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# Synthesis, structure and magnetism of a unique dodecanuclearcopper(II) 'picture frame' held in a 4 × 4 grid-like assembly†

**Craig J. Matthews,*[a] Stuart T. Onions,[a] Gérald Morata,[a] Margarita Bosch Salvia,[a] Mark R. J. Elsegood[b] and Daniel J. Price[c]**

[a] *Department of Chemistry and Physics, Nottingham Trent University, Clifton Lane, Nottingham, UK NG11 8NS. E-mail: craig.matthews@ntu.ac.uk; Fax: +(0)115 848 6636; Tel: +(0)115 848 3137*

[b] *Chemistry Department, Loughborough University, Loughborough, Leicestershire, UK LE11 3TU*

[c] *Department of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ*

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**The synthesis, structure and preliminary magnetic studies of a novel dodecanuclearcopper(II) grid-like assembly are reported.**

The field of supramolecular coordination chemistry has yielded a plethora of transition metal ion containing assemblies, which have contributed to the understanding of self-assembling processes between organic ligands and kinetically labile transition metal ions. Often the topology of the assembly can be predicted in advance when relatively rigid organic ligands are combined with transition metal ions that have a definite coordination preference.[1] However, quite unexpected structures can be formed by combining flexible multidentate ligands with Cu(II) because of the variety of coordination environments it can adopt.[2] In this context we describe the synthesis,‡ structural characterisation§ and magnetic properties of a unique dodecanuclearcopper(II) assembly $[Na \subset Cu_{12}(pd2am\text{-}2H)_8](BF_4)_9{\cdot}21H_2O{\cdot}2CH_3OH$ (**1**) that encapsulates a single sodium cation and is formed through the self-assembly of the flexible multidentate ligand pd2am (Scheme 1) and Cu(II) ions.

The structure of the cation in (**1**) (Fig. 1) can be best described as a dodecanuclearcopper(II) ′picture frame′ assembly and is composed of twelve Cu(II) ions, eight $pd2am^{2-}$ ligands and one encapsulated sodium cation. The ligand $pd2am^{2-}$ adopts two coordination modes (Scheme 1) with respect to the Cu(II) ions; four hexadentate ligands form the cross-section of a 4 × 4 square grid,[3] whilst the remaining four ligands behave in a decadentate fashion and complete the edges of the grid-like arrangement. This is in contrast to the hexadentate coordination mode adopted by $pd2am^{-}$ in the trinuclearnickel(II) chain like assembly $[Ni_3(pd2am\text{-}H)_3H_2O](NO_3)_3{\cdot}2H_2O$ previously reported.[4] The twelve Cu(II) centres are held at the corners and edges of the square grid by two groups of four roughly eclipsed parallel ligands, with π interactions associated with aromatic ring separations of approximately 3.4–4.2 Å, that lie above and below the mean plane of the twelve Cu(II) ions. This results in the formation of a puckered ′frame′ (Fig. 2) consisting of twenty eight atoms; twelve Cu(II) ions, eight μ-O alkoxide and four N–N pyridazine bridging groups around a central cavity, which contains a ′picture′ of a single encapsulated sodium cation. Two different types of Cu(II) centres are found within the structure; four corner Cu(II) centres have a *cis*-$N_4O_2$ pseudo octahedral environment (Cu–O 2.081(8) − 2.302(8) and Cu–N 1.894(11) − 2.314(9) Å) and eight edge Cu(II) centres have a nearly perfect $N_3O_2$ square based pyramidal geometry (Cu-O 1.932(7)–2.239(7) and Cu–N 1.839(10)–2.326(9) Å). In every case the axial ligands are significantly longer (Corner Cu: 2.20–2.31 Å, Edge Cu: 2.13–2.33 Å) than the equatorial ligands

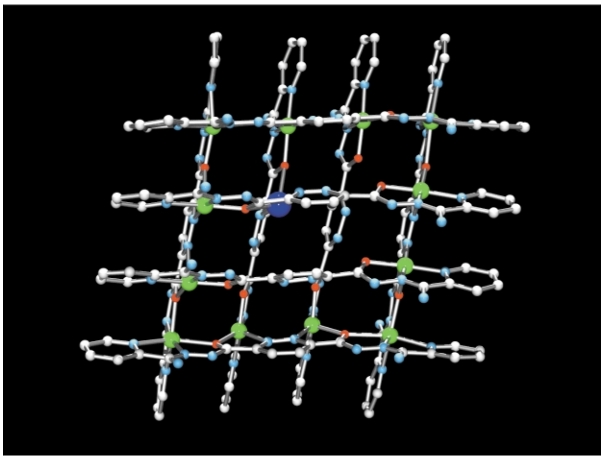


**Fig. 1** POV-Ray structural representation of the cation $[Na \subset Cu_{12}(pd2am\text{-}2H)_8]^{9+}$ in (**1**) (hydrogen atoms omitted for clarity). Silver (C); Red (O); Sky Blue (N); Green [Cu(II)]; Blue [Na(I)].

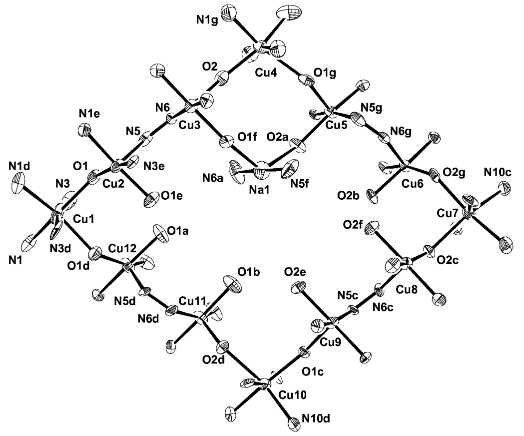
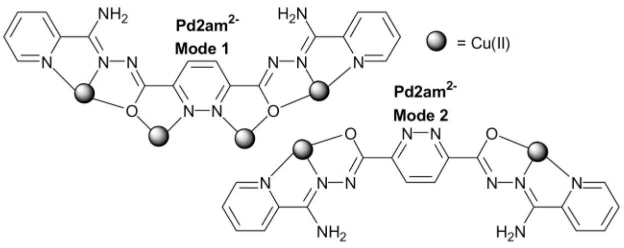


**Fig. 2** Ortep structural representation of the dodecanuclear core. Selected bond lengths [Å] and angles [°]: Corner Cu long bonds: Cu1–O1d 2.234(7), Cu1–N1d 2.199(10), Cu4–N1g 2.273(14), Cu4–O1g 2.302(8), Cu7–N10c 2.314(9), Cu7–O2c 2.271(7), Cu10–N10d 2.277(11), Cu10–O2d 2.258(7); Edge Cu long bonds: Cu2–N5 2.289(10), Cu3–O2 2.230(7), Cu5–O1g 2.226(8), Cu6–N6g 2.326(9), Cu8–N6c 2.286(8), Cu9–O1c 2.239(7), Cu11–O2d 2.131(7), Cu12–N5d 2.220(8); Cu–O–Cu 125.1(4)–141.6(4).



**Scheme 1**

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† Electronic supplementary information (ESI) available: plot of magnetic susceptibility of **1** *versus* temperature. See http://www.rsc.org/suppdata/cc/b2/b210891g/

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(Corner Cu: 1.89–2.14 Å, Edge Cu: 1.84–2.09 Å), which is indicative of the Jahn–Teller distortion often found in Cu(II) coordination compounds. The central cavity is composed of eight $N_{pyridazine}O$ coordination sub-units lying perpendicular to one another forming four $N_2O_2$ tetrahedral coordination pockets. Cu(II) rarely adopts this coordination environment with polypyridyl ligands of this type and this arguably explains the incomplete metal coordination sites found within the cavity of the grid. The single sodium ion found within the central cavity is located at a single position and is not statistically distributed over the four possible sites. The presence of the Na ion in (**1**) has also been confirmed *via* flame photometry and is not believed to play a role in the formation of the grid-like assembly in contrast to the formation of some metallocoronates.[5] The Na ion is encapsulated through the addition of $NaBF_4$ subsequent to the self-assembly process, since precipitation with $NH_4BF_4$ yields a similar grid-like motif.[6] The sodium ion adopts a severely distorted $N_2O_2$ tetrahedral geometry with average Na–O and Na–N bond lengths of 2.39 and 1.83 Å respectively and bond angles in the range of 78.9(4)–174.6(6)°. Adjacent pyridazine N–N and μ–O alkoxide bridged copper–copper separations fall in the range of 3.758–3.826 and 3.575–4.278 Å respectively and Cu–O–Cu angles fall in the range 125.1(4)–141.6(4)°, which are similar to those exhibited for the purely $M(II)_4(\mu\text{-}O)_4$, $M(II)_9(\mu\text{-}O)_{12}$ square grids and $M(II)_5(\mu\text{-}O)_6$ trigonal bipyramids.[7] A roughly square grid with inner core dimensions of 10.93 × 10.82 Å and overall external dimensions of approximately 19.4 × 19.4 Å places this system well into the nanoscale range.

On cooling (**1**) in an applied magnetic field¶ the susceptibility increases monotonically. This field independent behaviour is consistent with a paramagnetic phase down to the lowest experimental temperature of 2 K. Data below 200 K is not well modelled by Curie–Weiss law, but a good fit is obtained for higher temperatures (200–290 K) with $C = 0.367(1)$ cm$^3$ mol$^{-1}$ K (per Cu), $\theta = +16.1(7)$ K. This high temperature moment corresponds to an average *g*-value of 1.98. The deviation from simple paramagnetic behaviour is most evident in the plot (ESI) of the product $\chi T(T)$. On cooling a gradual increase to a broad maximum is observed at about 120 K ($\chi T = 0.41$ cm$^3$ mol$^{-1}$ K), followed by a decrease to a minimum at 14 K ($\chi T = 0.32$ cm$^3$ mol$^{-1}$ K) before increasing as the temperature is further reduced. The sign of the gradient is commonly taken as an indication of the sign of the dominant coupling interaction (negative gradient = ferromagnetic interaction, positive gradient = antiferromagnetic interaction). The presence of both maximum and minimum points to a complex irregular spin state structure. None of the features of the $\chi T(T)$ curve are reproduced by a simple fully-symmetric nearest-neighbour ring model, which varies monotonically for all values of *J*. The inadequacy of this simple approach is not surprising given the complete lack crystallographic symmetry and the variation in Cu–Cu superexchange pathways. A comparison of each Cu geometry and Cu–Cu coupling pathway leads us to suspect that a range of strong antiferromagnetic (Cu1–Cu2, Cu6–Cu7), weaker antiferromagnetic (Cu2–Cu3, Cu5–Cu6, Cu8–Cu9, Cu11–Cu12) and weak to moderate strength ferromagnetic couplings (Cu3–Cu4, Cu7–Cu8, Cu9–Cu10, Cu12–Cu1) are present. However the variation in geometries and metal separations within these coupling groups implies that only a fully realistic model with 12 distinct couplings would be satisfactory and even then coupling values could not be simply ascribed to a particular bond.

In summary, multidentate ligands such as pd2am have previously been employed in the designed assembly approach but the formation of (**1**) further illustrates that it is often difficult to predict the outcome of a self-assembly process that combines ligands of this type with a transition metal ion, such as Cu(II), having a variety of coordination preferences. Nevertheless, such a combination has produced the largest Cu(II) assembly formed exclusively by a linear single stranded ligand, which is also the largest structurally characterised square grid-like assembly reported to date. Ongoing research of analogous flexible ligand systems is currently underway since there is considerable interest in paramagnetic assemblies that display interesting magnetic phenomena.[8]

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## Notes and references

‡ Reaction of ligand pd2am[4] with copper(II) acetate dihydrate (1 : 1 or 3 : 4) in methanol at room temperature for 24 h afforded a clear deep green–brown solution from which a green solid precipitated on addition of a concentrated aqueous solution of $NaBF_4$; this was filtered and recrystallised from aqueous methanol (5/1, v/v). Dark green needle-shaped crystals of (**1**) (65–70% yield) suitable for X-ray structural analysis were formed after standing for a three-week period. Found (vacuum dried sample): C, 33.33; H, 2.97; N, 21.33. Calc. for $[Na \subset Cu_{12}(C_{18}H_{14}N_{10}O_2)_8](BF_4)_9\cdot 21H_2O\text{-}\cdot 2CH_3OH$: C, 33.54; H, 3.12; N 21.43%. $\nu_{max}$/cm$^{-1}$ (Nujol) $\nu = 3425$ ($H_2O$), 3344, 3177 (NH), 1679 (C=O), 1656 (C=N) and 1062 (py). $\lambda_{max}$/nm (Nujol): 680, (DMF): 680 (595).

§ *Crystal data* for (**1**): $C_{146}H_{172}B_9Cu_{12}F_{36}N_{80}NaO_{39}$, $U = 5238.40$, triclinic, space group $P1$ (No.2), $a = 21.3049(11)$, $b = 21.3272(11)$, $c = 24.7637(13)$ Å, $\alpha = 75.286(2)$, $\beta = 77.638(2)$, $\gamma = 65.984(2)°$, $V = 9862.5(9)$ Å$^3$, Z = 2, $\mu$(Mo-K$\alpha$) = 1.395 mm$^{-1}$, $T = 150(2)$ K. 74145 reflections measured, 25752 unique ($R_{int} = 0.0689$). Final $wR2 = 0.2543$ for all unique data, conventional $R = 0.0839$ on $F$ values of 13846 reflections with $F_o^2 > 2\sigma(F_o^2)$; 2864 parameters; 1317 restraints. H atoms included for Ar*CH* only. 20 water molecules and 8 of the $BF_4^-$ anions were modelled as point atoms, some disordered. It was not possible to fully resolve the last anion, though a central B atom with surrounding electron density peaks was seen in difference maps. Platon Squeeze[9] was used to model the remaining electron density as diffuse regions. The formula probably varies in water and methanol content from crystal to crystal. Programs: Bruker AXS SMART (control), SAINT (integration) and SHELXTL (structure solution and refinement) and local programs. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 188180. See http://www.rsc.org/suppdata/cc/b2/b210891g/ for crystallographic files in CIF or other electronic format.

¶ Magnetisation studies were performed with an MPMS Quantum Design SQUID magnetometer. A diamagnetic correction of $-182 \times 10^{-6}$ cm$^3$ mol$^{-1}$ was estimated from Pascal′s constants.[10] Field cooled dc magnetisation measurements were run between 2 and 290 K in fields of 100 and 500 G, field dependent measurements were also performed at both 10 and 290 K using fields up to 55 000 G.

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