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Circular serendipity: *in situ* ligand transformation for the self-assembly of an hexadecametallic [Cu^{II}₁₆] wheel†

Andreas K. Kostopoulos,^a Athanassios D. Katsenis,^a Jamie M. Frost,^b
Vadim G. Kessler,^c Euan K. Brechin^{*b} and Giannis S. Papaefstathiou^{*a}

A [Cu^{II}₁₆] wheel was isolated serendipitously from the reaction of acetylacetonate dioxime with copper(II) chloride and lanthanide ions in a reaction initially designed to produce heterometallic 3d–4f cages. The ligand has been transformed *in situ* to three different forms, all found within the [Cu₁₆] wheel, with the original ligand completely absent.

Synthetic methodologies for the construction of polymetallic cages of paramagnetic metal ions have (rightly) always spanned the entire spectrum from serendipity to designed assembly.¹ There is clear method in the madness of the former approach: the choice of metal dictates the nature of the magnetic properties of the resulting cluster, and careful thought is exercised in ligand design so that metal ions of a particular type, oxidation state and geometry can be linked in a particular fashion. It is the flexibility in the coordination of both metal and ligand, and the presence of (templating) hydroxide or oxide ions, that renders absolute structure prediction difficult, even if the building blocks – the small fragments dictating topology – are known. Perhaps it is this serendipity that often sees beautiful and novel structural types remaining un referenced by those outside the community, but the sheer variety and aesthetically pleasing nature of these molecules – beyond the imagination of the humble scientist – is undeniable and reason enough to justify the approach. Such examples include, but are not limited to, the spectacular [Mn₈₄] torus,² the [Mn₃₂] double-decker wheel,³ the [Fe₁₇] all-ferric analogue of magnetite obtained from the simple dissolution of FeBr₃ in wet pyridine,⁴ the chiral [Er₆₀]⁵ stabilized by eight μ₆-CO₃²⁻ ions derived from ligand decomposition, the giant

[Cu₁₇Mn₂₈]⁶ cage comprising six formates derived from the hydrolysis of the solvent (DMF), the enormous [Fe₆₄]⁷ and [Fe₁₆₈]⁸ cubic-shaped cages, the [Fe₃₀] icosidodecahedron encapsulated inside a {Mo^{VI}₇₂Fe^{III}₃₀} POM – a finite-size version of a Kagomé lattice,⁹ and the [Na₄Mn₄₀] and [Mn₄₄] loop-of-loops.¹⁰ Many in the molecular magnetism community would also argue that the most ‘*magnetically interesting*’ complexes of recent times also have their origins in serendipity. The structures of the molecular magnets Mn₁₂, Fe₈, Fe₄, Ni₄, Mn₄, Mn₆, and Cr₇M families (to name but a few) for example, could not have been predicted, but thorough exploitation thereafter has seen many fascinating physical properties uncovered and exploited.¹¹

The level of structural control over reaction product(s) is decreased yet further when the ligand(s) undergo(es) *in situ* metal-assisted transformation(s). Di-2-pyridyl ketone (py₂CO), for example, is known to undergo metal-assisted transformations, with more than ten different forms of py₂CO having been identified.¹² In some cases, two different forms of py₂CO have been found within the same cluster.¹³ Indeed there are a number of polynuclear metal complexes comprising two different forms of a ligand obtained by *in situ* metal-assisted transformations with the initially used ligand either present¹⁴ or absent.^{13,15}

Herein, we present an example of such serendipity in the form of the first example of a polynuclear metal complex, namely the [Cu₁₆(L¹)₄(L²)₈(L³)₈]·8H₂O (1·8H₂O)[†] wheel, comprising three different forms of acetylacetonate dioxime (acacdoH₂, Scheme 1), in which the initially employed ligand (acacdoH₂) is absent. Indeed, our initial idea was to utilize acacdoH₂ for the synthesis of heterometallic 3d–4f clusters acting as either SMMs or Magnetic Refrigerants.

To this end, we reacted CuCl₂·2H₂O with acacdoH₂ in EtOH, to obtain a bright, light green solution. If this solution remains undisturbed, bright green X-ray quality single-crystals of [Cu₂Cl₄(acacdoH₂)₂]² are obtained in 75% yield; addition of an aqueous solution of Ln(MeCO₂)₃·xH₂O (Ln = Nd, Gd, Er) into the above solution followed by gentle heating (~40–50 °C) results in a clear dark green solution. Slow evaporation of the latter affords dark green X-ray quality single-crystals of 1·8H₂O in

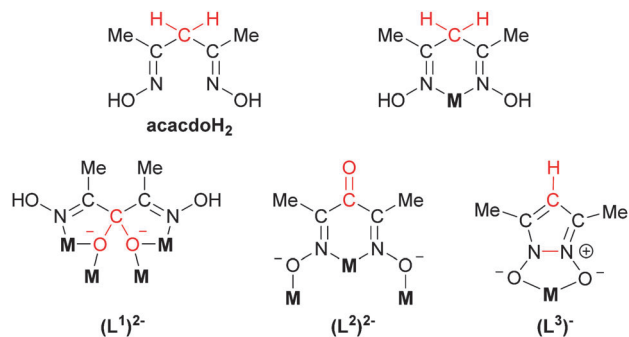
^a Laboratory of Inorganic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, 157 71 Zografou, Greece. E-mail: gspapaef@chem.uoa.gr; Fax: +30 210 727 4782; Tel: +30 210 727 4840

^b EaStCHEM School of Chemistry, The University of Edinburgh, David Brewster Road, Edinburgh, EH9 3FJ, UK. E-mail: ebrechin@staffmail.ed.ac.uk; Fax: +44 (0)11 275 4598; Tel: +44 (0)131 650 7545

^c Department of Chemistry, Swedish University of Agricultural Sciences, Box 7015, 750 07 Uppsala, Sweden

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Scheme 1 Ligands discussed in the text and their coordination modes.

moderate yields (28–37%, depending on the lanthanide ion). Although the lanthanide ion does not appear in the final product, its presence in the reaction mixture is essential since reactions in its absence do not lead to complex **1**. Addition of H₂O or aqueous solutions of MeCO₂M·xH₂O (M⁺ = NH₄⁺, Li⁺, Na⁺ or K⁺) or M'(MeCO₂)₂·xH₂O (M' = Zn^{II}, Cu^{II}, Ni^{II}, Co^{II} or Mn^{II}) instead of Ln(MeCO₂)₃·xH₂O does not lead to complex **1**.

Complex **2** crystallizes in the monoclinic space group *C2/c*. It comprises a Cu(μ₂-Cl)₂Cu core with a Cu··Cu separation of 3.608 Å (Fig. 1). The two halves of the dimer are related by a crystallographic two-fold axis. The Cu(μ₂-Cl)₂Cu unit is essentially planar with the Cu and Cl ions deviating from the least-squares plane by 0.083 Å. The geometry around the Cu ions is best described as distorted square pyramidal ($\tau = 0.17$). The basal plane contains two *cis* N atoms from the acacdoH₂ ligand and two *cis* Cl ions, with the apical site occupied by the Cl2 ion from the other monomer unit. Two intramolecular hydrogen bonds between the

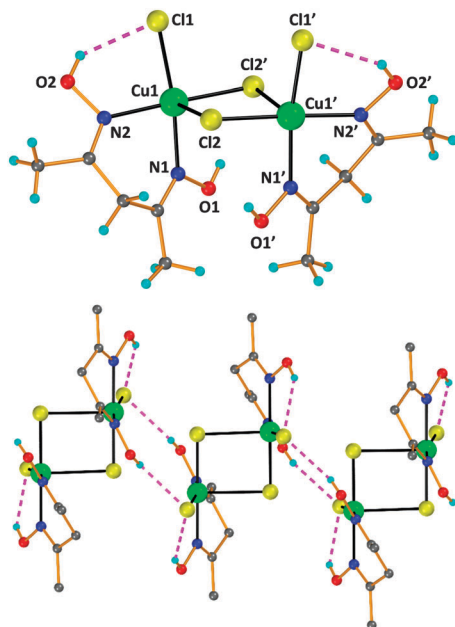


Fig. 1 The structure of **2** (top) and its hydrogen-bonded chain along *c* (bottom). Most hydrogen atoms have been omitted for clarity. Symmetry code: (') 1 - *x*, *y*, 1.5 - *z*. Colour code: Cu: green, O: red, N: blue, Cl: yellow, C: grey, H: cyan.

oximic OH groups and the terminal Cl1 ions stabilize the dimer. The dimers are further hydrogen bonded through the second oximic OH and the terminal Cl1 ion to form a 1D H-bonded chain along the crystallographic *c* axis. A salient feature of this structure is that both terminal Cl ions are on the same side of the Cu(μ₂-Cl)₂Cu plane. Indeed, this is the second example of a molecule in which two terminal Cl ions in a [LClCu(μ₂-Cl)₂CuL] (L = *N,N*-chelate ligand) dimer reside on the same side of the [Cu₂] plane.¹⁶

Complex **1** crystallizes in the tetragonal space group *P4/nnc*. The asymmetric unit comprises two Cu ions, one (L³)⁻, one (L²)²⁻ and half a (L¹)²⁻ ligand (Fig. 2 and Scheme 1). The two Cu ions (Cu1 and Cu2) are bridged by one alkoxide (RO⁻) and an oximato (N-O⁻) group with a Cu··Cu separation of 3.253 Å. Two such dimers are related by a crystallographic two-fold axis

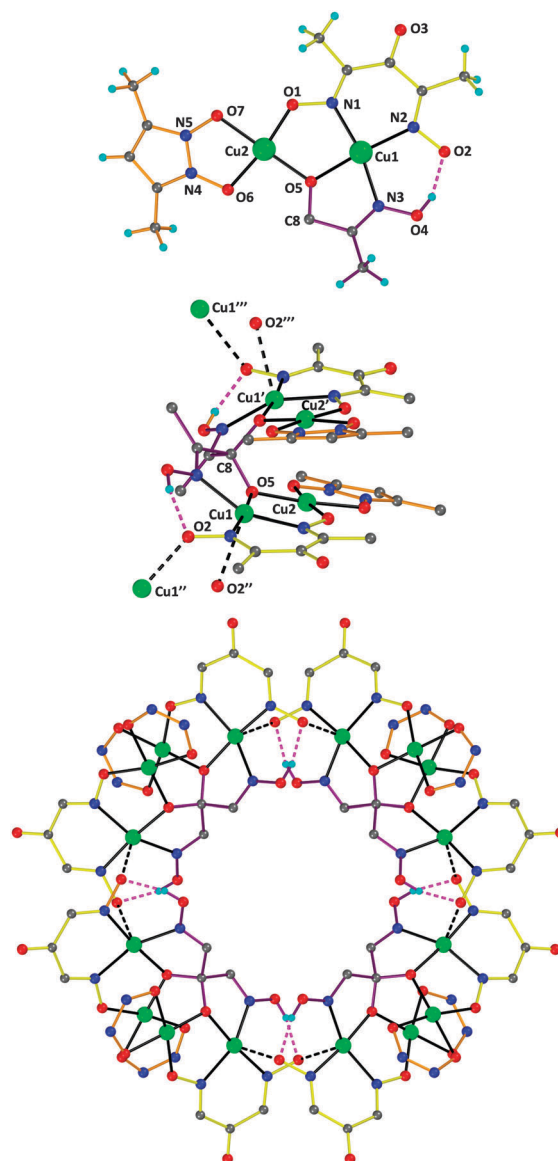


Fig. 2 The asymmetric unit of **1** (top), the [Cu₄] assembly showing the connections to neighbouring [Cu₄] units (middle) and the [Cu₁₆] wheel (bottom). Symmetry codes: (') 0.5 - *y*, 0.5 - *x*, 0.5 - *z*; (') 1.5 - *x*, *y*, 0.5 - *z*; (') 0.5 - *y*, -1 + *x*, *z*. Colour code: same as in Fig. 1.



passing through C8 of ligand $(L^1)^{2-}$ to form a tetranuclear assembly with formula $[Cu_4(L^1)(L^2)_2(L^3)_2]$. Ligand $(L^1)^{2-}$ which is the hydrate of the oxidized form of $acacdoH_2$ bridges all Cu ions within the tetranuclear assembly through the deprotonated hydroxyl groups adopting the $\mu_4-\eta^1:\eta^2:\eta^2:\eta^1$ coordination mode; the oximic OH groups remain protonated and are hydrogen bonded to the neighbouring deprotonated oximate O2 atoms of $(L^2)^{2-}$ which is the oxidized form of $acacdoH_2$. The latter, $(L^2)^{2-}$, chelates Cu1 through the two oximate N1 and N2 atoms and bridges Cu2 through the deprotonated oximate O1 atom adopting the $\mu_2-\eta^1:\eta^1:\eta^1$ coordination mode. The monoanion $(L^3)^-$ simply chelates Cu2. The second deprotonated oximate O2 atom of $(L^2)^{2-}$ is weakly bound to a Cu1 from a neighbouring tetranuclear assembly $[Cu_1-O_2(1.5-x, y, 0.5-z) = 2.548 \text{ \AA}]$ to form the hexadecanuclear wheel $[Cu_4(L^1)(L^2)_2(L^3)_2]_4$. The overall coordination mode of $(L^2)^{2-}$ is thus $\mu_3-\eta^1:\eta^1:\eta^1$. The geometry around Cu1 is best described as distorted square pyramidal ($\tau = 0.32$). The basal plane contains two *cis* N atoms from the $(L^2)^{2-}$, the oximic N3 atom and the O5 atom from the hydrate $(L^1)^{2-}$, with the apical site occupied by the oximate O2 ($1.5-x, y, 0.5-z$) atom of $(L^2)^{2-}$ from a neighbouring $[Cu_4]$. Cu2 is in a distorted square planar coordination environment, being chelated by two *cis* O atoms from $(L^3)^-$, the oximate O1 atom and the O5 atom from the hydrate $(L^1)^{2-}$. In the lattice, the molecules of **1** pack in off-set rows along the *a* and *b* axes having their $[Cu_{16}]$ mean-planes parallel along the *c* axis with separations of 8.245 Å and 16.490 Å as shown in Fig. 3. Complex **1** joins a small family of eleven $[Cu_{16}]$ clusters,^{17,18} three of which are cyclic (wheels or wheel-like).¹⁸

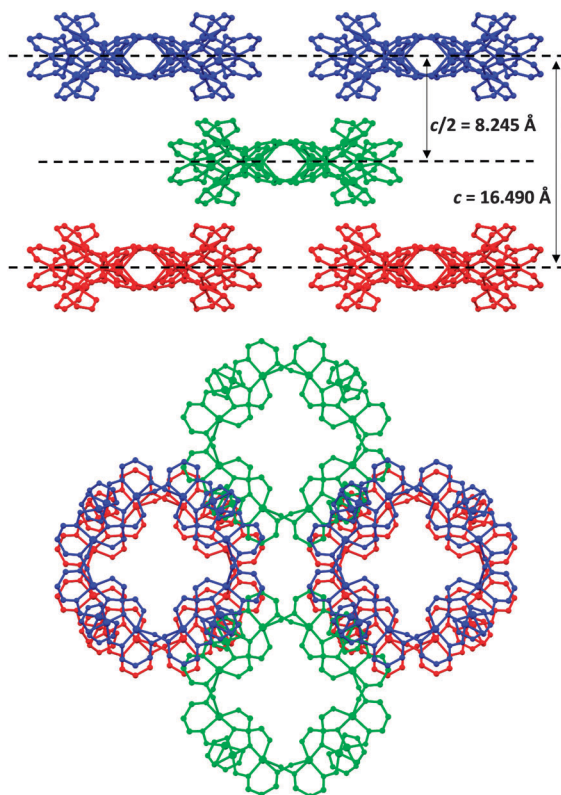


Fig. 3 The packing of complex **1** along *a* (top) and *c* (bottom) axes.

Although the transformation of $acacdoH_2$ to $(L^1)^{2-}$, $(L^2)^{2-}$ and $(L^3)^-$ was not anticipated, the formation of these anions can be fully rationalized. Methylene moieties ($-CH_2-$) attached to electron withdrawing groups can be aerially oxidized to the corresponding ketones with or without the presence of metal ions.¹⁹ In our case the oxidized form of $acacdoH_2$, $(L^2)^{2-}$, is probably metal-assisted since the 1H -NMR spectra of pure $acacdoH_2$ in D_2O or CD_3OD remains unchanged for several months. Ketones, like $(L^2)^{2-}$ may undergo nucleophilic addition of H_2O to the carbonyl C atom to form the respective hydrate, $(L^1)^{2-}$. The electrophilic character of the carbonyl C atom may be increased by coordination of the carbonyl O atom to a metal ion (direct polarization) or by coordination of the oximic N or O atoms (induced polarization). Such metal-assisted transformations occur often in py_2CO chemistry.^{12,13} Alternatively, $acacdoH_2$ may first oxidize to the hydrate (H_2L^1) which upon dehydration forms the ketone form H_2L^2 . Pyrazole *N*-oxides, like $(L^3)^-$, have been previously reported to form by metal-assisted transformations of β -diketone dioximes.²⁰

Dc magnetic susceptibility data for **1** were recorded between 300 and 5 K in an applied field of 1.0 kG. The plots of $\chi_M T$ and χ_M versus *T* for **1** are shown in Fig. 4. The $\chi_M T$ value at 300 K is $2.87 \text{ cm}^3 \text{ K mol}^{-1}$ and is significantly lower than the expected spin-only ($g = 2$) value for 16 non-interacting Cu^{II} centres of $6 \text{ cm}^3 \text{ K mol}^{-1}$, suggesting the presence of dominant and strong antiferromagnetic exchange. The $\chi_M T$ product decreases rapidly upon cooling to a value of $\sim 0.44 \text{ cm}^3 \text{ K mol}^{-1}$ at 100 K and then decreases smoothly until 5 K ($0.17 \text{ cm}^3 \text{ K mol}^{-1}$). The low-temperature data denote the presence of $\sim 2.8\%$ paramagnetic impurity per Cu ion. Considering the structural parameters a 2-*J* model (inset in Fig. 4) was utilised to fit the experimental data which considers the $[Cu_{16}]$ wheel as four weakly interacting $[Cu_4]$ moieties (the magnetic $d_{x^2-y^2}$ orbitals of Cu1 and Cu1' belonging to neighbouring $[Cu_4]$ units being approximately parallel to each other).²¹ In this model, J_1 denotes the exchange pathway between the Cu^{II} ions (Cu1...Cu2) bridged by one alkoxide (RO^-) and an oximate ($N-O^-$) group, and J_2 the exchange pathways between the Cu^{II} ions (Cu1...Cu1', Cu1...Cu2', Cu2...Cu1' and Cu2...Cu2') bridged by the (CO_2) moiety of the hydrate $(L^1)^{2-}$.

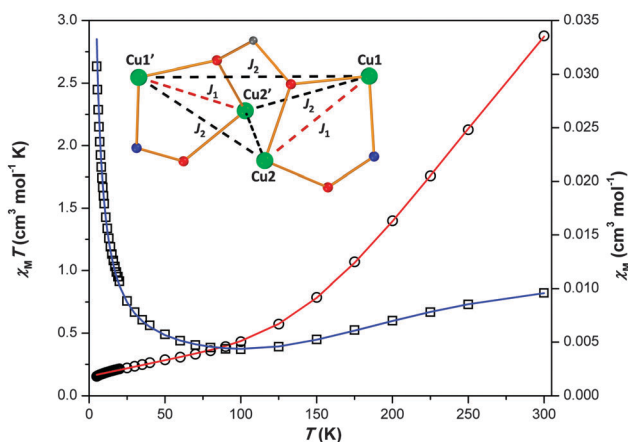


Fig. 4 $\chi_M T$ (○) and χ_M (□) vs. *T* plots for complex **1**. The solid lines represent the best fits of the experimental data – see text for details.



The experimental data were satisfactorily fitted using the program PHI²² employing the spin Hamiltonian in eqn (1). The best fit (solid lines in Fig. 4) gave the following parameters: $J_1 = -241.88 \text{ cm}^{-1}$, $J_2 = -3.42 \text{ cm}^{-1}$, $g = 2.18$, $zJ = -0.027 \text{ cm}^{-1}$, and an impurity = 0.1 (*i.e.* 2.5% per Cu atom) (zJ describes the intermolecular interactions in a mean field approximation). For such a $[\text{Cu}_4]$ model this results in a spin ground state $S = 0$, with the first excited state ($S = 1$) located $\sim 483 \text{ cm}^{-1}$ above the ground state. The large difference in the magnitude of J_1 and J_2 is expected: the former describes a one alkoxo, one oximato bridge which is known to provide very effective superexchange,²³ while the latter is a three atom exchange pathway (Cu–O–C–O–Cu) mediated by the hydrate moiety known to mediate weak exchange.²⁴

$$\hat{H}_{\text{ex}} = -2J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_3 \cdot \hat{S}_4) - 2J_2(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_4) \quad (1)$$

Our initial forays into the use of acetylacetone dioxime (acacdoH₂) as a ligand for the synthesis of polynuclear metal complexes has afforded a dinuclear Cu^{II} complex and an aesthetically pleasing hexadecanuclear Cu^{II} wheel. The acacdoH₂ ligand has been transformed into three different species, all of which are found within the wheel. To the best of our knowledge, the $[\text{Cu}_{16}]$ is the first polynuclear metal complex comprising three different forms of a ligand that has undergone metal-assisted transformation, without the originally employed ligand being present in the reaction product. It is becoming apparent that, given the rich reactivity of acacdoH₂,²⁰ this ligand may play a major role in the synthesis of a variety of novel polynuclear metal complexes in the future. Indeed, when comparing the coordination chemistry of acacdoH₂ with that of py₂CO, which has afforded numerous metal-assisted transformations in approximately 40 years of research,^{12,13} it is self-evident that the former has the potential to surpass the cluster-forming ability of the latter.

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