Hexacyanometalates as templates for heteropolynuclear complexes and molecular magnets: synthesis and crystal structure of $[Fe\{(CN)Cu(tpa)\}_6][ClO_4]_8{\cdot}3H_2O$, [tpa = tris(2-pyridylmethyl)amine]

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Reaction of $[Fe(CN)_6]^{3-}$ with $[Cu(tpa)(OH_2)]^{2+}$ produces a bimetallic heptanuclear complex, $[Fe\{(CN)Cu(tpa)\}_6][ClO_4]_8{\cdot}3H_2O$, which is characterised by single-crystal X-ray diffraction and shown to consist of an iron(II) centre connected by cyano bridges to six copper(II) centres forming spherical units of $[Fe\{(CN)Cu(tpa)\}_6]^{8+}$.

There is a rapidly growing interest in molecular-based ferromagnets derived from paramagnetic precursor complexes.[1] This has led to the application of hexacyanometalates as building blocks for constructing bimetallic assemblies which exhibit spontaneous magnetization.[2–5] Some of these studies have taken advantage of the bridging capabilities of the cyano group and its ability to promote ferromagnetic interactions between metal centres.[6] Okawa and co-workers have demonstrated the versatility of the $[Fe(CN)_6]^{3-}$ ion as a template for the preparation of two- and three-dimensional lattices which act as molecular magnets.[7–10] One of the synthetic challenges in the field of molecular magnetism is to create discrete polynuclear entities with high-spin ground states.[11–13] Mallah *et al.*, have recently reported a cyano-bridged heptanuclear complex,[14] $[Cr\{(CN)Ni(tetren)\}_6][ClO_4]_9$ (tetren = tetraethylenepentamine), consisting of a $[Cr(CN)_6]^{3-}$ centre linked to six $[Ni(tetren)]^{2+}$ units. The complex has an $S = 15/2$ ground state and exhibits ferromagnetic interaction between Cr^{III} ($S = 3/2$) and the surrounding Ni^{II} ($S = 2/2$) metal ions mediated by the cyano bridges. More recently, Scuiller *et al.*, again using $[Cr(CN)_6]^{3-}$ as the central building block, produced another heptanuclear complex[15] with composition $[Cr\{(CN)Mn(trispicMeen)\}_6][ClO_4]_9{\cdot}3thf$ [trispicMeen = *N,N,N'*-tris(2-pyridylmethyl)-*N'*-methylethane-1,2-diamine], a complex with a low-lying $S = 27/2$ ground state. At the present time, however, no crystal structures have been reported for these types of heptanuclear complexes. Our interest in magnetic materials[16] has led us to explore synthetic strategies to produce heteropolynuclear metal complexes based on hexacyanometalates. We report here the synthesis and structure of $[Fe\{(CN)Cu(tpa)\}_6][ClO_4]_8{\cdot}3H_2O$, the first heptanuclear complex of this type to be structurally characterised.

The bimetallic complex was prepared by the addition of $K_3[Fe(CN)_6]$ to 6 equiv. of $[Cu(tpa)(OH_2)][ClO_4]_2$ [tpa = tris(2-pyridylmethyl)amine] in water at pH 7 and the crude product was recrystallised from hot water. The Cu^{II} tpa precursor was prepared, *in situ*, by reaction of equimolar amounts of the ligand and $Cu(ClO_4)_2{\cdot}6H_2O$. The reaction afforded a dark purple precipitate (yield 74%) with a composition corresponding to $[Fe\{(CN)Cu(tpa)\}_6][ClO_4]_8{\cdot}3H_2O$ **1**. Complex **1** has been characterised using a variety of physicochemical techniques and its single-crystal X-ray structure determined.† In the IR spectrum, a hypsochromic shift of the CN stretching frequency (from 2042 cm^{-1} in ferrocyanide to 2109 cm^{-1} in complex **1**), is consistent with the formation of bridging cyano groups, while the presence of the tpa ligand is confirmed by bands due to the skeletal vibrations of the pyridine ring at 1607, 1482 and 1440 cm^{-1}. The room-temperature magnetic moment of 4.2 μ_B for complex **1** is typical of six independent d^9 Cu^{II} atoms surrounding a diamagnetic Fe^{II} centre. Curie behaviour was observed in variable-temperature magnetic susceptibility measurements. The Mössbauer spectrum of complex **1** recorded at 77 K, shows a strong, narrow single line with δ −0.049 mm s^{-1} and a half width maximum of 0.135 mm s^{-1}. This is indicative of a unique iron environment, with a symmetrical ligand field around the iron leading to zero quadrupole splitting. The isomer shift is close to zero, similar to the shifts observed for $K_3[Fe(CN)_6]$ (δ 0.0 mm s^{-1} ΔE_Q 0.47 mm s^{-1})[17] and $K_4[Fe(CN)_6]$, (δ 0.04 mm s^{-1} ΔE_Q 0 mm s^{-1}).[17] The slightly negative value observed for **1** is in accord with that observed for the related heptanuclear iron(II) complex, $[Fe\{(CN)Cu(tren)\}_6][ClO_4]_8{\cdot}10H_2O$ [δ −0.06 mm s^{-1} ΔE_Q 0 mm s^{-1}, tren = tris(2-aminoethyl)amine].[18] The reason for the reduction of Fe^{III} to Fe^{II} is unclear and is under further investigation. However, when the reaction is repeated using a 1 : 2 ratio of the iron(III) and copper(II) complexes but in the presence of an oxidising agent (such as $K_2S_2O_8$), the product isolated was a trinuclear complex $[(CN)_4Fe\{(CN)Cu(tpa)\}_2][ClO_4]_2$. The product contains two *trans* oriented $[Cu(tpa)]^{2+}$ ions and four terminal cyano groups.[19] Complex **1** is obtained in 84% yield when $K_4[Fe(CN)_6]$ is substituted for $K_3[Fe(CN)_6]$.

The molecular structure of complex **1** and selected interatomic parameters are shown in Fig. 1, which shows the encapsulation of the $[Fe(CN)_6]^{4-}$ core by six $[Cu(tpa)]^{2+}$ units forming an almost spherical complex. Since this is the first example of this type of $Fe^{II}Cu^{II}$ complex to be structurally characterised, comparisons will be made with cyano bridged $Fe^{III}Cu^{II}$ complexes and a polynuclear $Fe^{II}Cu^{II}$ complex.[20–24] Complex **1** adopts a minimally distorted octahedral environment around the iron centre: the C–Fe–C(*cis*) and the C–Fe–C(*trans*) angles are close to 90 and 180°, respectively. The Fe–C–N angles in complex **1** show only slight deviation from linearity [175(2)–178(2)°], which is consistent with literature values.[20–24] This observation, and the correspondence of the Fe–C bond distances in **1** (1.85–1.90 Å) to those reported for $[Fe(CN)_6]^{4-}$ and other Fe–Cu complexes, further highlights the fact that cyano–iron complexes are little distorted when incorporated into heteropolynuclear complexes.[7–9,22–25] The Fe···Cu distances in **1** of 4.90–4.95 Å, are towards the lower end of literature values for discrete molecules and lattice networks.[20–24] The interatomic distances between copper and the cyano nitrogen centres compare favourably to literature values of discrete molecules[20–24] in which the geometry about the Cu centre is trigonal bipyramidal and the cyano group occupies an axial site. Longer Cu–N distances have been observed in lattice network structures and discrete molecules where the cyano group binds to an axial site in geometries that are close to square pyramidal or octahedral.[20,21,24] Unlike the Fe–C–N angles, the Cu–N–C angles in complex **1** are in the range 163(1)–171(2)° showing significant deviation from linearity. This can be attributed to steric interactions between the tpa ligands on adjacent Cu centres. Such deviations have been observed in

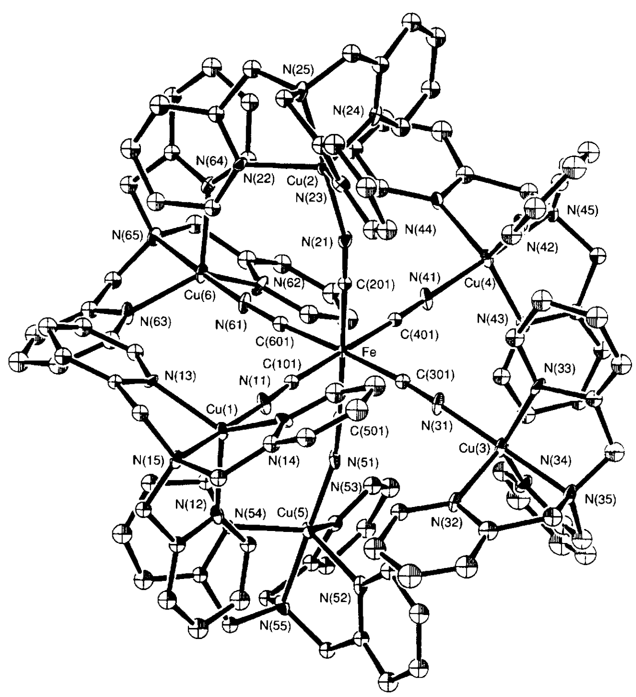

Fig. 1 An ORTEP diagram of $[Fe\{(CN)Cu(tpa)\}_6][ClO_4]_8 \cdot 3H_2O$ **1**. For clarity only atoms in $Fe\{(CN)Cu(N_4)\}_6$ are labelled. Selected ranges of bond angles (°) and distances (Å): Fe···Cu 4.899(4)–4.929(4), Fe–C 1.85(2)–1.90(2), Cu–N(cyano) 1.90(2)–1.95(1), Cu–N(amine) 2.01(1)–2.07(1), Cu–N(py), 1.98(2)–2.15(2); C–Fe–C(*cis*) 87.7(7)–91.5(7), C–Fe–C(*trans*) 177.5(8)–179.2(2), Fe–C–N 175(2)–178(2), Cu–N–C(cyano) 163(1)–171(2), N(amine)–Cu–N(py), 80.0(6)–83.7(6), N(py)–Cu–N(cyano) 96.1(6)–99.7(6).

other discrete molecules,[20–24] but the distortion in many of these complexes is smaller highlighting the steric effect of tpa in complex **1**. On the other hand, substantial variations in Cu–N–C angles (107–174°) have been reported for lattice network complexes.[20–21] The geometry about each Cu^{II} centre in complex **1** is best described as distorted trigonal bipyramidal with the pyridyl rings on each tpa ligand occupying equatorial positions around the Cu centre and the amine nitrogen the axial position *trans* to the cyano bridges. Significant variations in both Cu–N distances and N–Cu–N angles are found in the equatorial plane. The five-membered chelate rings confer several structural features on the Cu geometry. The N(py)–Cu–N(amine) angles are reduced from 90° and, to compensate for this, the N(py)–Cu–N(cyano) angles are greater than 90°. The Cu centres sit outside the plane formed by the pyridyl nitrogens towards the bridging cyano groups.

The applicability of hexacyanoiron(II/III) complexes in the synthesis of discrete heteropolynuclear complexes has been confirmed through the crystal structure characterisation of a heptanuclear $FeCu_6$ complex. The further development of hexacyanometalates as templates for heteropolynuclear metal complexes is currently under examination.

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Footnote

† *Crystal structure* of $[Fe\{(CN)Cu(tpa)\}_6][ClO_4]_8 \cdot 3H_2O$ **1**. *Crystal data*: $C_{114}H_{120}Cl_8Cu_6FeN_{30}O_{38}$; M = 3239.13. Crystal size 0.32 × 0.16 × 0.16 mm, monoclinic, space group $P2_1$ (no. 4), a = 16.673(2), b = 24.909(3), c = 18.060(3) Å, β = 114.74°, U = 6812(2) $Å^3$, Z = 2, $F(000)$ = 3308.0, D_c = 1.579 g cm^{-3}, μ(Mo-Kα) = 40.47 cm^{-1}, 10771 unique reflections were collected at 193 K with $2\sigma_{max}$ = 120.1°. The data were collected on a Rigaku AFC6R diffractometer using graphite-monochromated Cu-Kα (λ = 1.54178 Å) radiation operating in ω scan mode at a scan rate of 32.0° min^{-1}. The intensity data were corrected for Lorentz-polarization and absorption effects. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques (DIRDIF94). Due to insufficient data (due in part to substantial crystal decay) only non-C and -H atoms were refined anisotropically. Hydrogen atoms were included at calculated positions where possible. Water hydrogens could not be located and were omitted from the calculations. The handedness of the molecule was fixed by refinement in each enantiomorph. The final cycle of full-matrix least-squares refinement was based on 7991 observed reflections [$I > 3.00\sigma(I)$] and 1203 variable parameters and converged with unweighted and weighted agreement factors of R = 0.076 and R_w = 0.083 where the maximum peak in the final difference map was 1.36 e $Å^3$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/290.

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