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A new type of oxygen bridged Cu^{II}_{36} aggregate formed around a central $\{KCl_6\}^{5-}$ unit†

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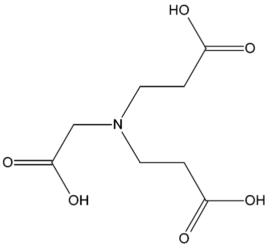
A magnetically coupled Cu^{II}_{36} aggregate forms around a potassium chloride unit.

The synthesis of high nuclearity aggregates made up of paramagnetic metal centres is currently the focus of much research with a goal of producing species with non-zero spin ground states. In some cases these systems display slow relaxation of the magnetisation to give hysteresis effects, leading to the label of "Single Molecule Magnet" (SMM) with $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ as the best-known example.[1,2] One strategy utilises relatively rigid ligands in order to direct structure.[3] However, the synthesis of magnetically interesting aggregates (including the Mn_{12} series) still largely results from what can be termed "serendipitous self-assembly".[4] Our synthetic strategy[5] uses polydentate amino-carboxylic acid chelating ligands (L) to trap intermediate species of general formula $\{M_xL_n(O)_y(OR)_z(HOR)_p\}^{\pm b}$ from water or alcohol solutions. This results in aggregates possessing a variety of superexchange pathways provided by the different sorts of bridging species and can result in high spin molecules.[5] We have recently been applying this strategy to a series of Cu(II) systems using the ligand carboxyphenyliminodiacetic acid[5b–d] where a nonanuclear aggregate and a series of compounds built up from a dodecanuclear aggregate prove to have non-zero spin ground states. In the presence of the ligand (nitrilodipropionic)acetic acid, H_3ndpa, (Scheme 1) in aqueous solution we found that tetranuclear species formed and these have dominant ferromagnetic interactions.[5e] We find that if we instead use methanol as solvent and potassium hydroxide as base we can reproducibly isolate small amounts of single crystals containing the Cu^{II}_{36} aggregates $[Cu^{II}_{36}(\mu_3\text{-}OH)_{32}(\mu\text{-}OR)_8Cl_6(ndpa)_8(H_2O)_5\{KCl_6\}]^{3-}$ (R is H or Me).‡

The crystals turn out to fall into two categories depending on whether reagent grade or absolute methanol is used. Crystals of **1** form in solutions of reagent grade methanol over a period of two weeks whereas crystals of **2** from absolute methanol could only be isolated after 2 months. The crystal structures§ of the two compounds reveal that whilst the core structures are essentially identical, in the case of **2**, there are two copper(I) centres also attached to the aggregate which presumably result from the ability of Cu(II) to oxidise alcohols.[6] The crystal structure analysis and magnetic behaviour are consistent with this assignment.

The structure of the Cu^{II}_{36} aggregate in **1** is shown in Fig. 1. Since the structure is rather complicated, in Fig. 2 it is shown broken down into its concentric structural motifs. An intriguing feature of the structure of the Cu^{II}_{36} aggregate (Fig. 1) is the central $\{KCl_6\}^{5-}$ fragment which appears to act as a sort of scaffold around which an inorganic hydroxo/methoxo-bridged Cu_{28} framework is constructed. Finally, this framework is encapsulated by $\{Cu(npda)Cl\}^{2-}$ and $\{Cu_2Cl(npda)_2\}^{3-}$ units, which inhibit further cluster growth (Fig. 2).



Scheme 1 H_3ndpa.

The copper centres are linked in a variety of ways and display 5 and 6 coordinate stereochemistries precluding a detailed analysis of the magnetic behaviour. The χT *vs.* T and χ^{-1} *vs.* T plots of polycrystalline **1** and **2** (Fig. 3) show a Curie–Weiss behaviour

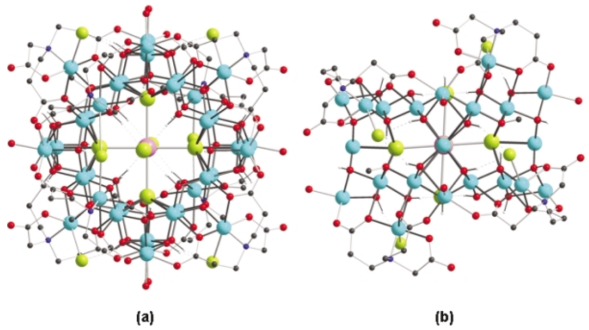


Fig. 1 The Cu^{II}_{36} aggregate. In (a) the crystallographic 2-fold axis is vertical, (b) is the view down this axis. Cu light blue; K pink; Cl green; O red; N dark blue; C black.

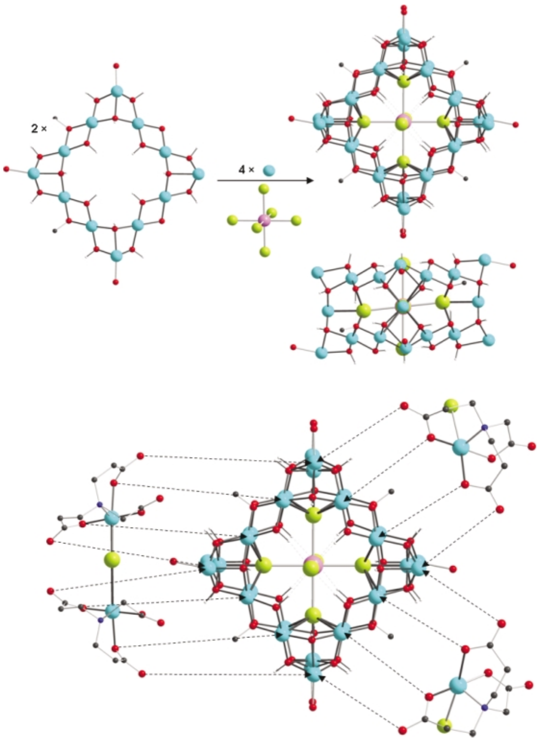


Fig. 2 Breakdown of the Cu_{36} aggregate into its constituent structural motifs: top, the central $\{KCl_6\}^{5-}$ unit and the O-bridged Cu_{28} framework (views as for Fig. 1) and bottom, the encapsulating copper/ligand units.

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† Electronic supplementary information (ESI) available: magnetic data as χ *versus T* and EPR data. See http://www.rsc.org/suppdata/cc/b4/b403735a/

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above *ca.* 50 K, with $C = 15.3$ emu K mol^{-1}, $\theta = -41$ K for **1** and $C = 16.0$ emu K mol^{-1}, $\theta = -39$ K for **2**. The Curie constants are consistent with 36 Cu^{II} centres, with g-values of 2.13 for **1** and 2.18 for **2**, in agreement with the EPR measurements, with the negative Weiss constants indicative of dominant antiferromagnetic interactions. Below about 50 K, the magnetic data deviate significantly from Curie–Weiss behaviour as a result of the molecular nature of the compounds. The field dependence of the magnetisation measured at 1.8 K shows that as the field increases up to 7 T the magnetisation rises smoothly without reaching saturation up to 14.2 μ_B for **1** and 13.3 μ_B for **2**. This result suggests that low lying excited spin states are significantly populated even at 1.8 K. It is thus not possible to assign a ground spin state from these data.

Although the yields of crystals for this system are rather low, the aggregate is reproducible and displays the rather unusual feature of an organic–inorganic cluster hybrid forming around a purely inorganic potassium chloride template. Although anion templated self-assembled systems are well known,[7] we are not aware of any other aggregate forming around a potassium chloride nucleus. Whilst we do not know whether the $\{KCl_6\}^{5-}$ scaffold arises from the arrested formation of KCl or if the chloride bridged aggregate captures a K$^+$ ion acting like a crown ether, we note that the crystallisation solutions must first be filtered to remove KCl (identified from X-ray powder diffraction) which begins to form on mixing the reagents. Adding a few drops of water to the system results in the formation of one of the tetramers we previously reported.[5e] Experiments using different MOH bases did not produce any similar compounds and neither did the use of other copper(II) salts, such as the bromide. We thus conclude that this particular set of conditions allows for the formation of small quantities of this novel aggregate which also represents along with the compound of Abedin, *et al.*[3] the largest copper(II) cluster so far reported.

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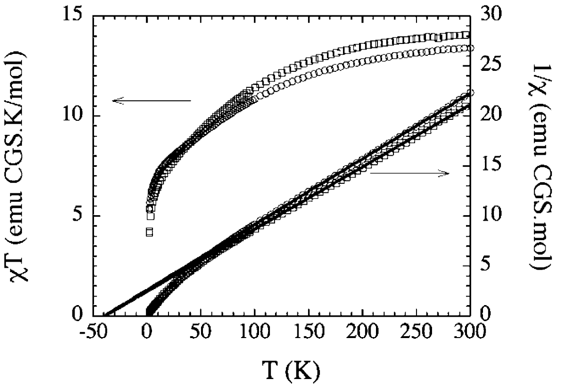

Fig. 3 Magnetic behaviour for **1** (open circles) and **2** (open squares). Solid lines are best fit to a Curie–Weiss law.

Notes and references

‡ **1** $\{K_4(\mu\text{-MeOH})_4\}[Cu^{II}_{36}(\mu_3\text{-OH})_{32}(\mu\text{-OH})_4(\mu\text{-OMe})_4Cl_6(ndpa)_8(H_2O)_5\{KCl_6\}]\cdot Cl\cdot 16MeOH$

H$_3$ndpa (0.055 g, 0.25 mmol) and KOH (0.056 g, 1 mmol) dissolved in MeOH (20 ml) were added with stirring to $CuCl_2\cdot 2H_2O$ (0.170 g, 1 mmol) in MeOH (20 ml). After filtration, slow evaporation of the resulting pale yellow–green solution gave pale blue square shaped crystals in 8% yield of **1** after 2 weeks. Found: C 17.23, H 3.46, N 1.67; calc. for $C_{88}H_{218}N_8O_{113}Cu_{36}Cl_{13}K_5$: C 17.26, H 3.32, N 1.83.

2 $\{Cu^{I}_2K_4Cl_3(H_2O)_3\}[Cu^{II}_{36}(\mu_3\text{-OH})_{32}(\mu\text{-OH})_5(\mu\text{-OMe})_3Cl_6(ndpa)_8(H_2O)_4\{KCl_6\}]\cdot 22MeOH$

H$_3$ndpa (0.055 g, 0.25 mmol) and KOH (0.056 g, 1 mmol) dissolved in absolute MeOH (20 ml) were added with stirring to $CuCl_2\cdot 2H_2O$ (0.170 g, 1 mmol) in absolute MeOH (20 ml) and left to stir for a further 30 min. After filtration, slow evaporation of the resulting green solution resulted in pale green–blue rectangular shaped crystals of **2** after 2 months. Yield 10%. Found: C 14.65, H 2.90, N 1.81; calc. for $C_{71}H_{176}Cl_{15}Cu_{38}K_5N_8O_{99}$ (corresponds to the crystallographic formula with the loss of 17 MeOH) : C 14.71, H 2.74, N 1.91

§ *Crystal data*. **1**: $C_{88}H_{202}Cl_{13}Cu_{36}K_5N_8O_{113}$, $M = 6124.37$ g mol^{-1}, monoclinic, $C2/m$, $a = 28.678(3)$, $b = 20.6184(13)$, $c = 16.8709(16)$ Å, $\beta = 105.883(11)°$, $V = 9594.9(14)$ Å^3, $Z = 4$, $\rho_{calc} = 2.12$ Mg m^{-3}, $F_{000} = 6100$, μ(Mo–Kα) = 4.284 mm^{-1}; 18179 data measured (3.3° < 2θ < 54.7°), 9294 unique ($R_{int} = 0.1134$). 635 parameters, 7 restraints, $wR_2 = 0.3338$, $S = 1.023$ (all data), $R_1 = 0.1081$ (4417 data with $I > 2\sigma(I)$). All non-H atoms anisotropic except disordered methanol solvent and chloride counterion. The final R-factors reflect disorder and poor crystal quality. **2**: $C_{80}H_{220}Cl_{15}Cu_{38}K_5N_8O_{120}$, 6424.56 g mol^{-1}, triclinic, $P\bar{1}$, $a = 17.2684(13)$, $b = 17.3396(13)$, $c = 18.4210(13)$ Å, $\alpha = 75.531(1)$, $\beta = 70.208(1)$, $\gamma = 79.806(1)°$, $V = 4999.4(6)$ Å^3, $Z = 1$, $\rho_{calc} = 2.11$ Mg m^{-3}, $F_{000} = 3168$, μ(Mo–Kα) = 4.348 mm^{-1}. 24084 data measured (3.2° < 2θ < 56.1°), 21206 unique ($R_{int} = 0.0544$). 1185 parameters, 11 restraints, $wR_2 = 0.1622$, $S = 0.982$ (all data), $R_1 = 0.0639$ (9383 data with $I > 2\sigma(I)$). All non-H atoms anisotropic except disordered methanol solvent. The assignment of the trigonally-coordinated Cu(19) to a +I oxidation state is consistent with Cl–Cu–Cl angles 154.9(1), 105.3(1), 99.8(1)° (sum = 360.0°) and the Cu–Cl bond lengths of 2.172(4), 2.217(3) and 2.457(3) Å which compare well with the Cu^{I}–Cl distances (2.346 Å) in CuCl.

CCDC 213431 and 213432. See http://www.rsc.org/suppdata/cc/b4/b403735a/ for crystallographic data in .cif or other electronic format.

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