# $\{[Cu^{II}(tn)]_2[Fe^{II}(CN)_6]\} \cdot KCl \cdot 5H_2O$ (tn=1,3-diaminopropane): a two-dimensional bimetallic layered material with "$Cu_4Fe_3$" defective cubane units

Letter

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**The new two-dimensional coordination compound $\{[Cu^{II}(tn)]_2[Fe^{II}(CN)_6]\} \cdot KCl \cdot 5H_2O$ (1) (tn = 1,3-diaminopropane), generated by six –Fe–CN–Cu– bridges, shows weak ferromagnetic interactions between the nearest Cu(II) ions through the diamagnetic $[Fe(CN)_6]^{4-}$ anion.**

Cyano-bridged bimetallic extended structures have attracted much attention because of their interesting magnetic, magneto-optical and optoelectronic properties.[1] Syntheses of such molecular solids can be seen as self-assembly processes between the hexacyanometallate building block anion $[M(CN)_6]^{n-}$ ($M = V^{II}$, $Cr^{III}$, $Mn^{III}$, $Fe^{II}$, $Fe^{III}$) and transition metal aqua complexes affording a new family of three-dimensional cyano-bridged bimetallic assemblies with Prussian blue-like structures, exhibiting spontaneous magnetisation at $T_c$ as high as 376 K.[1] In addition to these three-dimensional high-symmetry systems, a second family of low-symmetry cyano-bridged co-ordination polymers was obtained when cationic assembler units of $[M'L_x]^{n+}$ type ($M' = Mn^{II}$, $Mn^{III}$, $Ni^{II}$, $Cu^{II}$; L = diamine, triamine, tetraamine macrocyclic ligand, Schiff base, *etc.*), having selected free coordination sites, were used instead of simple aqua complexes.[2–5] These systems display rich structural architectures ranging from discrete polynuclear complexes to fascinating three-dimensional networks;[2–7] some of them exhibit ferro- or ferrimagnetic ordering.[2a–c,2f] Restricting our attention to the extended systems containing $[Cu^{II}L_x]^{2+}$ assembler units, only a few examples have been studied.[3] Most of them concern bimetallic compounds, containing $Fe^{II}$–$Cu^{II}$, $Fe^{III}$–$Cu^{II}$ and $Cr^{III}$–$Cu^{II}$ cyanide bridges, with a four-coordinate copper complex as an assembler unit ($[Cu^{II}L_2]^{2+}$; L = diamine ligand) acting as a $\mu_2$-bridging "complex ligand". Herein, we report the synthesis, structural characterisation and magnetic properties of the new bimetallic layered material $\{[Cu^{II}(tn)]_2[Fe^{II}(CN)_6]\} \cdot KCl \cdot 5H_2O$ (1) (tn = 1,3-diaminopropane) as the first "CuFe" cyanide bridged compound in which the two-coordinate $[Cu^{II}(tn)]^{2+}$ unit acts as a $\mu_3$-bridging "assembler complex-ligand".

Compound **1** was obtained as brown plate-like crystals by reaction of $K_3[Fe(CN)_6]$ (4 mmol) with a large excess of $CuCl_2$ dihydrate (24 mmol) and tn (24 mmol) in concentrated NaOH aqueous solution. Elemental analysis (see Experimental) shows that the iron(III) was reduced to iron(II) during the synthesis as observed in previously reported parent complexes.[7] The reason for this reduction is not clear for the moment, even if basic aqueous solutions of $[Fe(CN)_6]^{3-}$ are known for their oxidising character. However, magnetic measurements and the crystal structure (see below) support also the presence of iron(II) in **1**.

The infrared spectrum of **1** shows two strong absorption bands at 2091 and 2079 $cm^{-1}$; this is consistent with the cyanide bridges revealed by the X-ray structure since formation of such bridges increases the CN stretching wavenumber in comparison with that observed for terminal CN ligands in $K_4[Fe(CN)_6]$ (2040 $cm^{-1}$).[8]

Fig. 1 shows an ORTEP[9] drawing of the asymmetric unit with the atomic numbering scheme and the coordination polyhedrons of the metal ions (Fe, Cu1 and Cu2) in **1**. The extended molecular arrangement is shown in Fig. 2. The pertinent bond distances and bond angles of **1** are listed in Table 1. The asymmetric unit contains one $[Fe(CN)_6]^{4-}$ anion and two $[Cu(tn)]^{2+}$ (Cu1 and Cu2) cations, located on general positions. The two non-equivalent copper(II) cations (Cu1 and Cu2) exhibit a square pyramidal $CuN_5$ geometry (Fig. 1), arising in both cases from two nitrogen atoms of the chelating tn ligand (N7, N8 for Cu1 and N9, N10 for Cu2) and from three nitrogen atoms from the cyano groups [N3, N4(f) and N5(d) for Cu1; N1(a), N2 and N6(c) for Cu2; Fig. 1]. In both cases, the Cu–N apical bond length (Cu1–N5 and Cu2–N1) are significantly longer (2.122 and 2.230 Å, respectively) than the equatorial ones (average 2.01 Å; see Table 1 and Fig. 1). Each iron cation, which has an almost regular octahedral geometry, is linked to six copper(II) cations *via* six cyanide bridges, while each copper cation is linked to three equivalent iron(II) cations.

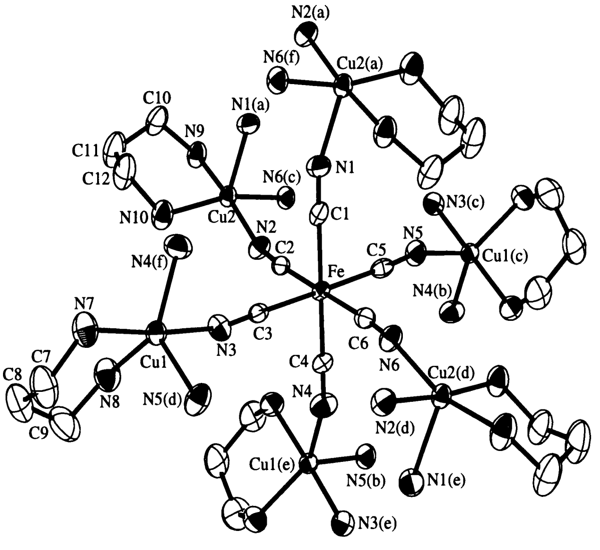

**Fig. 1** ORTEP view showing the atomic labeling scheme and the metal cation (M = Fe, Cu1 and Cu2) environments in **1** (40% probability ellipsoids). Codes of equivalent positions: (a) $-x, -y, 1-z$; (b) $-x, -y, 2-z$; (c) $-x, -1/2+y, 3/2-z$; (d) $-x, 1/2+y, 3/2-z$; (e) $x, 1/2-y, 1/2+z$; (f) $x, 1/2-y, -1/2+z$.

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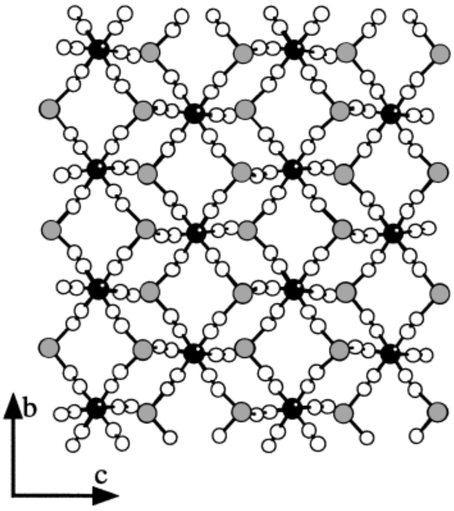

**Fig. 2** Projection in the *bc* plane showing the two-dimensional structure in **1**. The tn chelating ligands are omitted for clarity.

The Fe–C–N units are essentially linear while the Cu–N–C angles deviate significantly from linearity (see Table 1), as observed in the related cyano-bridged compound [{Cu(ept)}$_3$Fe$^{II}$(CN)$_6$](ClO$_4$)$_2$·5H$_2$O≡[ept = *N*-(2-aminoethyl)-1,3-diaminopropane].[4] This leads to an infinite [Cu(tn)]$_2$-[Fe(CN)$_6$] lamellar structure, which can be also described as a two-dimensional layered structure generated by the defective cubane units "Cu$_4$Fe$_3$" as shown in Fig. 2. These neutral parallel sheets are separated by the *a* parameter [15.1478(3) Å] and they are eclipsed with each other to give infinite tetragonal tunnels containing the chloride anions, the potassium cations and the water molecules.

The magnetic susceptibility measurements were performed at 0.1 T in the temperature range 2–300 K with an MPMS-XL-5 SQUID magnetometer from Quantum Design. The molar susceptibility was corrected for the sample holder and diamagnetic contributions of all atoms (Pascal tables). The magnetic properties of **1** are displayed in Fig. 3 as the thermal dependence of the $\chi_m T$ product, where $\chi_m$ is the magnetic susceptibility per mole of **1**, that is per Cu$^{II}_2$Fe$^{II}$ group. The room temperature $\chi_m T$ value of 0.85 emu K mol$^{-1}$ is in good agreement with the expected value for two isolated Cu(II) ions with local spin of 1/2. Upon cooling down, the $\chi_m T$ product remains constant down to approximately 20 K, then it increases and exhibits a value of 1.12 emu K mol$^{-1}$ at $T = 2$ K. These observations suggest weak ferromagnetic interactions between the nearest Cu(II) ions through the diamagnetic [Fe(CN)$_6$]$^{4-}$ anions. The magnetic susceptibility above 20 K obeys the Curie–Weiss law with $C = 0.85$ emu K mol$^{-1}$ ($g = 2.12$) and a positive Weiss constant ($\theta$) of +0.44 K, which also proves the ferromagnetic coupling in compound **1**. From these observations, it appears that the diamagnetic anion [Fe(CN)$_6$]$^{4-}$ propagates the weak ferromagnetic coupling between the Cu(II) centres.

In summary, we have described here the first "CuFe" cyano-bridged compound in which the two-coordinate [Cu$^{II}$(tn)]$^{2+}$ assembler unit acts as a $\mu_3$-bridging "complex-ligand" to lead to a new two-dimensional bimetallic material with "Cu$_4$Fe$_3$" defective cubane units. Extended "Fe(II)–Cu(II)" cyano-bridged compounds are scarcely reported and as far as we are aware, only two examples have been stucturally characterised: [{Cu(ept)}$_3$Fe(CN)$_6$](ClO$_4$)$_2$·5H$_2$O[4] has been reported as a paramagnetic compound while [Cu(dmen)]$_2$[Fe(CN)$_6$] (dmen = 2-dimethylaminoethylamine)[5] shows ferromagnetic behaviour, similar to that observed for **1**, but whose origin was not clearly elucidated since this Fe(II)–Cu(II) cyano-bridged compound also contains Cu$_2$ dinuclear units. Therefore, compound **1** is the first example in which the ferromagnetic coupling clearly results from the interaction between the Cu(II) ions through the diamagnetic [Fe(CN)$_6$]$^{4-}$ anions.

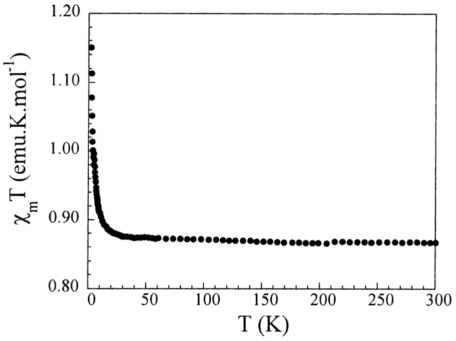

**Fig. 3** Thermal variation of the magnetic susceptibility in the form $\chi_m T$ *vs.* *T* for **1**.

## Experimental

### Synthesis

Under aerobic conditions, 1,3-diaminopropane (2.0 mL, 24.0 mmol) was slowly added with stirring to a concentrated aqueous solution of copper(II) chloride dihydrate (4.09 g, 24.0 mmol). A concentrated aqueous solution of NaOH (24.0 mmol) was then added, leading to a clear solution that was boiled for 10 min and then filtered. When an aqueous solution of K$_3$[Fe(CN)$_6$] (1.31 g, 4.0 mmol) was added to the resulting hot filtrate, brown crystals of {[Cu$^{II}$(tn)]$_2$[Fe$^{II}$(CN)$_6$]}·KCl·5H$_2$O (**1**) formed immediately. Anal. calcd. for C$_{12}$H$_{30}$ClCu$_2$-FeKN$_{10}$O$_5$: C, 22.1; H, 4.6; Cl, 5.4; Cu, 19.5; Fe, 8.6; K, 6.0; N, 21.5; found: C, 22.5; H, 4.8; Cl, 5.4; Cu, 19.5; Fe, 8.4; K, 5.6; N, 21.2. IR $\nu$/cm$^{-1}$: 3441br, 3301s, 3223s, 3145s, 2883w, 2091s, 2079s, 1604m, 1178m, 1106w, 1072w, 1027m, 929m, 591m, 489w.

### X-Ray crystallography

**Crystal data for 1.** C$_{12}$H$_{30}$ClCu$_2$FeKN$_{10}$O$_5$, $M = 651.92$, monoclinic, space group $P2_1/c$ (no. 14), $a = 15.1478(3)$, $b = 14.6941(4)$, $c = 12.6533(4)$ Å, $\beta = 109.95(9)°$, $u = 2647$ Å$^3$, $Z = 4$, $D_c = 1.64$ g cm$^{-3}$, $\mu = 24.37$ cm$^{-1}$, $F(000) = 1328$, $T = 288$ K, Nonius Kappa CCD, Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å),

**Table 1** Selected bond distances (Å) and bond angles (°) in **1**

| Fe–C–N–Cu | Fe–C | C–N | N–Cu | Fe–C–N | C–N–Cu | Fe···Cu |
|---|---|---|---|---|---|---|
| Fe–C1–N1–Cu2(a) | 1.929(6) | 1.138(8) | 2.230(5) | 175.4(4) | 156.0(4) | 5.194(1) |
| Fe–C2–N2–Cu2 | 1.918(5) | 1.145(6) | 2.005(4) | 175.3(5) | 161.2(5) | 4.980(1) |
| Fe–C3–N3–Cu1 | 1.899(4) | 1.159(6) | 2.002(4) | 178.3(4) | 162.0(5) | 4.997(1) |
| Fe–C4–N4–Cu1(e) | 1.895(6) | 1.147(8) | 2.027(6) | 178.5(4) | 160.1(4) | 4.991(1) |
| Fe–C5–N5–Cu1(c) | 1.931(4) | 1.137(6) | 2.122(4) | 176.7(5) | 159.0(5) | 5.114(1) |
| Fe–C6–N6–Cu2(d) | 1.919(5) | 1.138(6) | 2.008(4) | 175.8(5) | 163.0(5) | 4.998(1) |

$2\theta_{\max} = 60°$, final $R = 0.044$, $wR = 0.064$ for 3177 observed reflections $[I > 3.0\sigma(I)]$ and 263 variables. The structure was solved by direct methods and refined by full-matrix least-squares on $F$.[10]

CCDC reference number 175834. See http://www.rsc.org/suppdata/nj/b1/b108521m/ for crystallographic data in CIF or other electronic format.

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