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Engineering of ferrimagnetic Cu_{12}-cluster arrays through supramolecular interactions†

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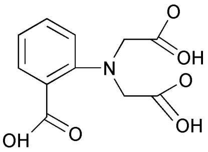
Ferrimagnetic oxo-bridged Cu_{12} aggregates can be organised into a variety of arrays by utilising structure-directing effects of counter ions, solvent molecules and linker units.

In previous work we have shown how hydrolytically-active Fe(III) ions in the presence of chelating ligands can be aggregated into 'ferrimagnetic' clusters when the activated water molecules provide hydroxo and oxo bridges.[1–5] Such aggregates have been termed ferrimagnetic when they demonstrate the property of overall antiferromagnetic coupling between individual pairs of paramagnetic centres but an increasing magnetic moment with decreasing temperature.[6] We have explored this synthetic strategy further using Cu(II) with the ligand carboxyphenyliminodiacetic acid, H_3cpida, in the presence of base and with methanol as protic solvent under ambient conditions.

H_3cpida



We have characterised a variety of aggregated Cu(II) species including a dodecanuclear aggregate $[Cu_{12}(\mu_3\text{-}OMe)_2(\mu\text{-}OMe)_6(cpida)_6]^{2-}$, $[\mathbf{1}]^{2-}$ (Fig. 1), which can be crystallised‡ § in a variety of arrays with the aggregates either separated by large areas of non-interacting solvent molecules or else joined together through alkali-metal ion linkages or by $\{Cu_2(\mu\text{-}OMe)_2\}^{2+}$ bridges. In this way a magnetically interesting, zero-dimensional building block can be arranged into 1, 2 and 3-dimensional arrays (Fig. 2).

The $[Cu_{12}(\mu_3\text{-}OMe)_2(\mu\text{-}OMe)_6(cpida)_6]^{2-}$ aggregate is made up of two triangular $\{Cu_3(\mu_3\text{-}OMe)(cpida)_3\}^{4-}$ units, within

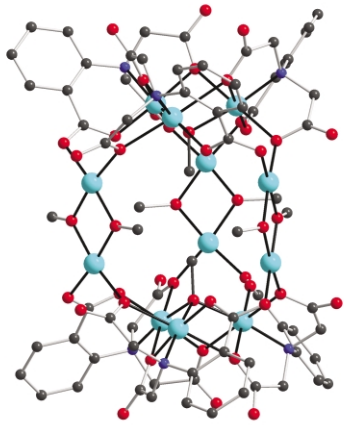


Fig. 1 $[Cu_{12}(OMe)_8(cpida)_6]^{2-}$, $[\mathbf{1}]^{2-}$. Pale blue = Cu, red = O, dark blue = N, black = C.

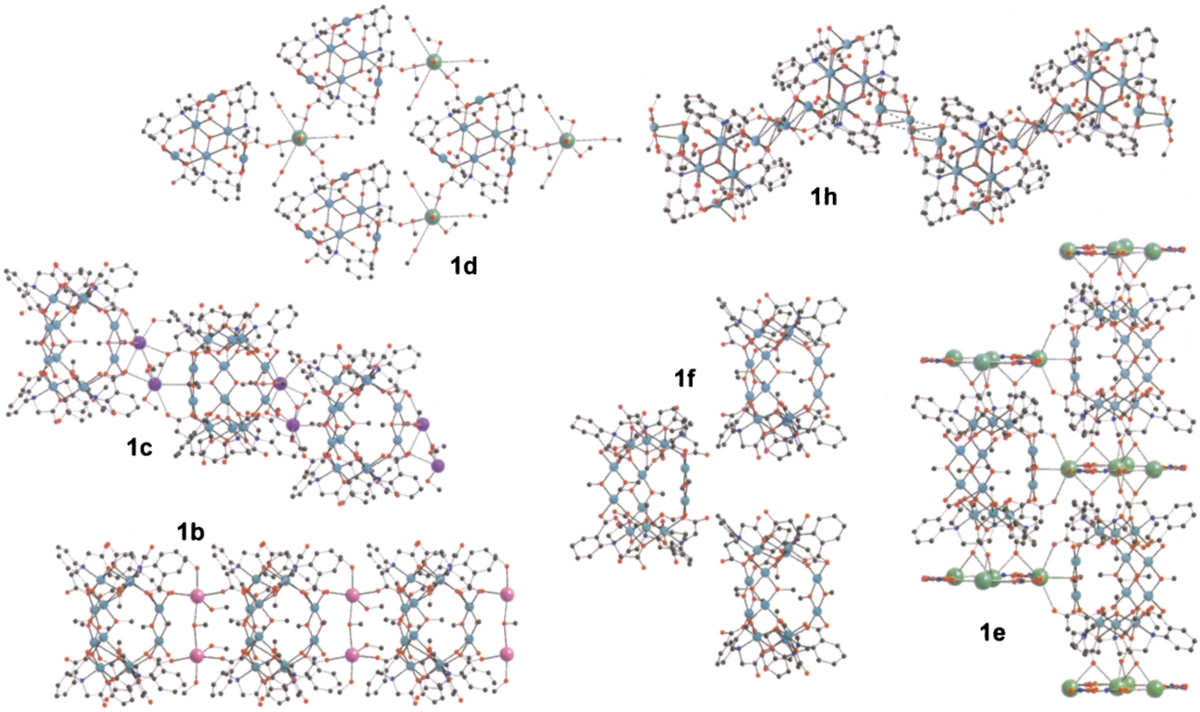


Fig. 2 Arrays of $[Cu_{12}(OMe)_8(cpida)_6]^{2-}$ aggregates with differing dimensionalities: 0-D (**1f**), 1-D (**1b**, **1c**), 2-D (**1d**), 3-D (**1e**), 1-D with magnetic linkages (**1h**).

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† Electronic supplementary information (ESI) available: χT *vs.* T plot for K^+ salt **1b** at magnetic fields of 1 and 10 kOe. See http://www.rsc.org/suppdata/cc/b2/b201585b/

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which the octahedral Cu(II) centres are linked *via* a μ_3-OMe and by three equivalent carboxylate oxygen bridges. The coordination sphere of each copper in the triangles is completed by coordination from the imino-N. The two triangles are linked through three dinuclear $\{Cu_2(\mu\text{-}OMe)_2\}^{2+}$ units. Each copper centre in the triangular units is linked *via* a *syn–anti* carboxylate bridge to a copper in one of the dimers, and *via* a carboxylate oxygen bridge to a copper in a different dimer, such that each copper is planar four-coordinate. This results in an overall framework with approximate C_{3h} symmetry.

In the case of the isomorphous potassium and sodium salts M_2[**1**]$\cdot$14MeOH, M = Na (**1a**), K (**1b**), the cluster aggregates are linked into chains through coordination of outer carboxylate oxygens not otherwise involved in the cluster framework to the alkali metal cations in $\{M_2(MeOH)_6\}^{2+}$ linking groups. Rather different one-dimensional chains are also found in Rb_2[**1**]$\cdot$14.5MeOH$\cdot H_2O$, **1c**, with the additional coordination of μ-OMe ligands to the Rb^+ cations. With Cs^+, two different structures can be obtained. In Cs_2[**1**]$\cdot$16MeOH$\cdot 2H_2O$, **1d**, $\{Cs_2(MeOH)_9(H_2O)_2\}^{2+}$ units link the aggregates into hexagonal two-dimensional sheets, whereas in Cs_4[**1**]$(NO_3)_2\cdot$9MeOH$\cdot$5H_2O, **1e**, trigonal-planar $\{Cs_4(NO_3)_2(H_2O)_2\}^{2+}$ units both link aggregates into columns and also bridge across to the three adjacent columns giving a three-dimensional array. If triethylamine is used as the base, the clusters are not linked but well separated by the heavily disordered solvent in $(Et_3NH)_2$[**1**]$\cdot x$(solvent), **1f**. If more Cu^{2+} is supplied to the reaction, the clusters are linked by further $\{Cu_2(OMe)_2\}^{2+}$ units. In [(**1**)$\{Cu_2(OMe)_2(MeOH)_3(NO_3)\}_2$ (**1**)$\{Cu_2(OMe)_2(MeOH)_2\}$]$\cdot$30MeOH, **1g**, the aggregates are linked by alternating double and single $\{Cu_2(OMe)_2\}^{2+}$ units whereas in [(**1**)$\{Cu_2(OMe)_2(H_2O)_2\}$(**1**)$\{Cu_2(OMe)_2(MeOH)(H_2O)\}$]$\cdot$60MeOH **1h** the links are simply single $\{Cu_2(OMe)_2\}^{2+}$ units.

These different packing arrangements result in slight distortions to the framework which could have important consequences on the overall magnetic behaviour observed. So far we have collected preliminary magnetic data on the K^+ salt **1b** where the aggregates, although linked, are relatively well-separated by diamagnetic centres so that we can ignore inter-cluster interactions which are expected to be extremely small and only evident at very low temperatures. The variation of χT with T (Fig. S1, ESI†) shows ferrimagnetic behaviour within the clusters. The value of χT at room temperature is 3.8 emu K mol^{-1}, compared with a value of 5.2 emu K mol^{-1} expected for non-interacting copper centres with *g*-value = 2.15, as determined by X-band EPR, and is indicative of overall antiferromagnetic couplings in the framework. This value rises to a maximum of 4.85 emu K mol^{-1} at *ca.* 10 K which is still lower than expected for twelve non-interacting Cu(II) centres and shows the behaviour typically observed for other ferrimagnetic cluster systems,[2,6] and then decreases sharply to 4.05 emu K mol^{-1} at 2 K. Looking at the structure of the framework we can identify several features which can influence the nature of the pairwise interactions between copper centres. Firstly, within the dinuclear units there is a variation in the angles at the oxygen atoms of the bridging methoxide units. Previous work on hydroxide and alkoxide-bridged copper dimers has shown that this parameter is critical in determining whether there is antiferromagnetic, ferromagnetic or zero interaction between the centres.[7] In all cases here the interaction is expected to be antiferromagnetic with Cu–O–Cu angles ranging from 99.9 to 103.7°, which corresponds to *J*-values ranging from -120 to -400 cm^{-1}. Secondly, the trinuclear μ_3-methoxide bridged units might be expected to display the spin frustration phenomena characteristic of triangular units.[8] Lastly, it is possible that the carboxylate bridges can also transmit magnetic information.[9] Detailed further studies on these systems are required in order to elucidate both the likely pathways within the clusters and the role of the linking units in modifying the magnetic behaviour.

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Notes and references

‡ A solution of H_3cpida (0.25 mmol) and NaOH (1.25 mmol) in 10 ml MeOH was added to a solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.5 mmol) in 10 ml MeOH. After 24 h, dark blue crystals of **1a** formed in 12% yield. **1b** (30%), **1c** (8%), **1d** (5%) and **1f** (*ca.* 35%) were prepared similarly, using the appropriate MOH or Et_3N as base; for **1f**, crystals were only obtained by diffusion of ether into the solution, and lose solvent very readily. **1e** was prepared using 1 mmol CsOH (35%). **1g** was prepared using 1.25 mmol $Cu(NO_3)_2\cdot 3H_2O$ and 1.25 mmol KOH (15%). **1h** was made using 1.75 mmol $Cu(NO_3)_2\cdot 3H_2O$ and 1.75 mmol KOH; diamond-shaped crystals formed after 24 h (15%), but if left in the mother-liquor they redissolved, finally yielding needle-shaped crystals of **1g**.

§ *Crystal data.* **1a**: $C_{88}H_{128}Cu_{12}N_6Na_2O_{58}$, $M = 3006.42$, monoclinic, $P2_1/m$, $a = 12.1348(9)$, $b = 32.0453(18)$, $c = 14.5001(11)$ Å, $\beta = 91.920(8)°$, $V = 5635.4(7)$ Å^3, $T = 200(2)$ K, $Z = 2$, $F(000) = 3064$, $\mu = 2.324$ mm^{-1}; 27890 data, 11000 unique ($R_{int} = 0.0540$), $wR_2 = 0.1341$, $S = 0.872$ (all data), $R_1 = 0.0508$ (6754 with $I \geqslant 2\sigma(I)$).

1b: $C_{88}H_{128}Cu_{12}K_2N_6O_{58}$, $M = 3038.64$, monoclinic, $P2_1/m$, $a = 12.2497(6)$, $b = 32.628(3)$, $c = 14.5421(9)$ Å, $\beta = 92.655(7)°$, $V = 5805.9(7)$ Å^3, $T = 180(2)$ K, $Z = 2$, $F(000) = 3096$, $\mu = 2.320$ mm^{-1}; 25478 data, 10801 unique ($R_{int} = 0.0438$), $wR_2 = 0.0955$, $S = 0.949$ (all data), $R_1 = 0.0357$ (8428 with $I \geqslant 2\sigma(I)$).

1c: $C_{88.5}H_{132}Cu_{12}N_6O_{59.5}Rb_2$, $M = 3137.37$, monoclinic, $P2_1/c$, $a = 35.956(3)$, $b = 12.3567(7)$, $c = 26.9198(18)$ Å, $\beta = 105.403(10)°$, $V = 11531(2)$ Å^3, $T = 200(2)$ K, $Z = 4$, $F(000) = 6348$, $\mu = 3.104$ mm^{-1}; 44621 data, 20031 unique ($R_{int} = 0.0793$), $wR_2 = 0.1624$, $S = 0.809$ (all data), $R_1 = 0.0625$ (8964 with $I \geqslant 2\sigma(I)$).

1d: $C_{90}H_{140}Cs_2Cu_{12}N_6O_{62}$, $M = 3326.38$, hexagonal, $P6_3/m$, $a = 14.7809(7)$, $c = 31.4530(19)$ Å, $V = 5951.1(5)$ Å^3, $T = 200(2)$ K, $Z = 2$, $F(000) = 3352$, $\mu = 2.802$ mm^{-1}; 12459 data, 3854 unique ($R_{int} = 0.0979$), $wR_2 = 0.1593$, $S = 0.806$ (all data), $R_1 = 0.0611$ (1654 with $I \geqslant 2\sigma(I)$).

1e: $C_{83}H_{118}Cs_4Cu_{12}N_8O_{64}$, $M = 3545.97$, hexagonal, $P6_3/m$, $a = 18.7889(8)$, $c = 19.0882(8)$ Å, $V = 5835.8(4)$ Å^3, $T = 200(2)$ K, $Z = 2$, $F(000) = 3592$, $\mu = 3.477$ mm^{-1}; 29318 data, 4641 unique ($R_{int} = 0.0903$), $wR_2 = 0.1411$, $S = 1.253$ (all data), $R_1 = 0.0802$ (3494 with $I \geqslant 2\sigma(I)$).

1f: hexagonal, $P\bar{6}$, $a = 20.7773(16)$, $c = 19.9374(15)$ Å, $V = 7453.8(6)$ Å^3, $T = 200(2)$ K, $Z = 2$. The clusters refine well, but heavily disordered $(NHEt_3)^+$ cations and methanol of solvation (30–35% of total scattering power) have precluded complete refinement.

1g: $C_{192}H_{314}Cu_{30}N_{14}O_{138}$, $M = 6932.77$, triclinic, $P\bar{1}$, $a = 17.912(2)$, $b = 18.034(2)$, $c = 23.367(3)$ Å, $\alpha = 104.864(15)$, $\beta = 90.031(14)$, $\gamma = 103.885(15)°$, $V = 7066.8(15)$ Å^3, $T = 180(2)$ K, $Z = 1$, $F(000) = 3538$, $\mu = 2.300$ mm^{-1}; 55069 data, 25415 unique ($R_{int} = 0.0813$), $wR_2 = 0.1348$, $S = 0.744$ (all data), $R_1 = 0.0504$ (11372 with $I \geqslant 2\sigma(I)$).

1h: $C_{215}H_{414}Cu_{28}N_{12}O_{158}$, $M = 7474.70$, triclinic, $P\bar{1}$, $a = 18.0778(11)$, $b = 22.4167(15)$, $c = 23.3107(15)$ Å, $\alpha = 63.190(5)$, $\beta = 71.862(5)$, $\gamma = 74.133(5)°$, $V = 7913.0(9)$ Å^3, $T = 200(2)$ K, $Z = 1$, $F(000) = 3864$, $\mu = 1.935$ mm^{-1}; 54761 data, 32526 unique ($R_{int} = 0.0586$), $wR_2 = 0.1984$, $S = 1.027$ (all data), $R_1 = 0.0706$ (20633 with $I \geqslant 2\sigma(I)$).

CCDC reference numbers 179671–179677. See http://www.rsc.org/suppdata/cc/b2/b201585b/ for crystallographic data in CIF or other electronic format.

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