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Structure and magnetic properties of two cyanide-bridged one-dimensional M–Cu^{II} (M = Fe^{III} or Fe^{II}) bimetallic assemblies from ferricyanide and CuN_4^{2+} (N_4 = 1,4,8,11-tetraazacyclotetradecane and *N*,*N′*-bis(2-pyridylmethylene)-1,3-propanediamine) building blocks

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Two bimetallic assemblies K[Cu(cyclam)][$Fe(CN)_6$]·$4H_2O$ **1** and [Cu(L)][Cu(L^1)][$Fe(CN)_6$]·$6.5H_2O$ **2** (cyclam = 1,4,8,11-tetraazacyclotetradecane; L = *N*,*N′*-bis(2-pyridylmethylene)-1,3-propanediamine and L^1 = *N*-2-pyridylmethylene-1,3-propanediamine) have been prepared from the reaction of $[Fe(CN)_6]^{3-}$ and the precursors $[Cu(cyclam)]^{2+}$ and $[Cu(L)]^{2+}$, respectively, and their structure and magnetic properties studied. The structure of **1** consists of polymeric zigzag chains of alternating $[Fe(CN)_6]^{3-}$ and $[Cu(cyclam)]^{2+}$ units, K^+ cations and crystal water molecules. In the crystals the chains are linked by CN–K–NC interactions, to form a two-dimensional layer structure. Magnetic measurements show a weak ferromagnetic intrachain interaction based on the strict orthogonality of the magnetic orbitals of the Fe^{III} and Cu^{II}. In the structure of **2** each $[Cu(L^1)]^{2+}$ unit is bonded to centrosymmetric $[Fe(CN)_6]^{4-}$ and [Cu(L)$Fe(CN)_6$Cu(L)] units through two *cis* bridging cyanide ligands. Owing to the symmetry, a unique one-dimensional zigzag chain structure is formed through *trans* bridging cyanide ligands of the two crystallographically non-equivalent $[Fe(CN)_6]^{4-}$ groups. In the course of the reaction the $[Fe(CN)_6]^{3-}$ ion undergoes a reduction to $[Fe(CN)_6]^{4-}$ whereas the $[Cu(L)]^{2+}$ ion partly hydrolyses to $[Cu(L^1)]^{2+}$. Compound **2** is essentially paramagnetic within the chain.

In the last few years there has been a considerable interest in the design and elaboration of polymetallic molecular systems with extended structures and predictable catalytic and electronic properties, mainly molecular-based magnets and inorganic materials with inner cavities or channel mimicking zeolites.[1,2] The most successful and often the sole strategy for preparing these materials consists in assembling two building blocks that usually are transition metal complexes, one with terminal ligands that are able to act as bridging ligands and another with empty or available co-ordination sites. A typical example of paramagnetic ligands that can be used to this end is the family of the cyanometalate complexes,[3,4] which react with transition metal aqua complexes to afford three-dimensional cyanide-bridged bimetallic assemblies with Prussian-like structure. These materials exhibit spontaneous magnetisation at T_c as high as 315 K[4] and interesting electrochemical, optoelectronic and magneto-optical properties.[3,5] When metal complexes containing polydentate ligands, that block selected co-ordination sites, are used instead of simple aqua complexes a great variety of cyanide-bridged bimetallic systems can be obtained. These systems exhibit fascinating structures, that range from discrete entities to 3-D extended networks, and interesting magnetic properties.[6–29] The structure, dimensionality and properties of the assembled compound depend directly on the nature of the building blocks. The major part of these systems has been constructed from transition metal complexes with two-available co-ordination sites of the type NiN_4^{2+} (N_4 = bis(diamine) or tetraamine macrocyclic ligand) or $MnN_2O_2^+$ (N_2O_2 = Schiff base ligand) and $[M(CN)_6]^{3-}$ (M = Cr^{III} or Fe^{III}). Since copper(II) complexes exhibit a great stereochemical plasticity, they are expected to give rise to a large variety of assembled compounds with hexacyanometalates. Nevertheless, only a few fully structurally characterised cyanide-bridged bimetallic complexes constructed from copper(II) complexes and hexacyanometalates have been reported so far. They are limited to one trinuclear, [$Fe^{II}(CN)_6$][Cu(tren)$]_2$·$12H_2O$[27] (tren = tris(2-aminoethyl)amine), one heptanuclear, [$Fe^{II}(CN)_6$][Cu(tpa)$]_6$-[$ClO_4]_8$·$3H_2O$[26] (tpa = tris(2-pyridylmethyl)amine), and two isostructural 1-D systems [Cu(dien)$]_3$[M(CN)$_6]_2$·$6H_2O$[20,21] (dien = diethylenetriamine and M = Cr^{III} or Fe^{III}). We report here, as a part of our work on magnetic extended materials based on cyanometalates, the synthesis, structure and magnetic properties of two 1-D chain assemblies, K[Cu(cyclam)]-[$Fe(CN)_6$]·$4H_2O$ **1** and [Cu(L)][Cu(L^1)][$Fe(CN)_6$]·$6.5H_2O$ **2** [L = *N*,*N′*-bis(2-pyridylmethylene)-1,3-propanediamine, L^1 = *N*-2-pyridylmethylene-1,3-propanediamine], the latter exhibiting a unique structure.

Experimental

Physical measurements

Elemental analyses were carried out at the Technical Services of the University of Granada on a Fisons-Carlo Erba analyser model EA 1108. The IR spectra were recorded on a Perkin-Elmer 983 G spectrometer using KBr pellets. Variable-temperature magnetic susceptibility data were collected on powdered samples of the compounds with use of a SQUID-based sample magnetometer on a Quantum Design Model MPMS instrument. Data were corrected for the diamagnetism

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of the ligands using Pascal's constants. Variable-temperature EPR spectra were measured with a Bruker ESP 300E spectrometer.

Preparations

K[Cu(cyclam)][Fe(CN)$_6$]·4H$_2$O 1. To an aqueous solution of [Cu(cyclam)][ClO$_4$]$_2$[30] (0.21 mmol, 0.1 g) in 30 cm^3 of water was added K$_3$[Fe(CN)$_6$] (0.21 mmol, 0.071 g) in 15 cm^3 of water with stirring at room temperature. Brown microcrystals precipitated, which were filtered off, washed with water and air dried. Yield: 70%. Calc. for $C_{16}H_{32}CuFeKN_{10}O_4$: C, 32.74; H, 5.45; N, 23.87. Found: C, 32.61; H, 5.50; N, 24.21%. Suitable crystals for X-ray analysis were obtained by slow evaporation of the filtrate.

[Cu(L)][Cu(L^1)][Fe(CN)$_6$]·6.5H$_2$O 2. To an aqueous solution of [Cu(L)][ClO$_4$]$_2$[31] (0.2 mmol, 0.1 g) in 20 cm^3 of water was added K$_3$[Fe(CN)$_6$] (0.2 mmol, 0.67 g) in 15 cm^3 of water with continuous stirring at room temperature. The green precipitate thus produced was filtered off and from the filtrate, by slow evaporation at room temperature, black crystals suitable for X-ray analysis were obtained, which were filtered off and dried in air. Yield: 20%. Calc. for $C_{30}H_{42}Cu_2FeN_{13}O_{6.5}$: C, 41.33; H, 4.80; N, 20.80. Found: C, 41.22; H, 4.30; N, 20.50%. This compound can also be prepared from the reaction of K$_3$[Fe(CN)$_6$] and a 1 : 1 mixture of [Cu(L^1)]$^{2+}$ and [Cu(L)]$^{2+}$ in aqueous solution.

Crystallography

K[Cu(cyclam)][Fe(CN)$_6$]·4H$_2$O 1. *Crystal data.* $C_{16}H_{32}CuFeKN_{10}O_4$, $M = 587.01$, monoclinic, space group $C2/m$, $a = 14.405(3)$, $b = 12.284(3)$, $c = 9.836(2)$ Å, $\beta = 131.59(3)°$, $U = 1301.7(5)$ Å^{-3}, $T = 293(2)$ K, $Z = 2$, μ(Mo-Kα) = 1575 mm^{-1}, $F(000) = 608$, 1156 unique reflections collected ($2.65 < \theta < 25°$), $R1$ ($I > 2\sigma(I)$) = 0.0819 ($wR2 = 0.2355$) for 91 parameters.

The unit cell parameters were determined and the data collected on a Siemens STADI4 diffractometer at 20 °C. The data were corrected for Lorentz-polarisation effects and for absorption (empirical ψ scan). The structure was solved by direct methods using the SHELXS 86 program[32] and refined (full-matrix least squares on F^2) by using the program SHELX 97.[33] All non-hydrogen atoms were refined anisotropically but hydrogen atoms, except those belonging to the crystal water molecule, were included in calculated positions and treated as riding atoms using the SHELX 97 default parameters. The position of the potassium ion is partially occupied, and refinement of the site occupation parameter for K$^+$ gave 0.572(12), but the parameter was fixed at 0.5 in the final refinement.

[Cu(L)][Cu(L^1)][Fe(CN)$_6$]·6.5H$_2$O 2. *Crystal data.* $C_{30}H_{42}Cu_2FeN_{13}O_{6.5}$, $M = 871.70$, triclinic, space group $P\bar{1}$, $a = 11.592(6)$, $b = 12.226(6)$, $c = 14.737(5)$ Å, $\alpha = 102.78(4)$, $\beta = 101.86(4)$, $\gamma = 109.95(5)°$, $U = 1822.4(14)$ Å^3, $T = 193(2)$ K, $Z = 2$, μ(Mo-Kα) = 1612 mm^{-1}, $F(000) = 898$, 5412 unique reflections collected ($2.56 < \theta < 25°$), $R1$ ($I > 2\sigma(I)$) = 0.0671 ($wR2 = 0.1296$) for 476 parameters.

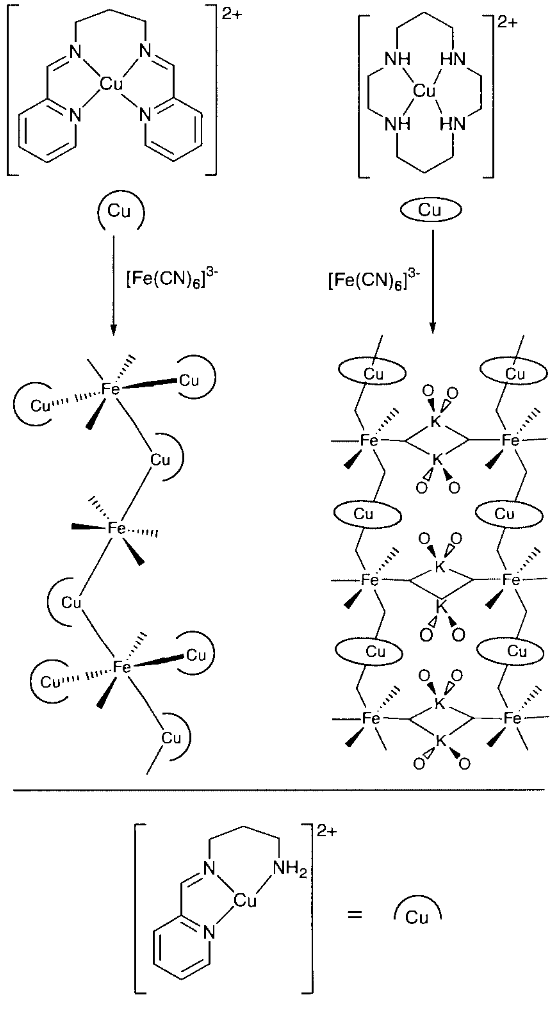
The unit cell parameters were determined and the data collected on a Rigaku AFC7S diffractometer at −80 °C. The data were corrected for Lorentz-polarisation effects and an empirical correction for absorption was carried out using the TEXSAN program.[34] The structure was solved and refined as above. Hydrogen atoms of the water molecules were not determined. The crystal water molecules O5, O6 and O7 are disordered, each occupying two positions.

CCDC reference number 186/1786.

See http://www.rsc.org/suppdata/dt/a9/a908485a/for crystallographic files in .cif format.

Results and discussion

The complexes [Cu(cyclam)][ClO$_4$]$_2$ and [Cu(L)][ClO$_4$]$_2$ react with K$_3$[Fe(CN)$_6$] in aqueous solution to yield the 1-D cyanide-bridged complexes K[Cu(cyclam)][Fe(CN)$_6$]·4H$_2$O **1** and [Cu(L)][Cu(L^1)][Fe(CN)$_6$]·6.5H$_2$O **2**, respectively (see Scheme 1). The IR spectra exhibit two sharp bands at 2119 and 2105 cm^{-1} for **1** and 2116 and 2077 cm^{-1} for **2**, which are assignable to CN stretching vibrations of bridging and terminal cyanide groups, respectively. The low frequency value for the terminal cyanide groups in **2** is consistent with ferrocyanide rather than ferricyanide (2042 cm^{-1} for K$_4$[Fe(CN)$_6$] and 2119 cm^{-1} for K$_3$[Fe(CN)$_6$]). The presence of the ligands is confirmed by bands due to NH stretching vibrations of cyclam at 3370 and 3244 cm^{-1} for **1** and by bands due to skeletal vibrations of the pyridine ring at 1603, 1481 and 1448 cm^{-1} and by the band due to the C(H)=N stretching vibration at 1648 cm^{-1} for **2**. Noteworthy, in **2** the original bicondensed tetradentate ligand L and the monocondensed tridentate ligand L^1 coexist, thus indicating that L undergoes a partial hydrolysis during the reaction. As expected, **2** can also be prepared from the reaction of K$_3$[Fe(CN)$_6$] and a 1 : 1 mixture of [Cu(L^1)]$^{2+}$ and [Cu(L)]$^{2+}$ in aqueous solution. Moreover, the analytical, spectroscopic and magnetic data (see below) for **2** clearly support the reduction of [Fe(CN)$_6$]$^{3-}$ to [Fe(CN)$_6$]$^{4-}$. The mechanism for this reduction process remains unclear at this moment. Nevertheless, it should be pointed out that an analogous and unclear reduction process has been shown to occur in the formation of other cyanide-bridged Cu^{II}–Fe^{II} systems from K$_3$[Fe(CN)$_6$] and copper(II) complexes.[26] The Mössbauer spectrum of **1** at 293 K shows a doublet with isomer shift (δ) and quadrupole splitting (ΔE_Q) of



Scheme 1

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Cu–N(4)	2.012(6)	Cu–N(1)	2.492(9)
Fe–C(1)	1.952(9)	Fe–C(2)	1.933(8)
Fe–C(3)	1.933(8)	K–O	2.782(9)
K–N(2)	2.829(12)	K–N(2)^{i}	2.909(12)
N(4)^{ii}–Cu–N(4)^{iii}	180.0	N(4)^{ii}–Cu–N(4)^{iv}	86.2(4)
N(4)^{iii}–Cu–N(4)^{iv}	93.8(4)	N(4)^{ii}–Cu–N(4)	93.8(4)
N(4)^{iii}–Cu–N(4)	86.2(4)	N(4)^{iv}–Cu–N(4)	180.0
N(4)^{ii}–Cu–N(1)	88.6(2)	N(4)^{iii}–Cu–N(1)	91.4(2)
N(4)^{iv}–Cu–N(1)	91.4(2)	N(4)–Cu–N(1)	88.6(2)
N(4)^{ii}–Cu–N(1)^{iv}	91.4(2)	N(4)^{iii}–Cu–N(1)^{iv}	88.6(2)
N(4)^{iv}–Cu–N(1)^{iv}	88.6(2)	N(4)–Cu–N(1)^{iv}	91.4(2)
N(1)–Cu–N(1)^{iv}	180.0	C(2)–Fe–C(2)^{v}	180.0
C(2)–Fe–C(3)^{v}	90.0	C(2)^{v}–Fe–C(3)^{v}	90.0
C(2)–Fe–C(3)	90.0	C(2)^{v}–Fe–C(3)	90.0
C(3)^{v}–Fe–C(3)	180.0	C(2)–Fe–C(1)^{v}	90.5(4)
C(2)^{v}–Fe–C(1)^{v}	89.5(4)	C(3)^{v}–Fe–C(1)^{v}	90.0
C(3)–Fe–C(1)^{v}	90.0	C(2)–Fe–C(1)	89.5(4)
C(2)^{v}–Fe–C(1)	90.5(4)	C(3)^{v}–Fe–C(1)	90.0
C(3)–Fe–C(1)	90.0	C(1)^{v}–Fe–C(1)	180.0

Symmetry relations: i $-x + 1, -y + 1, -z + 1$; ii $x, -y + 1, z$; iii $-x, y, -z + 1$; iv $-x, -y + 1, -z + 1$; v $-x + 1, -y + 1, -z + 2$.

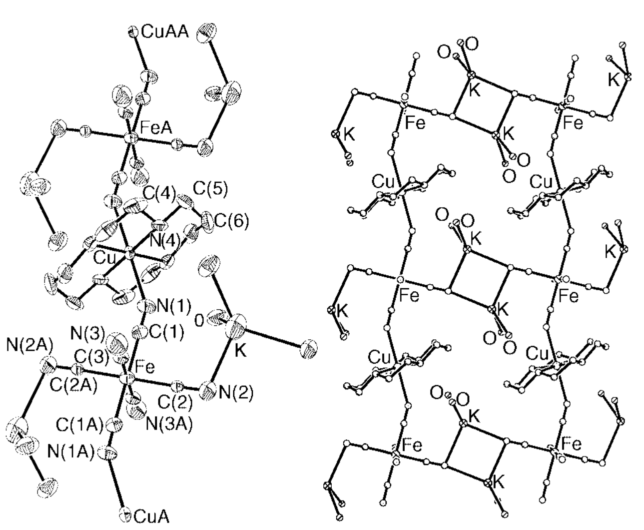


Fig. 1 Perspective views of a chain and a layer of chains for complex **1**. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

Fe(1)–C(1)	1.892(8)	Fe(1)–C(2)	1.925(8)
Fe(1)–C(3)	1.925(9)	Fe(2)–C(4)	1.904(8)
Fe(2)–C(5)	1.893(7)	Fe(2)–C(6)	1.913(8)
Cu(1)–N(4)	1.975(7)	Cu(1)–N(9)	2.007(7)
Cu(1)–N(7)	2.011(7)	Cu(1)–N(8)	2.041(6)
Cu(1)–N(1)	2.162(6)	Cu(2)–N(12)	1.981(6)
Cu(2)–N(11)	2.015(6)	Cu(2)–N(10)	2.021(6)
Cu(2)–N(13)	2.110(6)	Cu(2)–N(5)	2.127(6)
C(1)^{vi}–Fe(1)–C(1)	180.0	C(1)^{vi}–Fe(1)–C(2)	89.1(3)
C(1)–Fe(1)–C(2)	90.9(3)	C(1)^{vi}–Fe(1)–C(2)^{vi}	90.9(3)
C(1)–Fe(1)–C(2)^{vi}	89.1(3)	C(2)–Fe(1)–C(2)^{vi}	180.000(2)
C(1)^{vi}–Fe(1)–C(3)	91.5(3)	C(1)–Fe(1)–C(3)	88.5(3)
C(2)–Fe(1)–C(3)	89.3(3)	C(2)^{vi}–Fe(1)–C(3)	90.7(3)
C(1)^{vi}–Fe(1)–C(3)^{vi}	88.5(3)	C(1)–Fe(1)–C(3)^{vi}	91.5(3)
C(2)–Fe(1)–C(3)^{vi}	90.7(3)	C(2)^{vi}–Fe(1)–C(3)^{vi}	89.3(3)
C(3)–Fe(1)–C(3)^{vi}	180.0	C(5)–Fe(2)–C(5)^{vii}	180.0
C(5)–Fe(2)–C(4)	90.4(3)	C(5)^{vii}–Fe(2)–C(4)	89.6(3)
C(5)–Fe(2)–C(4)^{vii}	89.6(3)	C(5)^{vii}–Fe(2)–C(4)^{vii}	90.4(3)
C(4)–Fe(2)–C(4)^{vii}	180.0	C(5)–Fe(2)–C(6)^{vii}	88.6(3)
C(5)^{vii}–Fe(2)–C(6)^{vii}	91.4(3)	C(4)–Fe(2)–C(6)^{vii}	90.6(3)
C(4)^{vii}–Fe(2)–C(6)^{vii}	89.4(3)	C(5)–Fe(2)–C(6)	91.4(3)
C(5)^{vii}–Fe(2)–C(6)	88.6(3)	C(4)–Fe(2)–C(6)	89.4(3)
C(4)^{vii}–Fe(2)–C(6)	90.6(3)	C(6)^{vii}–Fe(2)–C(6)	180.0
N(4)–Cu(1)–N(9)	90.6(3)	N(4)–Cu(1)–N(7)	92.9(3)
N(9)–Cu(1)–N(7)	173.9(3)	N(4)–Cu(1)–N(8)	151.8(3)
N(9)–Cu(1)–N(8)	94.1(3)	N(7)–Cu(1)–N(8)	80.5(3)
N(4)–Cu(1)–N(1)	109.8(2)	N(9)–Cu(1)–N(1)	92.3(3)
N(7)–Cu(1)–N(1)	91.2(3)	N(8)–Cu(1)–N(1)	97.8(3)
N(12)–Cu(2)–N(11)	92.0(2)	N(12)–Cu(2)–N(10)	167.3(2)
N(11)–Cu(2)–N(10)	80.8(2)	N(12)–Cu(2)–N(13)	81.1(2)
N(11)–Cu(2)–N(13)	156.3(2)	N(10)–Cu(2)–N(13)	101.3(2)
N(12)–Cu(2)–N(5)	93.8(2)	N(11)–Cu(2)–N(5)	108.6(2)
N(10)–Cu(2)–N(5)	98.4(2)	N(13)–Cu(2)–N(5)	94.6(2)

Symmetry relations: vi $-x + 1, -y, -z + 1$; vii $-x, -y, -z$.

-0.244 and 0.630 mm s^{-1}, respectively. The value for the latter is consistent with the asymmetric d-electron distribution for an octahedral low spin Fe^{III} with a $t_{2g}{}^5$ configuration. The δ and ΔE_Q parameters are very similar to those observed for the low spin complex Na$_3$[Fe(CN)$_6$] and other cyanide-bridged complexes containing [Fe(CN)$_6$]$^{3-}$ units.[35] The Mössbauer spectrum of **2** at 293 K exhibits a narrow single line with $\delta = -0.1$ mm s^{-1}, which is consistent with an octahedral low spin iron(II) ion ($t_{2g}{}^6$) and a symmetrical field around the iron, leading to zero quadrupole splitting. Similar δ and ΔE_Q have been reported for K$_4$[Fe(CN)$_6$] and other complexes with [Fe(CN)$_6$]$^{4-}$ bridging groups.[26,35]

Crystal structures

The structure of complex **1** consists of polymeric chains of alternating [Fe(CN)$_6$]$^{3-}$ and [Cu(cyclam)]$^{2+}$ units, disordered K$^+$ cations and crystal water molecules. A perspective view of the chain with the atom labelling scheme is given in Fig. 1 whereas selected bond lengths and angles are in Table 1. In the chain two CN$^-$ groups of each [Fe(CN)$_6$]$^{3-}$ unit bridge two copper(II) atoms with a Fe$^{III}\cdots$Cu^{II} distance of 5.389(3) Å. Both copper and iron atoms are located on symmetry elements 2/*m*. The Fe–C(1)–N(1) and Cu–N(1)–C(1) bond angles for the bridging cyanide groups of 178.8(11) and 151.4(9)°, respectively, indicate that the chain adopts a zigzag disposition. The Fe–C–N angles for the terminal cyanide groups in [Fe(CN)$_6$]$^{3-}$ are 177.8(7) and 180°. The iron centre in the [Fe(CN)$_6$]$^{3-}$ unit adopts a minimally distorted octahedral environment, all the *cis* C–Fe–C angles being exactly 90 or 90° within experimental errors and the *trans* C–Fe–C angles are 180°. The Fe–C bond distances for the terminal cyanide groups are 1.895(10) and 1.933(8) Å whereas those for the bridging cyanide groups are 1.952(9) Å. Owing to Jahn–Teller effects, the copper(II) centre assumes an axially distorted octahedral CuN$_6$ chromophore. The two axial positions are occupied by the nitrogen atoms of the cyanide bridging groups with Cu–N distances of 2.492(9) Å and the equatorial positions by the N$_4$ set of donor atoms from the cyclam ligand with Cu–N distances of 2.012(6) Å. The *cis* N–Cu–N bond angles deviate somewhat from 90° whereas the *trans* N–Cu–N angles are 180°. In the crystal chains are linked by K–N interactions involving the terminal CN(2) groups to form a two-dimensional layer structure with distances of 2.829(12) and 2.909(12) Å (Fig. 1). In addition, K$^+$ are involved in K–O interactions with water molecules with a distance of 2.782(9) Å. These distances agree quite well with those observed for other K–N and K–O interactions.[9,36] Finally, the CN(3) terminal cyanide group and the water molecules are involved in hydrogen bond interactions with donor–acceptor distances N$\cdots$O and O$\cdots$O of 2.753(8) and 2.810(14) Å, respectively.

In the structure of complex **2** each [Cu(L^1)]$^{2+}$ unit is bonded to centrosymmetric [Fe(CN)$_6$]$^{4-}$ and [Cu(L)Fe(CN)$_6$Cu(L)] units through two *cis* bridging cyanide ligands. Owing to the symmetry, a unique one-dimensional zigzag chain structure is formed through *trans* bridging cyanide ligands of the two crystallographically non-equivalent [Fe(CN)$_6$]$^{4-}$ groups. A perspective view of the chain together with the atom labelling scheme is given in Fig. 2. Selected bond lengths and angles are listed in Table 2.

Within the [Cu(L)Fe(CN)$_6$Cu(L)] fragment two *trans* cyanide groups of the [Fe(CN)$_6$]$^{4-}$ unit bridge the Fe^{II} and Cu^{II} of the

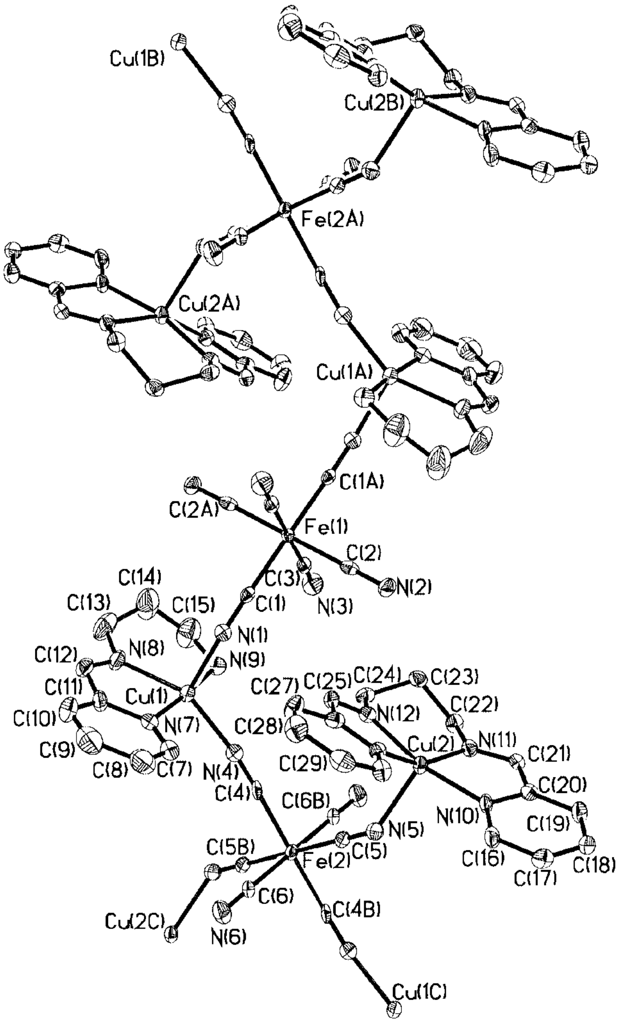


Fig. 2 A perspective view of the chain complex **2**. Hydrogen atoms are omitted for clarity.

$[Cu(L)]^{2+}$ units with a Cu···Fe distance of 4.811(4) Å. Atoms Cu(1) and Cu(2) belonging to $[Cu(L^1)]^{2+}$ and $[Cu(L)]^{2+}$, respectively, are five-co-ordinated with geometries that are intermediate between trigonal bipyramidal (C_{3v}) and square-based pyramidal (C_{4v}). According to the procedure described by Addison *et. al.*,[37] Cu(1) and Cu(2) have τ values ($\tau = (\theta_1 - \theta_2)/60$, where θ_1 and θ_2 are the largest angles in the co-ordination sphere) of 0.37 and 0.18, thus indicating that the CuN_5 co-ordination polyhedra can be better described as distorted square-based pyramidal. In the $Cu(1)N_5$ polyhedron the nitrogen atoms of the tridentate L^1 ligand and the N(4) nitrogen atom of one bridging cyanide ligand occupy the basal positions with bond distances in the range 1.975(7)–2.041(6) Å, whereas N(1) of another cyanide bridging ligand is bonded in apical position at a distance of 2.162(6) Å. In the $Cu(2)N_5$ co-ordination polyhedron the equatorial positions are occupied by the N_4 set of donor atoms of the L ligand with bond distances in the range 1.981(6)–2.110(6) Å and the apical position by the N(5) nitrogen atom of the cyanide bridging ligand at a distance of 2.127(6) Å. As usual, in both polyhedra the copper ions are lifted from the mean basal plane toward the apical nitrogen atoms by 0.275(3) and 0.310(3) Å, for Cu(1) and Cu(2), respectively. Both iron atoms, Fe(1) and Fe(2), which are located on centres of symmetry, exhibit a minimally distorted octahedral environment, where the *cis* C–Fe–C angles are close to 90° and the *trans* angles have crystallographically imposed values of 180°. The Fe(1)–C bond distances for bridging cyanide groups are 1.892(8) Å and those for the terminal cyanide ligands 1.925(8) and 1.925(9) Å, whereas for Fe(2) those distances are 1.893(7) and 1.904(8) Å for bridging cyanide and 1.913(8) Å for terminal cyanide groups. These distances are similar to those found in other $[Fe(CN)_6]^{4-}$ containing systems.[26,27] The Fe–C–N angles are approximately linear or linear within experimental errors with values in the ranges 177.1(6)–179.1(7) and 178.2(7)–179.5(8)°, for Fe(1) and Fe(2), respectively. For the bridging cyanide ions the Cu–N–C angles are, however, considerably deviated from linearity with values as low as 136.4(6) and 140.8(6)° for Cu(2)–N(5)–C(5) and Cu(1)–N(1)–C(1) angles, respectively.

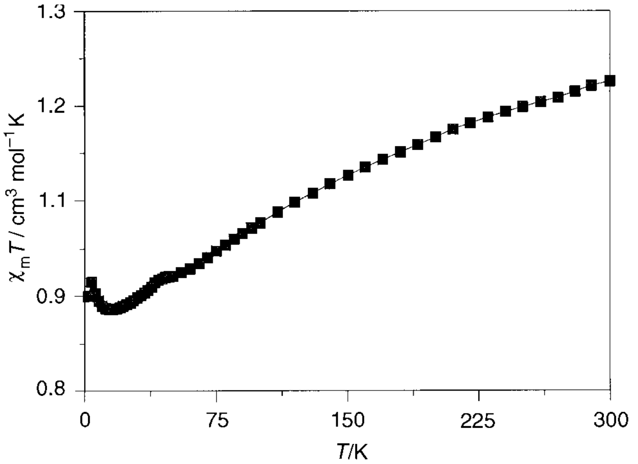


Fig. 3 Temperature dependence of $\chi_m T$ for complex **1**.

The copper–iron distances within the chain are 4.899(4) Å for Cu(1)···Fe(1) and 5.023(4) Å for Cu(1)···Fe(2). In the crystal, chains and water molecules are involved in an extensive and intrincated network of hydrogen bonds, the shortest interchain pathway involving the Fe–CN(6) groups and three water molecules.

Magnetic properties

The X-band EPR spectra of polycrystalline samples of complexes **1** and **2** at 100 K look axial with two main features attributable to $g_\parallel$ and $g_\perp$ (2.18 and 2.04 for **1**, 2.22 and 2.07 for **2**) indicating, as expected for axially distorted octahedral and square based pyramidal co-ordination polyhedra, respectively, a $(d_{x^2-y^2})^1$ electronic configuration for copper(II) ions. The spectra are devoid of any hyperfine structure or half-field signal.

The temperature dependence of the $\chi_m T$ product per FeCu unit in the range 2–300 K for complex **1** is shown in Fig. 3. The value at room temperature, 1.2 cm^3 mol^{-1} K, is significantly larger than the spin-only value of 0.75 cm^3 mol^{-1} K expected for isolated Cu^{II} and low spin Fe^{III} ($S = 1/2$), assuming $g_{Cu} = 2.0$ and $g_{Fe} = 2.0$, which is likely due to the orbital contribution to the magnetic moment of the low-spin Fe^{III}. As the temperature is lowered $\chi_m T$ steadily decreases to reach a minimum value of 0.91 cm^3 mol^{-1} K at 14 K. Such a magnetic behaviour is characteristic of a low-spin octahedral iron(III) system with spin–orbit coupling of the $^2T_{2g}$ ground term. A similar temperature dependence of $\chi_m T$ has been observed for the complex $[Zn(cyclam)]_3[Fe(CN)_6]_2\cdot 22H_2O\cdot EtOH$[38] containing paramagnetic $[Fe(CN)_6]^{3-}$ units. On further lowering the temperature from 14 K, $\chi_m T$ increases to reach a maximum of 0.94 cm^3 mol^{-1} K at 4 K and then decreases sharply to a value of 0.92 cm^3 mol^{-1} K at 2 K. Such magnetic behaviour is consistent with a ferromagnetic exchange interaction, small in magnitude, between Cu^{II} and Fe^{III} within the chain and weak interchain antiferromagnetic interactions, which are responsible for the decrease of $\chi_m T$ at very low temperature.

The intrachain magnetic interaction in complex **1** can be rationalised in terms of the strict orthogonality of the magnetic orbitals of the iron(III) and copper(II) ions. A low spin iron(III) in octahedral surrounding (t_{2g}^5) has the unpaired electron density on *xy*, *xz* and *yz* d orbitals, which are degenerate and π in character, whereas a copper(II) in an axially elongated octahedral geometry (D_{4h}) has one unpaired electron in the $x^2 - y^2$ d orbital (b_{1g}), which is σ in character. The σ/π interaction would lead to zero overlap and then to a strict orthogonality. It should be pointed out that, despite the long CN–Cu bond distance, as a consequence of the copper(II) Jahn–Teller effect, there exists an appreciable magnetic exchange interaction, which is of the same order of magnitude as that observed in other Fe^{III}–Cu^{II} cyanide-bridged compounds with similar Cu–C–N bent angles but shorter CN–Cu distances.[20] Indeed, more examples are needed in order to clarify these and other aspects of these scarce extended systems.

The χ_mT product at room temperature per Fe_2Cu_2 unit for complex **2** of 0.875 $cm^3\ mol^{-1}$ K is typical of two independent Cu^{II} and diamagnetic Fe^{II}. It remains almost constant in the temperature range 300–5 K and then decreases to 0.76 $cm^3\ mol^{-1}$ K at 2 K. These results indicate a negligible intrachain interaction between copper(II) ions through the diamagnetic $[Fe(CN)_6]^{4-}$ units and weak antiferromagnetic interchain interactions. A similar behaviour has been observed for the $Fe^{II}Cu^{II}{}_6$ heptanuclear complex $[Fe\{(CN)Cu(tpa)\}_6][ClO_4]_8\cdot H_2O$,[26] in which a diamagnetic $[Fe(CN)_6]^{4-}$ unit bridges six copper(II) atoms. Conversely, the complexes $[Ni(L)_2]_3[Fe^{II}(CN)_6]X_2$ (L = ethylenediamine or 1,3-propanediamine), recently reported by Ohba and co-workers,[19] exhibit a weak ferromagnetic exchange interaction between the Ni^{II} through diamagnetic $[Fe(CN)_6]^{4-}$ units. In view of these contradictory results, more examples of Fe^{II}–Cu^{II} cyanide-bridged systems are needed in order to clarify the exchange mechanism.

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