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$[Cu(tn)]_3[Cr(CN)_6]_2 \cdot 3H_2O$: a unique two-dimensional Cu–Cr cyano-bridged ferromagnet (tn = 1,3-diaminopropane)

Franck Thétiot,[a] **Smaïl Triki,***[a] **Jean Sala Pala,**[a] **Carlos J. Gómez-García**[b] **and Stéphane Golhen**[c]
[a] *UMR CNRS 6521, Univ. de Bretagne Occidentale, BP 809, 29285 Brest Cedex, France. E-mail: smail.triki@univ-brest.fr*
[b] *Instituto de Ciencia Molecular, Univ. de Valencia, 46100 Burjasot, Spain*
[c] *UMR CNRS 6511, Univ. de Rennes 1, 35042 Rennes Cedex, France*

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Reaction of the two-coordinate 'assembling complex-ligand' $[Cu(tn)]^{2+}$ with the building block $[Cr(CN)_6]^{3-}$ leads to a unique two-dimensional Cu–Cr cyano-bridged ferromagnet with unusual μ_3- and μ_4-bridging $[Cu(tn)]^{2+}$ units.

Bimetallic cyano-bridged assemblies of Prussian-blue type have attracted a great attention because of their remarkable magnetic, magneto-optical and optoelectronic properties.[1] However, the lack of structural details, due to the difficulty to obtain crystals suitable for X-ray structure determination, precludes a thorough magneto–structural correlation of these three-dimensional systems of high-symmetry. In order to tailor their dimensionality and connectivity, a second family of cyano-bridged coordination assemblies was envisaged by using cationic assembling units of the $[M'L_x]^{n+}$ type (L = polyamine, macrocycle ligand, Schiff base, *etc.*), having selected free coordination sites, instead of simple aqua complexes. These low-symmetry cyano-bridged assemblies display rich and fascinating structural architectures ranging from discrete polynuclear complexes to extended three-dimensional networks,[2–5] and in some cases, exhibit long-range magnetic ordering.[3,5] Most of them concern the extended bimetallic compounds $[M'^{II}(L)_x]_y[M(CN)_6]_z$ with a three- or four-coordinate $[M'(L)_x]^{2+}$ assembling unit which imposes the number of adjacent hexacyanometallate building blocks to two and/or a limited dimensionality of two. In contrast, examples in which the assembling block acts as a μ_4-bridging 'complex-ligand' are very scarcely reported.[4,5] In order to explore such extended bimetallic assemblies with higher connectivities and/or higher dimensionalities, we focus on the use of two-coordinate assembling units containing the Cu(II) ion, the versatility of which as regards to coordination number and geometry is well known. During the preparation of this manuscript, the three-dimensional assembly $[Cu(EtOH)_2][Cu(en)]_2[Cr(CN)_6]_2$ (**2**) was reported as a unique Cu–Cr cyano-bridged ferromagnet structurally characterized.[5] Herein, we report the synthesis, structural characterization and magnetic properties of $[Cu(tn)]_3[Cr(CN)_6]_2 \cdot 3H_2O$ (**1**), as the first two-dimensional ferromagnet involving '–Cu–NC–Cr–' linkages.

Under aerobic conditions, tn (1.0 mL, 12.0 mmol) was added with stirring to a concentrated aqueous solution of $CuCl_2 \cdot 2H_2O$ (2.04 g, 12.0 mmol) leading to the immediate appearance of a pale green precipitate. An aqueous solution of KOH (12.0 mmol) was added with stirring, the mixture was warmed (*ca.* 60 °C for about 5 min) and then filtered in order to eliminate the precipitate which remained. To the resulting blue filtrate, an aqueous solution of $K_3[Cr(CN)_6]$ (0.65 g, 2.0 mmol) was added. Blue crystals of **1**, suitable for X-ray diffraction,† were formed by slow evaporation at room temperature (yield *ca.* 40%).

The asymmetric unit of **1** contains one $[Cr(CN)_6]^{3-}$ and one $[Cu(tn)]^{2+}$ (Cu1) ion, both located on general positions, and a second $[Cu(tn)]^{2+}$ ion (Cu2) on special position (1/2, *y*, 1/4). Fig. 1(a) shows an ORTEP drawing of this asymmetric unit with the atom-labelling scheme and the coordination polyhedra of the metal ions. The Cu1 atom presents a distorted CuN_5 square pyramidal geometry (Fig. 1(a)) arising from two nitrogen atoms of a chelating tn ligand (N7, N8) and three nitrogen atoms from CN groups (N1, N2(a) and N3(f)); the Cu1–N2(a) apical bond length (2.195(7) Å) is significantly longer than the equatorial ones (Cu–N range 2.013–2.051 Å). The coordination polyhedron of the Cu2 atom differs markedly from that of Cu1 and can be described as a CuN_4N_2 elongated octahedron generated by a CuN_4 equatorial plane arising from the two equivalent nitrogen atoms of the chelating tn ligand (N9 and N9(a); Cu2–N9 2.003(6) Å) and two equivalent nitrogen atoms of CN groups (N4 and N4(a); Cu2–N4 2.005(6) Å), and two axial positions filled by two equivalent nitrogen atoms (N5(b) and N5(c); Cu2–N5 2.569(8) Å) of CN groups as shown in Fig. 1(a). In contrast, each chromium cation, although bound to six carbon atoms arising from one terminal and five bridging CN ligands,

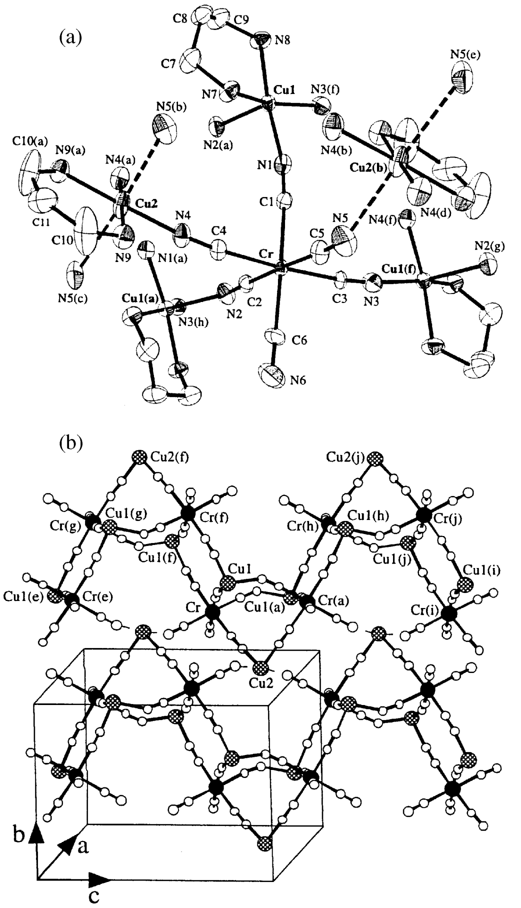

Fig. 1 (a) ORTEP view showing the atomic labelling scheme and the metal ion (Cr, Cu1 and Cu2) environments in **1** (30% probability ellipsoids). Cr–(CN)–Cu distances (Å): Cr···Cu1 5.153(1), Cr···Cu1(a) 5.164(1), Cr···Cu1(f) 5.187(1), Cr···Cu2 5.190(1), Cr···Cu2(b) 5.392(1); (b) Perspective view of the two-dimensional structure of **1** (the tn chelating ligands are omitted for clarity). Codes of equivalent positions: (a) 1 − *x*, *y*, 1/2 − *z*; (b) 1 − *x*, 1 − *y*, −*z*; (c) *x*, 1 − *y*, 1/2 + *z*; (d) *x*, 1 − *y*, −1/2 + *z*; (e) 1 − *x*, *y*, −1/2 − *z*; (f) 1 − *x*, −*y*, −*z*; (g) *x*, −*y*, −1/2 + *z*; (h) *x*, −*y*, 1/2 + *z*; (i) *x*, *y*, 1 + *z*; (j) 1 − *x*, −*y*, 1 − *z*.

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presents an almost regular octahedral coordination geometry (Cr–C bond lengths from 2.042 to 2.071 Å). The extended structure can be more clearly described taking the twelve-membered tetrametallocycle Cr–CN–Cu–NC–Cr–CN–Cu–NC as the elemental unit. The molecular arrangement can be seen as zigzag 'chains' of such 'CrCuCrCu' cycles sharing alternatively one side (Cu1Cr) and one vertex (Cu1); these 'chains' are connected each other through the CN bridges (Cr–C5N5–Cu2) to lead to the neutral two-dimensional structure as clearly shown in Fig. 1(b). Adjacent layers are distant of $a/2$ (11.557(4) Å) and the shortest metal–metal interlayer distance Cu1···Cr is 6.995 Å.

The magnetic susceptibility of **1** follows a Curie–Weiss law above 100 K with a Curie constant C = 4.97(1) emu K mol^{-1} and a Weiss constant θ = 46.0(2) K. The C value is very similar to the expected one (4.875 emu K mol^{-1} for g = 2) for two non-interacting Cr(III) (S = 3/2) and three non interacting Cu(II) (S = 1/2) ions. The positive sign of θ indicates the presence of dominant ferromagnetic interactions between neighbouring Cr(III) and Cu(II) ions. Below 10 K, χ_m sharply increases and tends to saturate at lower temperatures (Fig. 2(a)). This behaviour suggests the onset of a long-range magnetic transition. To confirm this transition and to determine its critical temperature, we have performed ac susceptibility measurements (Fig. 2(b)). These measurements show a peak in the in-phase (χ_m') signal at about 9 K which is frequency independent and an out-of-phase signal (χ_m'') which deviates from zero at T_c = 9.5 K (also frequency independent) and reaches a broad maximum at about 4.5 K. The ordering temperature of 9.5 K is lower than that reported for the only known example of cyano bridged Cu_3Cr_2 ferromagnet: $[Cu(EtOH)_2][Cu(en)]_2[Cr(CN)_6]_2$ (**2**) (where a T_c of 57 K is found).[5] This fact can be related to the lower dimensionality of our compound and/or to the lower Cu–Cr exchange integrals in **1**, as the Cu–CN–Cr angles are different. The nature of the magnetic transition corresponds to a ferromagnetic ordering, as demonstrated by the field dependence of the isothermal magnetisation performed at 2 and 5 K where rapid saturation of the magnetisation is observed to a maximum value of 9.2 μ_B above 1 T (inset in Fig. 2(a)). This latter value is the expected one for a ferromagnetic alignment of the interacting spins in the Cu_3Cr_2 unit (S_{Cu} = 1/2, S_{Cr} = 3/2; S = 9/2 per Cu_3Cr_2 unit) and is very similar to that found in **2** (9.05 μ_B). At 2 and 5 K this ferromagnet exhibits a small magnetic hysteresis with a coercive field of 1.5 mT.

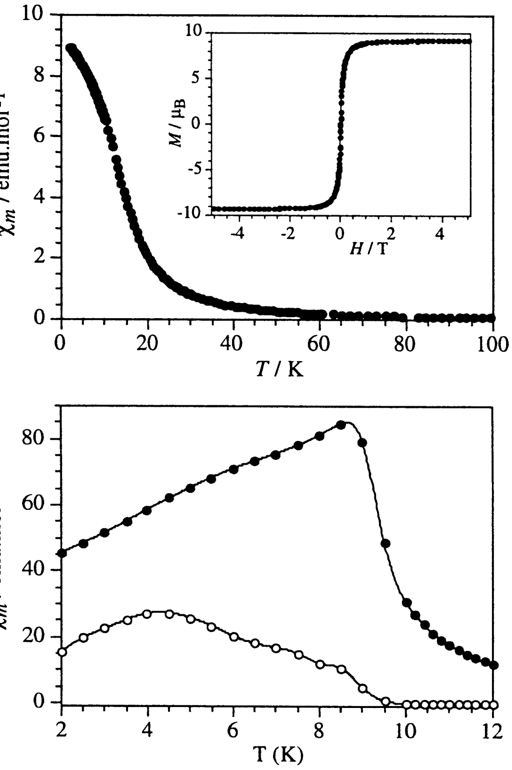

Fig. 2 (a) Thermal variation of the molar susceptibility for **1** showing the abrupt increase around 10 K. Inset: The isothermal magnetisation at 2 K showing the rapid saturation; (b) ac susceptibility for **1** (χ': filled circles, χ'': empty circles) at 110 Hz showing the appearing of a χ'' signal below 9.5 K. The χ'' values have been multiplied by a factor of 5.

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Notes and references

† *Crystal data* for **1**: $C_{21}H_{36}Cr_2Cu_3N_{18}O_3$, M = 883.30, orthorhombic, space group *Pbcn* (no. 60), a = 23.1148(4), b = 11.1692(6), c = 14.650(1) Å, V = 3782 Å^3, Z = 4, D_c = 1.55 g cm^{-3}, μ(Mo-Kα) = 2.26 mm^{-1}, F(000) = 1788, T = 288 K, final $R(F)$ = 0.066, $R_w(F^2)$ = 0.160, $\Delta\rho_{max}$ = 0.699 e Å^{-3}, and GOF = 1.053, for 2337 observed reflections [$I > 2\sigma(I)$] and 218 variables. CCDC reference number 175842. See http://www.rsc.org/suppdata/cc/b2/b201312f/ for crystallographic data in CIF or other electronic format.

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