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A cyclic hexacopper(II) fluoro complex that encapsulates two fluoride anions†

Xiaoming Liu,[a] Abbie C. McLaughlin,[b] Marcelo P. de Miranda,[a] Eric J. L. McInnes,[d] Colin A. Kilner[a] and Malcolm A. Halcrow*[a]

[a] *Department of Chemistry, University of Leeds, Woodhouse Lane, Leeds, UK LS2 9JT. E-mail: M.A.Halcrow@chem.leeds.ac.uk*
[b] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW*
[c] *Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge, UK CB3 0HE*
[d] *Department of Chemistry, University of Manchester, Oxford Road, Manchester, UK M13 9PL*

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The complex $[\{Cu_3(Hpz^{tBu})_4(\mu\text{-}pz^{tBu})_2(\mu\text{-}F)_2(\mu_3\text{-}F)\}_2]F_2$ (Hpz^{tBu} = 3{5}-*tert*-butylpyrazole) has a cyclic, C_{2v}-symmetric hexacopper core. The two non-coordinated F^- anions are encapsulated within cavities formed by three Hpz^{tBu} ligands.

We have recently reported the crystal structure and magnetochemistry of $[\{Cu_3(Hpz^{tBu})_6(\mu_3\text{-}Cl)(\mu_3\text{-}OH)_3\}_2Cu]Cl_6$ (**1**; Hpz^{tBu} = 5-*tert*-butylpyrazole), which was obtained by complexation of $CuCl_2$ and Hpz^{tBu} in basic MeOH.[1] The structure of **1** contains a $[\{Cu_3(Hpz^{tBu})_6(\mu_3\text{-}Cl)(\mu_3\text{-}OH)_3\}_2Cu]^{6+}$ vertex-sharing double cubane core, surrounded by a belt of six hydrogen-bonded Cl^- anions that are enclosed within a hydrophobic sheath of *tert*-butyl groups. This is an inversion of the usual scenario in polymetallic host:guest complexes, in that the Cl^- guests surround the periphery of the cluster core rather than being encapsulated within it.[2] We have now found that a similar reaction using CuF_2 gives a completely different and unprecedented product. Reaction of hydrated CuF_2 with Hpz^{tBu} and NaOH in a 1 : 2 : 1 molar ratio in MeOH at 290 K for 24 h yields a dark green solution.[3] Evaporation of this solution to dryness, extraction of the residues with CH_2Cl_2, and layering the extracts with pentane at 240 K affords **2** in *ca.* 50% yield. The turquoise solids **1** and **2** are indistinguishable in appearance. However, X-ray analysis of crystals of **2**$\cdot 2CHCl_3\cdot 0.5C_7H_{16}$,‡ grown by recrystallisation of **2** from these two solvents, revealed a different formulation of $[\{Cu_3(Hpz^{tBu})_4(\mu\text{-}pz^{tBu})_2(\mu\text{-}F)_2(\mu_3\text{-}F)\}_2]F_2$. Elemental analysis confirmed that the bulk sample of **2** also has this composition.§

Compound **2** contains a cyclic hexacopper complex dication with approximate C_{2v} symmetry, which is composed of two $[Cu_2(Hpz^{tBu})_3(\mu\text{-}F)_2]^{2+}$ units linked by two *cis*-$[CuF(Hpz^{tBu})(\mu\text{-}pz^{tBu})_2]^-$ moieties (Fig. 1, Scheme 1). The Cu centers in the molecule show τ = 0.12–0.34, corresponding to small distortions from the 'ideal' value of 0 for a square pyramid.[4] Cu(1) and Cu(4) have a Hpz^{tBu} ligand in their apical coordination sites, while the other Cu ions have apical bridging interactions to a F^- ligand bound to another Cu atom (Scheme 1). The two charge-balancing F^- anions are each hydrogen-bonded to three Hpz^{tBu} N-H protons, and are encapsulated within these ligands' *tert*-butyl groups (Fig. 2). There are also two intramolecular N–H···F hydrogen bonds spanning the cluster molecule (Fig. 2), to F(119) and F(120) (Fig. 1). These eight N–H···F interactions show N···F = 2.620(3)–2.653(3) Å and N–H···F = 163.9–172.4°.

At 300 K, $\chi_M T$ of **2** is 2.04 cm^3 mol^{-1} K, which is smaller than the value expected for 6 non-interacting Cu(II) ions with a reasonable *g*-value, of 2.5 cm^3 mol^{-1} K.[5] $\chi_M T$ decreases steadily as the temperature is lowered, reaching 0.86 cm^3 mol^{-1} K at 5 K. This low-temperature value is smaller than expected for an isolated S = 1 ground state ($\chi_M T$ = 1.1 cm^3 mol^{-1} K), but is more reasonable for two isolated Cu(II) spins (0.8 cm^3 mol^{-1} K).[5] These data were modelled using a C_2-symmetric Hamiltonian [eqn. (1)], which only considers interactions between Cu ions that are directly linked by basal–basal covalent bridges.¶

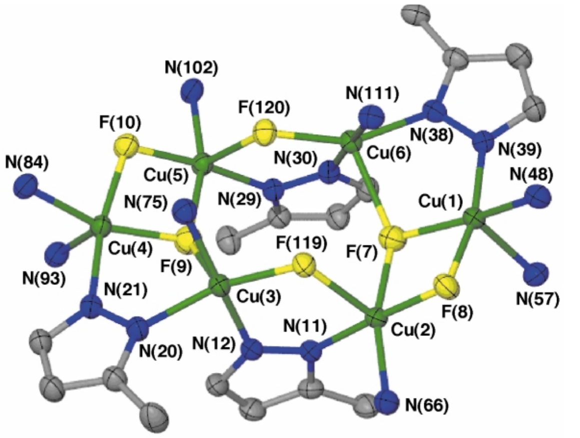
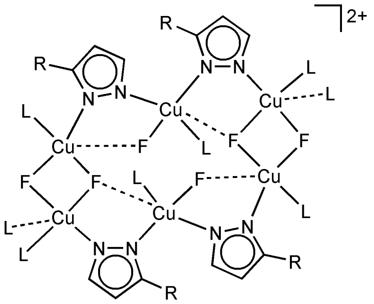


Fig. 1 View of the core of the $[\{Cu_3(Hpz^{tBu})_4(\mu\text{-}pz^{tBu})_2(\mu\text{-}F)_2(\mu_3\text{-}F)\}_2]^{2+}$ complex molecule in **2**$\cdot 2CHCl_3\cdot 0.5C_7H_{16}$. Only the coordinated N atoms of the Hpz^{tBu} ligands, and only the *ipso tert*-butyl C atoms of the $[pz^{tBu}]^-$ ligands, are shown. Thermal ellipsoids are at the 50% probability level. Colour code: C = grey, H = turquoise, Cu = green, F = yellow, N = blue. Selected bond lengths: Cu–F{basal} = 1.8990(18)–1.9993(19), Cu–F{apical} = 2.1891(18)–2.333(2), Cu–N{basal} = 1.966(2)–2.015(3), Cu–N{apical} = 2.232(3)–2.239(3) Å.

$$H = -2J_1(S_1\cdot S_2 + S_4\cdot S_5) - 2J_2(S_2\cdot S_3 + S_5\cdot S_6) - 2J_3(S_3\cdot S_4 + S_1\cdot S_6) \quad (1)$$

Using this model, two fits were obtained that fit the data almost equally well: g = 2.20, J_1 = −79, J_2 = −79 and J_3 =



Scheme 1 Connectivity of the cluster core in **2** (R = *tert*-butyl, L = 5-*tert*-butylpyrazole). Basal and apical copper-ligand bonds are represented as filled and dotted lines, respectively.

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† Electronic supplementary information (ESI) available: observed and simulated EPR spectra for **2**. See http://www.rsc.org/suppdata/cc/b2/b207923m/

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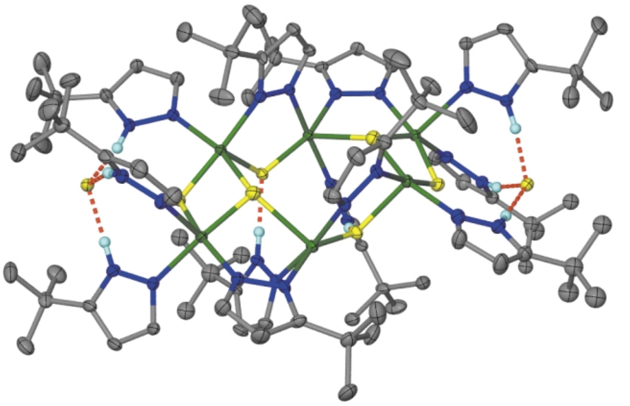

Fig. 2 View of the complete $[\{Cu_3(Hpz^{tBu})_4(\mu\text{-}pz^{tBu})_2(\mu\text{-}F)_2(\mu_3\text{-}F)\}_2]F_2$ molecule in the structure of $\mathbf{2}\cdot 2CHCl_3\cdot 0.5C_7H_{16}$. All C-bound H atoms have been omitted, while only one orientation of the disordered *tert*-butyl groups is shown. Other details as for Fig. 1.

0 cm^{-1} (fit **A**); and $g = 2.18$, $J_1 = -120$, $J_2 = 0$ and $J_3 = 0$ cm^{-1} (fit **B**) (Fig. 3).¶ These interpretations both lead to two lowest energy states lying within 0–10 cm^{-1} of each other, one with $S = 0$ and one with $S = 1$. This implies a ground configuration comprised of two very weakly interacting $S = 1/2$ spins, in agreement with the low-temperature value of $\chi_M T$.

Magnetochemical data are only available for one compound containing a basal, basal $[Cu_2(\mu\text{-}F)_2]^{2+}$ bridge of the type observed in **2**. This complex, $[\{Cu(\mu\text{-}F)(\mu\text{-}BF_4)(Hpz^{Me,Ph})_2\}_2]$ ($Hpz^{Me,Ph}$ = 3-methyl-5-phenylpyrazole), shows $J = -118$ cm^{-1} for a Cu–F–Cu angle of 98.9(1)°.[6] This is close to the average Cu–F–Cu angles of 100.2(1) and 100.5(1)° across the two $[Cu_2(\mu\text{-}F)_2]^{2+}$ bridges in **2**, which suggests that J_1 for **2** should also be close to this value.[7] The other superexchange pathways in **2** are mediated by one basal–basal $[pz^{tBu}]^-$ bridge, and a basal–apical-bridging F^- ligand which should contribute negligibly to these interactions.[8] All previous magnetochemical studies of mono-pyrazolido-bridged dicopper complexes have shown antiferromagnetic coupling, with $-32 \leq J \leq -12$ cm^{-1}.[9] For these reasons, it can be predicted that J_1 for **2** should be much more antiferromagnetic than J_2 or J_3. We therefore believe that fit **B** is a more reasonable description of the magnetic behaviour of **2**.

The Q-band EPR spectrum of powdered **2** at 290 K shows a single broad feature at $\langle g \rangle = 2.15$. This resonance sharpens upon cooling to 5 K, resolving into an apparently axial signal with a perpendicular feature at *ca.* 2.10 and two parallel features centred on $g = 2.28$ with linewidths of *ca.* 300 G. This can be simulated as a $S = 1$ system with the spin Hamiltonian parameters $g_1 = 2.28$, $g_{2,3} = 2.08$, $|D| = 0.02$ cm^{-1}, $|E| = 0$ (see ESI†). The small zero field splitting is consistent with the lack of a detectable half-field resonance at this frequency.[10] There is an additional weak feature in the spectrum near $g = 2.55$, which was not simulated but which might correspond to a singlet–triplet transition.[10] The X-band spectrum consists of a broad single line with a very weak resonance at half-field, and can be simulated using the same parameters used at Q-band. These spectra are consistent with **2** possessing either an $S = 1$ ground state, or a very low-lying $S = 1$ excited state.

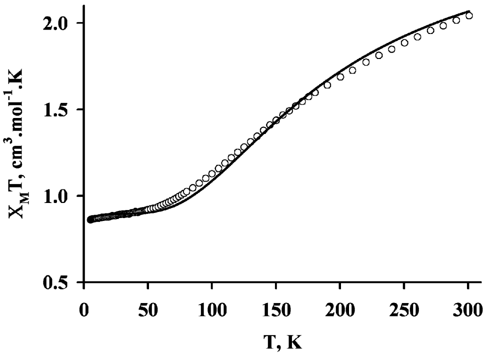

Fig. 3 Plot of $\chi_M T$ *vs.* T for a powder sample of **2** (circles), showing the theoretical fit **B** (line) quoted in the text.

These results demonstrate that the products obtained from the reaction of Cu(II) salts with Hpz^{tBu} depend drastically on the anion present in the reaction mixture. This emphasises that the exogenous, hydrogen-bonded anions in **1** and **2** play an important role in templating the structures of these cluster products. A full investigation of the influences of the anion, and of the pyrazole ligand, on the products obtained from these reactions will be reported in due course.

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Notes and references

‡ *Crystal data for* **2**. $2CHCl_3\cdot 0.5C_7H_{16}\cdot C_{89.5}H_{150}Cl_6Cu_6F_8N_{24}$, M_r = 2308.27, triclinic, $P1$, a = 12.9428(1), b = 20.4550(1), c = 24.9037(2) Å, α = 67.7688(4), β = 82.1704(4), γ = 74.9426(3)°, V = 5888.19(7) Å^3, Z = 2, μ(Mo-Kα) = 1.262 mm^{-1}, T = 150(2) K; 119167 measured reflections, 26888 independent, R_{int} = 0.060; $R(F)$ = 0.048, w$R(F^2)$ = 0.143.

The asymmetric unit contains one molecule of the complex, two molecules of $CHCl_3$ and a molecule of heptane, which is disordered over two equally occupied orientations giving a total occupancy of 0.5. Three *tert*-butyl groups in the complex are also disordered, over two orientations. All disordered C–C distances were restrained to 1.52(2) Å, and non-bonded 1,3-C···C distances within a given disorder orientation to 2.48(2) Å. All non-H atoms with occupancy > 0.5 were refined anisotropically, while H atoms were placed in calculated positions and refined using a riding model. CCDC 191749. See http://www.rsc.org/suppdata/cc/b2/b207923m/ for crystallographic data in CIF or other electronic format.

§ *Analytical data for* **2**. Found C, 50.0; H, 7.1; N, 16.4; F, 7.7%: calcd. for $C_{84}H_{140}Cu_6F_8N_{24}$ C, 50.0; H, 7.0; N, 16.6; F, 7.5%.

¶ Each S center corresponds to the equivalently numbered Cu ion in Fig. 1 [*i.e.* $S_1 \equiv$ Cu(1) *etc.*]. The methods used to derive the van Vleck equation for **2**, and to fit the data to this equation, are described in ref. 1. No TIP or paramagnetic impurity terms were included in the model. Estimated errors on g are ±0.01, and on J are ±2 cm^{-1} for fit **A**, and ±5 cm^{-1} for fit **B**.

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