (KBr): $\tilde{\nu}$ = 3288, 3237, 2935, 2858, 1603 cm^{-1}.

[Cu(*cis*-chxn)$_2$]$_3$[Fe(CN)$_6$]$_2$·7H$_2$O (1): Cu(NO$_3$)$_2$·3H$_2$O (72 mg, 0.3 mmol) and *cis*-chxn (68 mg, 0.6 mmol) were dissolved in the minimum amount of water. Slow diffusion of this solution and an aqueous solution of K$_3$[Fe(CN)$_6$] (66 mg, 0.2 mmol) produced brown crystals of the title compound. Complex **1** was also obtained by slow diffusion of [Cu(*cis*-chxn)$_2$(NO$_3$)$_2$] (125 mg, 0.3 mmol) and K$_3$[Fe(CN)$_6$] (66 mg, 0.2 mmol) in water. $C_{48}H_{98}Cu_3Fe_2N_{24}O_7$ (1425.80): calcd. C 40.44, H 6.93, N 23.58; found C 40.27, H 6.78, N 24.13. IR (KBr): $\tilde{\nu}$ = 3309 cm^{-1}, 3242 (N−H), 2930, 2853 (C−H), 2118, 2105 (C≡N).

[Cu(*cis*-chxn)]$_3$[Fe(CN)$_6$]$_2$·6H$_2$O (2): This compound was obtained by slow diffusion of Cu(NO$_3$)$_2$·3H$_2$O (72 mg, 0.3 mmol), *cis*-chxn (34 mg, 0.3 mmol) and K$_3$[Fe(CN)$_6$] (66 mg, 0.2 mmol) in water as described above for **1**. IR (KBr): $\tilde{\nu}$ = 3309 cm^{-1}, 3145 (N−H), 2925, 2853 (C−H), 2172, 2141, 2105, 2100, 2090 (C≡N).

Magnetic Measurements: Variable-temperature susceptibility measurements were carried out on polycrystalline samples in the 2−300 K temperature range at magnetic fields of 1 T (**1**) and 0.1 T (**2**) using a magnetometer (Quantum Design MPMS-XL-5) equipped with a SQUID sensor. Diamagnetic contributions were corrected with Pascal's constants. Isothermal magnetization measurements at 2 K were carried out up to 5 T by using the same equipment.

X-ray Crystallographic Study: X-ray diffraction data of **1** and **2** were collected at room temperature with a Nonius−KappaCCD diffractometer using a graphite monochromated Mo-K_α radiation source (λ = 0.71073 Å). Denzo and Scalepack[20] programs were used for cell refinements and data reduction. The structures were solved by direct methods using the SIR97[21] program with the WinGX[22] graphical user interface. The structure refinements were carried out with SHELX-97.[23] All non-hydrogen atoms were refined anisotropically. Multiscan absorption corrections, based on equivalent reflections, were applied to the data using the program SORTAV.[24] Crystallographic data are summarized in Table 2.

For **1**, three independent H$_2$O solvent molecules were found in the asymmetric unit and were well behaved. The sample, however, showed the presence of further disordered water molecules. Calculations with PLATON[25] indicated a solvent-accessible void centred around the inversion point (*1/2*, *1/2*, *1/2*) with an area of 73 Å^3. There was some indication of electron density at this site. The presumed solvent was heavily disordered and no realistic atomic model could be satisfactorily refined. Therefore, the SQUEEZE procedure of Spek and van der Sluis[26] was used to accommodate this extra density. A total of 20 electrons per unit cell were recovered and they fit quite well with one water molecule. This extra H$_2$O molecule was added to the final formula of **1**. H atoms of water molecules were found in difference maps and refined positionally with geometric restraints (O−H = 0.82 Å, N−H = 0.90 Å and H···H = 1.35 Å) and with U_{iso}(H) = 1.2U_{eq}(O). The remaining H atoms were placed in calculated positions and refined with a riding model, with C−H = 0.97 Å, N−H = 0.90 Å and U_{iso}(H) = 1.2U_{eq}(C, N).

In compound **2**, one of the three independent cyclohexanediamine ligands [coordinating to Cu(3)] shows a positional disorder over two sets of sites having refined occupancies of 0.668 and 0.332. This disorder only affects three atoms of the ligand: N(11), C(28) and C(29). H atoms on O(1 W), O(2 W), O(3 W) and N atoms were found in difference maps and refined positionally with geometric restraints as described previously. The H atoms on atoms O(4 W), O(5 W) and O(6 W) could not be found clearly in difference maps.

For both compounds, six low-angle reflections were omitted from the final cycles of refinement because the observed intensities were much lower than the calculated values, as a result of being partially obscured by the beam stop.

CCDC-213881 and -213882 contain the supplementary crystallographic data for this paper. These data can be obtained free of

Table 2. Crystal data and structure refinement for **1−2**

Compound	**1**	**2**
Empirical formula	$C_{48}H_{100}Cu_3Fe_2N_{24}O_8$	$C_{30}H_{48}Cu_3Fe_2N_{18}O_6$
Molecular mass	1443.84	1065.23
a (Å)	8.4720(2)	12.3931(8)
b (Å)	13.4430(3)	12.7006(7)
c (Å)	15.7510(4)	18.2838(5)
α (°)	106.304(5)	102.751(3)
β (°)	103.865(5)	96.370(2)
γ (°)	90.586(5)	119.062(3)
Z	1	2
d (mg·m^{-3})	1.439	1.492
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Crystal dimensions (mm)	0.40 × 0.30 × 0.20	0.20 × 0.10 × 0.10
T (K)	293(2)	293(2)
Θ range	1.78 < Θ < 27.44	2 < Θ < 27.70
Reflections collected	15772	103797
Independent reflections	7270	10862
Data/restraints/parameters	7270/10/398	10862/43/623
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0465, wR_2 = 0.1445	R_1 = 0.0427, wR_2 = 0.1190
R indices (all data)	R_1 = 0.0592, wR_2 = 0.1512	R_1 = 0.0587, wR_2 = 0.1314

charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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