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A novel nonanuclear Cu^{II} carboxylate-bridged cluster aggregate with an $S = 7/2$ ground spin state

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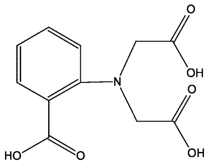
The Cu^{II} aggregate in $[Cu_9(cpida)_6(MeOH)_6]\cdot 6(MeOH)$ {H_3cpida = 2-(carboxyphenyl)iminodiacetic acid} is made up of two weakly ferromagnetically coupled carboxylate-bridged Cu_4 units that are antiferromagnetically linked through a central Cu^{II} to give a Cu_9 core with an $S = 7/2$ spin ground state.

The self-assembly approach to large cluster aggregates has led to the synthesis of high nuclearity species containing up to 36 paramagnetic transition metal centres, including Fe_{19},[1] Fe_{17},[2] Co_{24},[3] Ni_{24},[4] Mn_{30}[5] and Cu_{36},[6] with the aim of producing systems with non-zero ground spin states. The latter triakontahexanuclear cluster is in fact the largest of several Cu^{II} clusters reported in the literature.[7–11] We have previously reported a series of Cu_{12} aggregates with the ligand 2-(carboxyphenyl)iminodiacetic acid (H_3cpida) that were synthesised under ambient conditions in the presence of base using methanol as a protic solvent.[12]



Our general approach aims to involve the protic solvent in an intermediate metastable cluster aggregate, $\{M_xL_n(OR)_p(ROH)_q\}^{n\pm}$, that we can trap through crystallisation before the solvolysis reaction goes to completion.[2]

In the case of Cu_{12}, the methanol solvent molecules become deprotonated and perform an important bridging function between the Cu^{II} centres. By reducing the solvolysis gradient (*i.e.* using less base) we have found that the cluster aggregate $[Cu_9(cpida)_6(MeOH)_6]$ (**1**) can be isolated.† In contrast to the Cu_{12} aggregates, deprotonated solvent is not present in **1** as a bridging ligand. The fairly low yield of crystals reported here reflects this trapping and crystallisation strategy.

In the Cu_9 cluster **1**,‡ several carboxylate bridging modes are important in linking the metal centres and mediating a variety of magnetic interactions. The centrosymmetric aggregate can be regarded as two irregular tetrahedral $[Cu_4(cpida)_3(MeOH)_3]^-$ units linked *via* a central Cu^{II} ion, Cu(1), at its inversion centre (Fig. 1). The two basal planes of the tetrahedra are formed by Cu(2), Cu(3) and Cu(4), and Cu(2′), Cu(3′) and Cu(4′), where Cu(3) and Cu(3′) are six-coordinate, with the remaining basal Cu(II) ions adopting a five-coordinate distorted square-based pyramidal geometry. A tetradentately chelating $cpida^{3-}$ ligand coordinates to each of the six basal Cu^{II} ions, with the fifth coordination site being occupied by a carboxylate oxygen atom from a neighbouring $cpida^{3-}$ ligand. The latter results in a cyclic link between the three basal Cu^{II} ions in each tetrahedron *via syn* (equatorial)–*anti* (axial) carboxylate bridges (Fig. 2). The distorted octahedral geometry about Cu(3) and Cu(3A) is completed by a methanol molecule.

The apices of the two tetrahedral $[Cu_4(cpida)_3(MeOH)_3]^-$ units are occupied by the square-based pyramidal Cu^{II} ions, Cu(5) and Cu(5′). These apical ions are linked to the basal Cu^{II} centres *via* three *syn* (eq.)–*anti* (ax.) carboxylate bridges from the $cpida^{3-}$ ligands, with two methanol molecules completing the coordination sphere. Further carboxylate oxygens from the $cpida^{3-}$ ligands connect the three basal Cu^{II} centres in each tetrahedron through three monoatomic, two *syn* (eq.)–*anti* (ax.) and one *syn* (eq.)–*anti* (ax.) carboxylate bridges to the central linking Cu(1) ion, giving an overall [4 + 2] distorted octahedral environment about Cu(1) (Fig. 2).

Magnetic measurements (Fig. 3) show that the χT product is constant between 300 and 150 K at 3.9 emu K mol^{-1}. At lower temperatures, χT decreases to reach a minimum of 3.3 emu K mol^{-1} at 22 K and finally increases to 4.8 emu K mol^{-1} at 1.8 K. Fitting the data with a Curie–Weiss law above 60 K leads to C = 3.97 emu K mol^{-1}, which is in good agreement with that expected for nine independent Cu^{II} of $S = 1/2$ with a g factor of 2.17. An EPR measurement on a powder sample of **1** at 300 K is consistent with this value, exhibiting a Lorentzian resonance line ($\Delta H = 200$ Oe) at $g = 2.15$. The Weiss constant, θ, is −5.8 K, indicating a dominant antiferromagnetic interaction.

The Cu_9 clusters in **1** are relatively well separated and can be considered as isolated. The Cu_9 aggregate is held together by a number of different types of carboxylate bridge. Therefore, in order to simplify the magnetic model, we have considered only those modes which are known to mediate the strongest magnetic

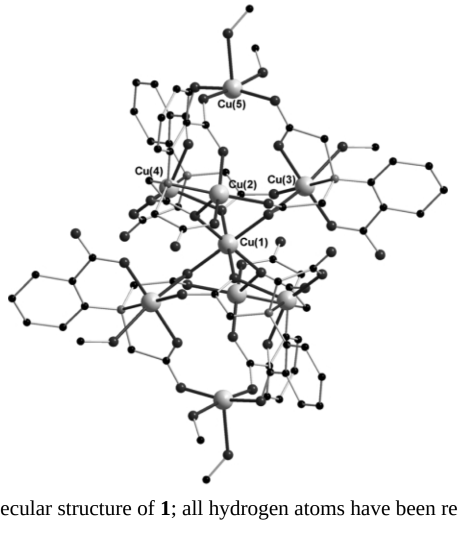


Fig. 1 Molecular structure of **1**; all hydrogen atoms have been removed for clarity.

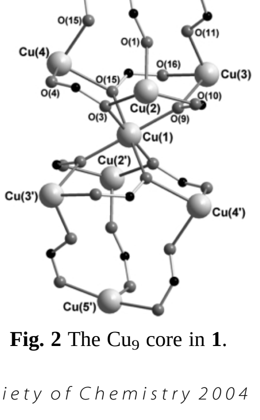


Fig. 2 The Cu_9 core in **1**.

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pathways.[12–14] These involve equatorial positions on both the Cu^{II} metal ions involved and, as shown in Scheme 1 and Fig. 2, there are two different types of magnetic interaction: (i) J_1 mediated by a *syn* (eq.)–*anti* (ax.) carboxylate bridge, expected to be antiferromagnetic,[13] and (ii) J_2 mediated by a *syn* (eq.)–*anti* (ax.) carboxylate bridge, expected to be ferromagnetic.[12,14] Due to the complicated topology of the Cu$_9$ cluster, an analytical model is difficult to obtain, hence the numerical approach using irreducible tensor methods in the program MAGPACK[15] was used. This can be regarded as an alternative approach to using variable field χT *vs*. T measurements to establish a unique set of parameters.[16] Excellent fits of both χT *vs*. T and the magnetisation at 1.85, 5 and 10 K were achieved with $J_1/k_B = -15(1)$ K, $J_2/k_B = +0.4(1)$ K and $g = 2.17$ (Fig. 3). No fit could be obtained when J_2 was set to zero. The sign and values of the magnetic interactions are in good agreement with the literature[12–14] and imply that the Cu$_9$ cluster in **1** possesses an $S = 7/2$ spin ground state.

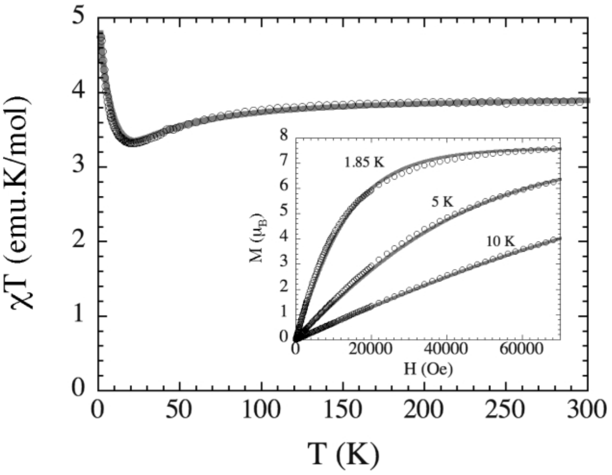
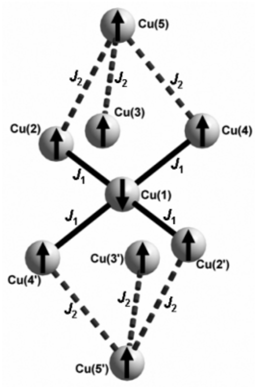


Fig. 3 Temperature dependence of the χT product (per nine Cu^{II}) for **1** at 1000 Oe. Inset: field dependence of the magnetisation (per nine Cu^{II} centres) for **1**. Solid lines are the best fits obtained with the model described in the text.



Scheme 1

The resultant spin topology is indicated in Scheme 1. A combination of the antiferromagnetic coupling to the central Cu^{II} and weaker ferromagnetic coupling within the tetrahedral units results in a magnetic spin ground state in which eight of the nine spins are aligned parallel, an unusually high proportion for an aggregate in which the antiferromagnetic coupling is dominant. This offers an attractive strategy for the construction of aggregates with high spin ground states, which is an important goal in the area of molecular magnetism.

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Notes and references

† Synthesis of **1**: a solution of H$_3$cpida (0.063 g, 0.25 mmol) and KOH (0.042 g, 0.75 mmol) in MeOH (20 ml) was added to a solution of Cu(NO$_3$)$_2$·2H$_2$O (0.121 g, 0.5 mmol) in MeOH (20 ml). After 3 to 4 days, X-ray quality dark green needle-shaped crystals of **1** were formed (10% yield). Elemental analysis: found C, 38.16; H, 3.60; N, 3.56; calc. C, 38.12; H, 3.94; N, 3.42%.

‡ *Crystal data* for **1**: $C_{78}H_{96}Cu_9N_6O_{48}$, $M = 2457.47$, monoclinic, $P2_1/c$, $a = 12.6762(9)$, $b = 17.3686(11)$, $c = 21.3680(18)$ Å, $\beta = 95.453(9)°$, $V = 4683.3(6)$ Å^3, $T = 200(2)$ K, $Z = 2$, $F(000) = 2502$, $\mu = 2.103$ mm^{-1}; 29723 data, 8575 unique ($R_{int} = 0.0667$), $wR_2 = 0.1293$, $S = 0.936$ (all data), $R_1 = 0.0521$ [5481 with $I \geq 2\sigma(I)$]. CCDC 226039. See http://www.rsc.org/suppdata/cc/b3/b316233h/ for crystallographic data in CIF or other electronic format.

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