

# An alcoholysis route to a Cu<sub>16</sub> cluster, and the influence of the alcohol†

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A systematic investigation of the alcoholysis of copper(II) pivalate (piv<sup>-</sup>) solutions has led to a series of Cu<sub>2</sub>, Cu<sub>6</sub>, and Cu<sub>16</sub> products, depending on the alcohol used as solvent. When Pr<sup>n</sup>OH or Bu<sup>n</sup>OH was employed, the products were the clusters [Cu<sub>16</sub>O<sub>4</sub>(OH)<sub>4</sub>(OR)<sub>8</sub>(piv)<sub>12</sub>(ROH)] (R = Pr<sup>n</sup>, Bu<sup>n</sup>) that are almost isostructural. The Cu<sub>16</sub> clusters are antiferromagnetically-coupled with an *S* = 0 spin ground state.

There are various reasons for the current interest by many groups around the world in the synthesis and study of high nuclearity 3d molecular metal clusters.<sup>1</sup> Among these is the search for various nuclearity oxide-bridged metal carboxylate clusters to model *M<sub>x</sub>* sites in biomolecules, including understanding the growth of the core of the ferritin protein,<sup>2</sup> the synthesis of the Mn site of water oxidation within the photosynthetic apparatus of green plants and cyanobacteria,<sup>3</sup> and the modeling of the Cu site within the complicated membrane protein (αβγ) methane monooxygenase.<sup>4</sup> Other reasons for this interest are varied, and include the aesthetically pleasing structures that many such molecular clusters possess<sup>5</sup> and the search for compounds with interesting magnetic properties.<sup>6</sup>

Crucial to such efforts and others is the continuing development of new synthetic procedures to high nuclearity species. However, there is no obvious and guaranteed route to such species. Much work over many years has been invested in exploring different strategies, and there are now several empirically established approaches to a variety of species.<sup>7</sup> Among these is the use of hydrolysis and alcoholysis reactions.<sup>7b</sup> In intermediate or high oxidation state Mn<sup>III</sup>, Mn<sup>III/IV</sup>, Mn<sup>IV</sup>,<sup>7b</sup> and Fe<sup>III</sup> chemistry, for example, alcoholysis in the presence of carboxylate groups, with or without chelating ligands, has proven to be a very useful method for obtaining both oxo and hydroxo-containing clusters. Another, more standard, approach, frequently applied in lower oxidation state M<sup>II</sup> (M = Cu, Co, Ni, *etc.*) chemistry, is to use chelates containing alcohol, pyrazoles, and/or 2-pyridyl oxime groups, since alkoxides, pyrazolates and oximates are good bridging groups and thus foster formation of polynuclear products.<sup>7,9</sup> In copper(II) cluster chemistry, for example, Raptis and co-workers have reported Cu<sub>18</sub>, Cu<sub>27</sub> and Cu<sub>31</sub> complexes bearing pyrazolato groups,<sup>10</sup> while Powell et al have prepared Cu<sub>36</sub> and Cu<sub>44</sub> cage-like clusters from the use of various carboxyphenyliminodiacetic acid

chelating/bridging ligands;<sup>11</sup> the latter Cu<sub>44</sub> complex is currently the highest-nuclearity Cu(II) cluster reported in the literature.<sup>11b</sup>

In contrast to the above well-established, chelate-induced formation of Cu<sup>II</sup><sub>*x*</sub> clusters, there is a lack of a systematic investigation of alcoholysis using simple alcohols, rather than alcohol-containing chelates, in copper(II) carboxylate chemistry.<sup>12</sup> We have therefore decided to explore this and have chosen bulky pivalate as the representative carboxylate to minimize the possibility of polymeric products. We have sought to identify to what extent variation of the alcohol identity might yield different nuclearity products with interesting structural motifs. We have employed the series MeOH, EtOH, Pr<sup>n</sup>OH and Bu<sup>n</sup>OH under otherwise identical conditions, and have identified a systematic difference in product as a function of the alcohol. It should be added that some Cu(II) clusters with alkoxide and carboxylate groups are already in the literature, such as [Cu<sub>4</sub>(OMe)<sub>4</sub>(O<sub>2</sub>CMe)<sub>4</sub>]<sup>13a</sup> and [Cu<sub>6</sub>(OEt)<sub>6</sub>(piv)<sub>6</sub>]<sup>13b</sup> but it is not clear whether the nuclearity differences are due to the different carboxylates, the different alkoxides, the different reaction conditions, or a combination of some or all of these. Thus, we have explored a reaction system where only the alcohol is varied.

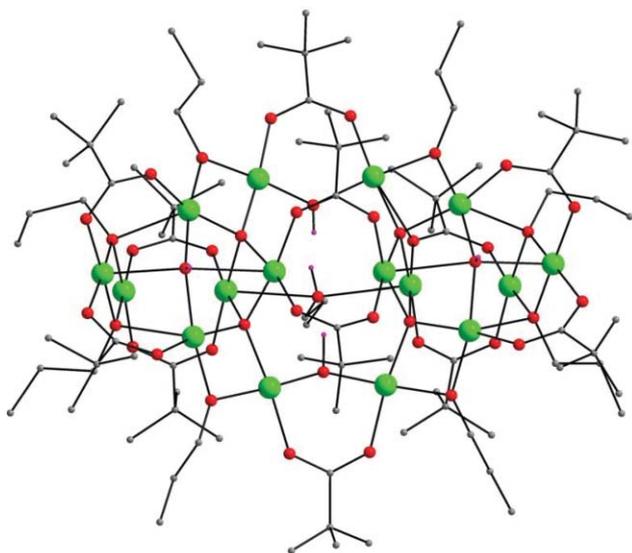
A blue solution of Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in MeOH was added to a solution of pivH in the same solvent and in a 1:1 molar ratio, and treated with an excess of NEt<sub>3</sub>. Slow evaporation of the resulting green solution gave blue crystals of [Cu<sub>2</sub>(piv)<sub>4</sub>(MeOH)<sub>2</sub>] (**1**) in ~50% yield. Complex **1** has the familiar paddlewheel-like structure of copper(II) acetate.<sup>14</sup> The same preparative and crystallization procedure was then employed with EtOH in place of MeOH, and now green crystals of [Cu<sub>6</sub>(OEt)<sub>6</sub>(piv)<sub>6</sub>] (**2**) were obtained in 35% yield.<sup>14a</sup> Complex **2** is a known compound possessing a triangular loop-like structure consisting of alternating {Cu(μ-OEt)<sub>2</sub>Cu} and {Cu(μ-piv)<sub>2</sub>Cu} units, and square-planar Cu(II) atoms.<sup>13b</sup> When the alcohol was changed to Pr<sup>n</sup>OH, the reaction now produced dark green crystals of what turned out to be the interesting hexadecanuclear [Cu<sub>16</sub>O<sub>4</sub>(OH)<sub>4</sub>(OPr<sup>n</sup>)<sub>8</sub>(piv)<sub>12</sub>(Pr<sup>n</sup>OH)]·3Pr<sup>n</sup>OH (3·3Pr<sup>n</sup>OH) in 50% yield.‡ This encouraged us to extend the reaction further to Bu<sup>n</sup>OH, and dark green crystals were again obtained of what proved to be [Cu<sub>16</sub>O<sub>4</sub>(OH)<sub>4</sub>(OBu<sup>n</sup>)<sub>8</sub>(piv)<sub>12</sub>(Bu<sup>n</sup>OH)]·2Bu<sup>n</sup>OH (4·2Bu<sup>n</sup>OH) in ~65% yield.‡

The structure‡ of **3** (Fig. 1) comprises sixteen Cu<sup>II</sup> ions held together by four μ<sub>4</sub>-O<sup>2-</sup>, two μ<sub>4</sub>-OH<sup>-</sup>, two μ<sub>3</sub>-OPr<sup>n-</sup>, four μ<sub>2</sub>-OPr<sup>n-</sup>, and a μ-Pr<sup>n</sup>OH and μ-OR (R = Me<sub>3</sub>CCO) groups to give a [Cu<sub>16</sub>(μ<sub>4</sub>-O)<sub>4</sub>(μ<sub>4</sub>-OH)<sub>2</sub>(μ<sub>3</sub>-OPr<sup>n-</sup>)<sub>4</sub>(μ<sub>2</sub>-OPr<sup>n-</sup>)<sub>4</sub>(μ-Pr<sup>n</sup>OH)(μ-OR)<sub>2</sub>]<sup>11+</sup> cage-like core. The latter (Fig. 2, top) may be conveniently described as two Cu<sub>8</sub> subunits [Cu(1,3,5,7,9,11,13,15) and Cu(2,4,6,8,10,12,14,16)] linked together through the oxygen atoms of two μ-OH<sup>-</sup> (O7, O8) and one μ-Pr<sup>n</sup>OH (O41) groups. Each Cu<sub>8</sub> subunit consists of two [Cu<sub>4</sub>(μ<sub>4</sub>-O<sup>2-</sup>)]<sup>6+</sup> and one [Cu<sub>4</sub>(μ<sub>4</sub>-OH)]<sup>7+</sup> distorted tetrahedra that are edge-shared; the latter moiety is

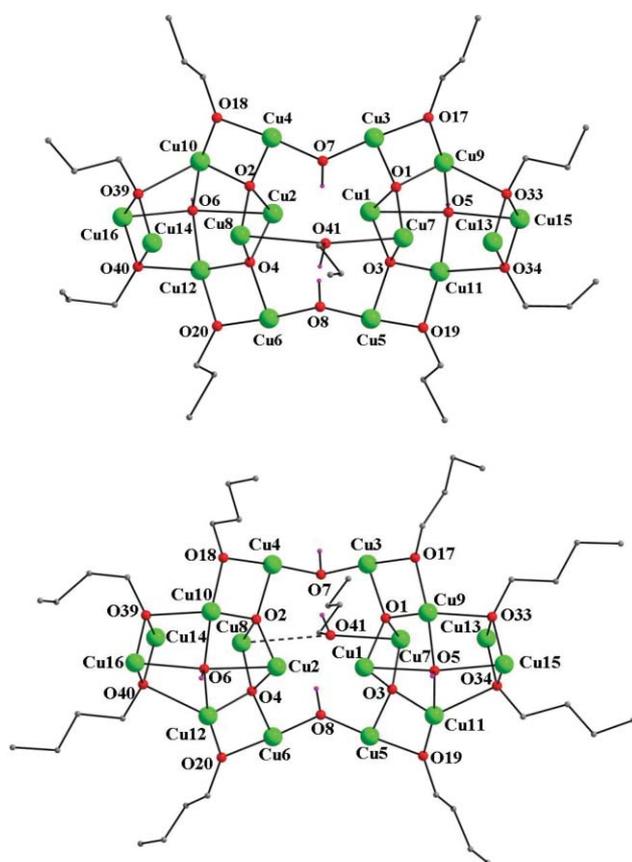
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† Electronic supplementary information (ESI) available: Structural figure for **4**. CCDC reference numbers 751642 & 751643. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c002925b



**Fig. 1** Molecular structure of **3**. Colour scheme: Cu<sup>II</sup>, green; O, red; C, grey; H, purple.



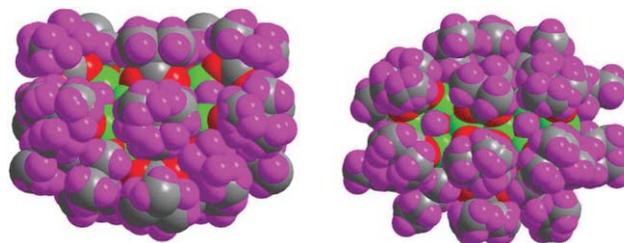
**Fig. 2** The core of complexes **3** (top) and **4** (bottom). Colour scheme: Cu<sup>II</sup>, green; O, red; C, grey; H, purple.

additionally bridged to an extrinsic Cu<sup>II</sup> ion (Cu13 or Cu14) by two  $\mu_3$ -OPr<sup>-</sup> groups. The protonation levels of O<sup>2-</sup>, OH<sup>-</sup>, OPr<sup>-</sup> and Pr<sup>n</sup>OH groups were confirmed by BVS calculations.<sup>15</sup> Peripheral ligation is provided by twelve  $\eta^1:\eta^1:\mu$  piv<sup>-</sup> groups.

Six Cu<sup>II</sup> atoms [Cu(3,4,5,6,13,14)] are four-coordinate with distorted square planar geometry (*cis*- and *trans*- angles in the 79.8–96.9° and 171.4–176.3° ranges). The remaining ten Cu<sup>II</sup> atoms are five-coordinate with almost ideal square pyramidal geometry ( $\tau$  values span the range 0.01–0.12, where  $\tau$  is 0 and 1 for perfect square pyramidal and trigonal bipyramidal geometries,<sup>16</sup> respectively). The central Pr<sup>n</sup>OH (O41) bridging Cu7 and Cu8 does so slightly asymmetrically (Cu7–O41 = 2.673 and Cu8–O41 = 2.879 Å). In addition, there are intramolecular hydrogen-bonds between the Pr<sup>n</sup>OH and the two adjacent OH<sup>-</sup> ions, O7 and O8 (O7...O41 = 2.716 and O8...O41 = 2.657 Å).

The structure† of **4** is very similar to that of **3**, essentially isostructural. The main difference is that the central Bu<sup>n</sup>OH group is now *very* asymmetrically bridging Cu7 and Cu8 (Fig. 2, bottom), so much so that it is perhaps better described as being semi-bridging: Cu7–O41 = 2.508 and Cu8–O41 = 3.163 Å. This is presumably due to increased steric congestion and packing forces, relative to **3**. Consequently, Cu8 is better described as square planar.

A space-filling representation (Fig. 3) shows that **3** and **4** possess an essentially spherical topology of dimensions  $\sim 20 \times 15$  Å and  $\sim 23 \times 20$  Å, respectively. Complexes **3** and **4** join a handful of Cu<sup>II</sup><sub>16</sub> complexes,<sup>17</sup> and are the first examples of any structural type to contain solely carboxylato and alkoxide groups, *i.e.*, without alkoxide-containing chelates, as discussed above.



**Fig. 3** Space-filling representations of **3** (left) and **4** (right). Colour scheme: Cu<sup>II</sup>, green; O, red; C, grey; H, purple.

The solid-state dc magnetic susceptibilities ( $\chi_M$ ) of 3-2Pr<sup>n</sup>OH and 4-Bu<sup>n</sup>OH were measured in the 5.0–300 K range in a 1 kG (0.1 T) field, and they are plotted as  $\chi_M T$  vs.  $T$  in Fig. 4.  $\chi_M T$  at 300 K is 3.87 cm<sup>3</sup> K mol<sup>-1</sup> for both compounds, much lower than the  $\sim 6.6$  cm<sup>3</sup> K mol<sup>-1</sup> calculated (with  $g = 2.1$ ) for a cluster of sixteen non-interacting Cu<sup>II</sup> ions, indicating the presence of strong antiferromagnetic exchange interactions. For 3-2Pr<sup>n</sup>OH,  $\chi_M T$  gradually decreases with decreasing  $T$  to a minimum of 0.39 cm<sup>3</sup> K mol<sup>-1</sup> at 5 K. This indicates an  $S = 0$  ground state, as expected for antiferromagnetic interactions between an even number of Cu<sup>II</sup> ions in a closed, cage-like arrangement.<sup>18</sup> For 4-Bu<sup>n</sup>OH,  $\chi_M T$  also decreases upon cooling, but more rapidly than for 3-2Pr<sup>n</sup>OH, dropping to a constant value of essentially zero (0.07 cm<sup>3</sup> K mol<sup>-1</sup>) in the 5–10 K range; the small plateau value will be due to temperature-independent paramagnetism (TIP). The coupling in 4-Bu<sup>n</sup>OH is thus overall stronger than in 3-2Pr<sup>n</sup>OH. No doubt the difference in the asymmetrically bridging ROH is a contributor, if only because it leads to a difference in the Cu7...Cu8 distance (5.192 vs. 5.316 Å, respectively) which will in turn cause small changes to other Cu–O<sup>2-</sup>–Cu and Cu–OR–Cu angles affecting the pairwise Cu<sub>2</sub> exchange interactions.<sup>19</sup> Given

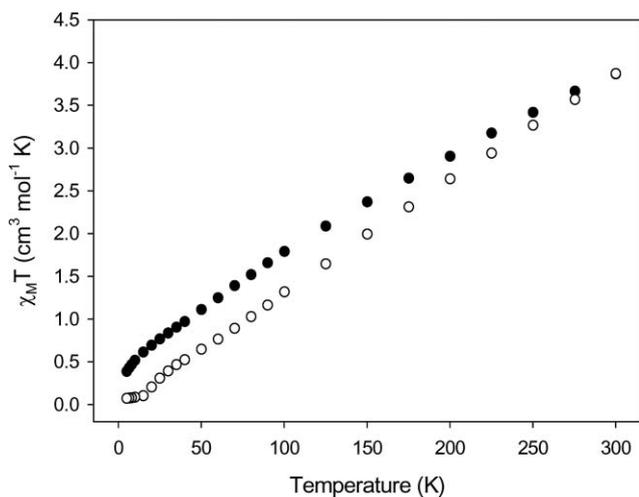


Fig. 4 Plot of  $\chi_M T$  vs.  $T$  for complexes  $3 \cdot 2\text{Pr}^n\text{OH}$  (●) and  $4 \cdot \text{Bu}^n\text{OH}$  (○).

the high nuclearity, low symmetry, and the resulting number of inequivalent exchange constants, it is not feasible to fit the data to determine the individual  $\text{Cu}_2$  exchange parameters.

In summary, surprising differences have been observed in the products isolated from an alcoholysis reaction in which the alcohol has been varied from MeOH to  $\text{Bu}^n\text{OH}$ . Of interest is the fact that, under our conditions at least, the MeOH reaction gives a non-methoxide product, although the green colour of the solution suggests one is present in solution. In addition, very different products are obtained for EtOH and  $\text{Pr}^n\text{OH}$ , surprisingly so given that we have deliberately used  $\text{Pr}^n\text{OH}$  rather than  $\text{Pr}^i\text{OH}$  to avoid complicating the present study with large changes to the steric bulk. The reaction systems thus probably contain several species in solution, and the primary effect of the lengthening alkoxide is to affect the relative solubilities and/or crystallization kinetics, giving significantly different products crystallizing out on concentration of the solution by slow evaporation. This also suggests that small changes to the reaction conditions, plus other factors such as alkoxide bulk, could lead to many new products of various nuclearities. Our conclusion is that the present and previous work in Cu/oxo/alkoxide/carboxylate chemistry has merely scratched the surface, and that there are many undoubtedly exciting clusters waiting to be discovered.

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## Notes and references

‡ Vacuum-dried solid analysed as  $3 \cdot 2\text{Pr}^n\text{OH}$ : Calcd. (found): C, 37.05 (37.11); H, 6.42 (6.52%). Vacuum-dried solid analysed as  $4 \cdot \text{Bu}^n\text{OH}$ : Calcd. (found): C, 38.80 (38.91); H, 6.64 (6.78%). Crystal structure data for  $3 \cdot 3\text{Pr}^n\text{OH}$ :  $\text{C}_{87}\text{H}_{176}\text{Cu}_{16}\text{O}_{41}$ ,  $M_w = 2895.06$ , triclinic, space group  $P\bar{1}$  with  $a = 14.6732(11)$  Å,  $b = 18.7987(13)$  Å,  $c = 27.5100(19)$  Å,  $\alpha = 103.941(1)^\circ$ ,  $\beta = 96.0710(10)^\circ$ ,  $\gamma = 110.847(1)^\circ$ ,  $V = 6727.5(8)$  Å<sup>3</sup>,  $T = 173(2)$  K,  $Z = 2$ , 46031 reflections collected, 30166 unique ( $R_{\text{int}} = 0.0501$ ),  $R1 [I > 2\sigma(I)] = 0.0575$ ,  $wR_2 = 0.1202$  ( $F^2$ , all data). CCDC 751642. Crystal structure data

for  $4 \cdot 2\text{Bu}^n\text{OH}$ :  $\text{C}_{100}\text{H}_{204}\text{Cu}_{16}\text{O}_{42}$ ,  $M_w = 3095.27$ , triclinic, space group  $P\bar{1}$  with  $a = 15.2832(10)$  Å,  $b = 18.7974(13)$  Å,  $c = 25.7722(17)$  Å,  $\alpha = 98.4020(10)^\circ$ ,  $\beta = 93.5150(10)^\circ$ ,  $\gamma = 108.185(1)^\circ$ ,  $V = 6913.5(8)$  Å<sup>3</sup>,  $T = 173(2)$  K,  $Z = 2$ , 47344 reflections collected, 31050 unique ( $R_{\text{int}} = 0.0442$ ),  $R1 [I > 2\sigma(I)] = 0.0592$ ,  $wR_2 = 0.1452$  ( $F^2$ , all data). CCDC 751643. In both compounds, all C and O atoms of the lattice solvent molecules were disordered too badly to be modeled. Their contributions to the observed intensity data were thus removed using program SQUEEZE, part of the PLATON package of crystallographic software.<sup>20</sup>

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