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Controlled hydrolysis of  $K_4Zr_2O(O^iPr)_6$  in the presence of  $CuCl_2$  in THF yields  $Cu_4Zr_2O_3(O^iPr)_8$ , which was characterized by  $^1H$  and  $^{13}C$  NMR and infrared spectroscopy, magnetic susceptibility and X-ray diffraction. Cell constants ( $-92^\circ C$ ):  $a = 12.673(8) \text{ \AA}$ ,  $b = 17.482(13)$ ,  $c = 10.877(8)$ ,  $\alpha = 104.85(3)$ ,  $\beta = 113.52(3)$ ,  $\gamma = 75.65(3)$  with  $Z = 1$  in space group  $P1$ . The compound has a central planar  $Cu_4O_3(O^iPr)_2$  unit terminated on two ends by  $Zr_2(O^iPr)_6$  units. The central of the three oxide ions has an unusual planar four-coordinate geometry. The central  $Cu_4^{8+}$  unit shows antiferromagnetic coupling, with  $\mu_{eff} = 1 \text{ BM/Cu}$  over the range 100-300K. The molecule retains its structure in toluene solution, as judged by  $^1H$  and  $^{13}C$  NMR.

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Alkoxide Chemistry**

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Kathleen L. Trojan, William E. Hatfield and Kenneth G. Caulton

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A PLANAR OXOCUPRATE(II) ARRAY VIA  
HETEROMETALLIC ALKOXIDE CHEMISTRY

by

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ABSTRACT

Controlled hydrolysis of  $K_4Zr_2O(O^iPr)_{10}$  in the presence of  $CuCl_2$  in THF yields  $Cu_4Zr_4O_3(O^iPr)_{18}$ , which was characterized by  $^1H$  and  $^{13}C$  NMR and infrared spectroscopy, magnetic susceptibility and X-ray diffraction. Cell constants ( $-92^\circ C$ ):  $a = 12.673(8)\text{\AA}$ ,  $b = 17.482(13)$ ,  $c = 10.877(8)$ ,  $\alpha = 104.85(3)$ ,  $\beta = 113.52(3)$ ,  $\gamma = 75.65(3)$  with  $Z = 1$  in space group  $P\bar{1}$ . The compound has a central planar  $Cu_4O_3(O^iPr)_2$  unit terminated on two ends by  $Zr_2(O^iPr)_8$  units. The central of the three oxide ions has an unusual planar four-coordinate geometry. The central  $Cu_4^{8+}$  unit shows antiferromagnetic coupling, with  $\mu_{eff} = 1$  BM/Cu over the range 100-300K. The molecule retains its structure in toluene solution, as judged by  $^1H$  and  $^{13}C$  NMR.

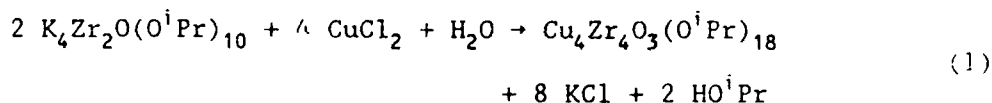
<sup>†</sup> Department of Education Fellow



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Application of the molecular precursor method<sup>1,2</sup> to the synthesis of copper-based high temperature superconductors<sup>3</sup> rests on our ability to produce copper-containing heterometallic alkoxides.<sup>4</sup> We have reported recently<sup>5,6</sup> on the chemistry of the anion  $\text{Zr}_2(\text{O}^i\text{Pr})_9^-$ , which is related to recent reports by the group of Mehrotra.<sup>7,8</sup> We report here our investigation of the coupling of this and related anions to  $\text{CuCl}_2$  of relevance to hydrolytic routes to copper/oxo superconductors.

The reaction of  $\text{K}_4\text{Zr}_2\text{O}(\text{O}^i\text{Pr})_{10}$ ,<sup>6</sup>  $\text{CuCl}_2$ , and water (2:4:1 mole ratio) in a refluxing THF solution produces a deep olive green solution. Workup (i.e., removal of solvent, extraction with pentane, concentration, and layering with isopropanol) yields a blue-green solid (25% yield) which was established<sup>9</sup> to have the formula  $\text{Cu}_4^{\text{II}}\text{Zr}_4^{\text{IV}}\text{O}_3(\text{O}^i\text{Pr})_{18}$ , **1**, eq. 1. The



centrosymmetric structure is shown in Fig. 1. The molecule contains a planar central  $\text{Cu}_4\text{O}_3(\text{O}^i\text{Pr})_2$  unit capped on two opposite ends by  $\text{Zr}_2(\text{O}^i\text{Pr})_8$  units. At the crystallographic center of symmetry is an unusual four-coordinate planar  $\text{O}^{2-}$  ion. Only two other examples of this geometry are known.<sup>10,11</sup> An alternative description of the structure is that two face-shared bioctahedral  $\text{Zr}_2\text{O}(\text{O}^i\text{Pr})_8^{2-}$  units bind through a pseudo-tetrahedral  $\mu\text{-O}$  and two terminal  $\text{O}^i\text{Pr}$  groups to a central planar  $\text{Cu}_4\text{O}(\text{O}^i\text{Pr})_2^{4+}$  unit. This view leads to the idea that the  $\text{Zr}_2(\text{O}^i\text{Pr})_8\text{O}^{2-}$  unit is a template (via 2  $\text{O}^i\text{Pr}$  and the oxide) for growth of the planar ribbon of composition  $\text{Cu}_4\text{O}(\text{O}^i\text{Pr})_2^{4+}$ . Growth of this ribbon into a sheet

(i.e., growth perpendicular to the  $(\mu_4-O)_3$  direction) is prevented by the iso-propyl groups on the oxygens which bridge the coppers.

Spectroscopic analysis confirms the chemical formula and structure. IR spectra lack any O-H stretches, thus excluding the presence of hydroxyl or coordinated alcohol. The NMR spectra<sup>12</sup> of 1 lack the expected shifting and broadening associated with paramagnetic species. The methine region of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum shows that the solid-state structure is maintained in solution: the expected five chemical shifts with approximately the correct integral ratio of 2:2:2:2:1 are found.<sup>12</sup> This conclusion is further supported by the methyl-group  $^1\text{H}$  and  $^{13}\text{C}$  NMR. These are sufficiently complex to indicate the retention of the solid-state structure (with diastereotopic methyls) in solution.

Based on the lack of paramagnetic characteristics in the NMR spectra, the magnetic susceptibility was investigated. This reveals that, while there are unpaired electron spins, these spins are coupled antiferromagnetically. The solution magnetic susceptibility (Evans method, 295K, THF) yields a  $\mu_{\text{eff}}$  of 0.9 BM/Cu. A variable temperature (56-230K) solid-state study shows the  $\mu_{\text{eff}}$  to remain nearly constant at 1.1 BM/Cu from 230-100K, then drop to 0.4 BM/Cu by 56K. A mononuclear  $\text{Cu}^{2+}$  ion would have  $\mu_{\text{eff}} = 1.73$  BM. Our initial exploration of the parameter space of the three J values (two  $J_{\text{cis}}$  and one  $J_{\text{trans}}$ ) of a Heisenberg Hamiltonian model appropriate to a centrosymmetric  $\text{Cu}_4^{8+}$  unit shows a singlet ground state. There is another singlet, a set of three triplets, and a quintet state at higher energies; one or more of the triplets become appreciably populated by 100K, causing the rise in  $\mu_{\text{eff}}$  from 56-100K, but up to now it has not been possible to simulate the

magnetic susceptibility data, and further work is in progress. The  $\mu_{\text{eff}}$  fails to rise further even at 300K because a quintet state lies too high to be significantly populated.

This heterometallic oxo alkoxide contains a planar  $\text{Cu}_4$  array previously unknown in the chemistry of Cu(II). This work suggests that electropositive partner metals in heterometallic species can "guide" the growth of Cu/O patches which mimic some of the structural features of high  $T_c$  superconductors.<sup>13</sup> We believe that the thermodynamically-favored unit (i.e.,  $\text{Zr}_2\text{X}_9$ ) of a "partner metal" in a heterometallic alkoxide can serve as a structural template for the planar  $\text{Cu}_4\text{O}$  array. In the present case, three colinear donor sites (i.e., one terminal alkoxide on each Zr together with the  $\mu\text{-O}^{2-}$ ) of two  $\text{Zr}_2(\text{O}^i\text{Pr})_8\text{O}^{2-}$  units are complementary to the growth of a copper(II) oxide "ribbon" two coppers wide. Further growth along the ribbon direction (i.e., the 05-05' axis) would require insertion of the repeat unit  $\text{Cu}_2\text{O}(\text{O}^i\text{Pr})_2$ .

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**Supplementary Material Available.** A table of positional and thermal parameters for compound 1. Ordering information is given on any current masthead page.

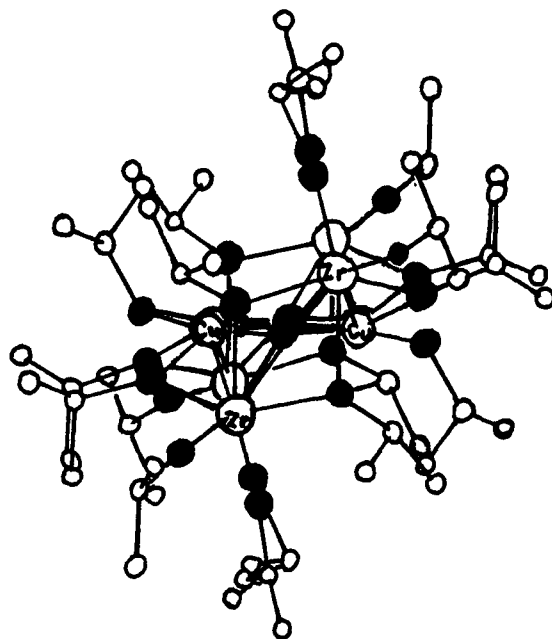
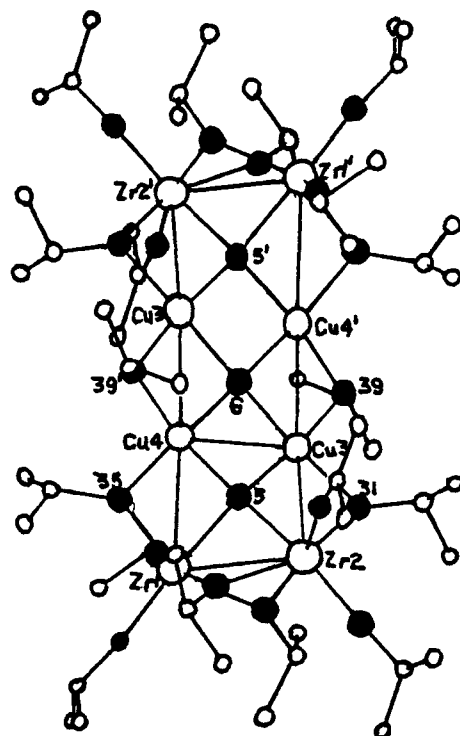
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12.  $^1\text{H}$  NMR (500 MHz, 20°,  $\text{C}_6\text{D}_6$ ): Methine peaks at 5.51 (septet,  $J = 6$  Hz), 5.03 (br), 4.34 (septet,  $J = 6$  Hz), 4.21 (m). Methyl peaks at  $\delta$  2.53, 2.09, 1.47, 1.26 (all overlapping doublets) and 1.32 (d,  $J = 6$ ).  $^{13}\text{C}(^1\text{H})$  NMR (125 MHz, 20°,  $\text{C}_6\text{D}_6$ ):  $\delta$  72.0, 71.3, 70.0, 66.3, 66.2 (CH, int = 2:2:2:2:1), 33.2 (br), 29.0, 28.4, 27.3 (m), 26.7 ( $\text{CH}_3$ , int = 1:1:1:5:1).
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## FIGURE CAPTIONS

Figure 1. ORTEP drawing of the nonhydrogen atoms of  $\text{Cu}_4\text{Zr}_4\text{O}_3(\text{O}^i\text{Pr})_{18}$ . a) viewed perpendicular to the  $\text{Cu}_4\text{O}_3$  plane and b) viewed along the edge of the  $\text{Cu}_4\text{O}_3$  plane. Oxygen atoms are stippled. Lines between metals are for clarity, and are not bonds. Primes indicate atoms related by a center of symmetry. Selected structural parameters: Cu3-O6, 1.968(3)Å; Cu4-O6, 1.966(2); Cu3-O5, 1.880(18); Cu4-O5, 1.896(11); Cu3-O39, 1.892(12); Cu4-O39', 1.901(12); Cu3-O31, 1.965(11); Cu4-O35, 1.966(11); Cu3-Cu4 = Cu3-Cu4, 2.781(8); *cis* angles O-Cu-O range from 84.5(5)° to 104.0(5)°.





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