

## The Oxidation of Ethane-1,2-diol resulting from Molecular Oxygen Activation by Copper: Formation of an Oxoethanoate Complex precedes Carbon–Carbon Bond Cleavage

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The aerial oxidation of ethane-1,2-diol in the presence of copper metal and pyridine (py) at room temperature and atmospheric pressure produces  $[\text{Cu}(\text{py})_2(\text{HCO}_2)_2] \cdot \text{H}_2\text{O}$  and  $[\text{Cu}_2(\text{py})_4(\text{OCH}_2\text{CO}_2)_2] \cdot (\text{CH}_2\text{OH})_2$ ; the structure of the latter has been fully elucidated by an X-ray study.

In a previous study we reported that dioxygen can be activated on a copper surface to allow smooth reaction of the dioxygen with weak Brønsted acids in the presence of organic bases.<sup>1</sup> With methanol as the reagent, copper methoxide was obtained, whereas in the case of phenols oxidation of the aromatic nucleus occurred, leading to hydroxylation, quinone formation and carbon–carbon bond coupling.<sup>2</sup> At present there is great interest in the interaction of molecular oxygen with copper (in its different oxidation states) as the active site as such interactions are connected with naturally occurring enzymatic oxidations.<sup>3</sup>

We report here new results concerning the unusual ability of metallic copper to promote the stepwise addition of oxygen to ethane-1,2-diol producing the coordinated oxoethanoate dianion and formate ion. Finely divided copper metal powder (200–315 nm), stirred in the presence of an excess of ethane-1,2-diol and pyridine (py), reacts slowly with atmospheric dioxygen at 298 K, and rapidly with pure dioxygen at 298 K and 310 kPa, to produce dark-green solutions which after several hours turn blue. By monitoring the  $\text{O}_2$  consumption under the conditions reported in Table 1 we observed an induction time (40 min) followed by a smooth gas uptake ( $0.1 \text{ mmol min}^{-1}$ ) which declined ( $0.01 \text{ mmol min}^{-1}$ ) after 2 h. At this point only a small amount of unreacted copper was present and on adding ethyl acetate to the filtered solution, green crystals of  $[\text{Cu}_2(\text{py})_4(\text{OCH}_2\text{CO}_2)_2] \cdot (\text{CH}_2\text{OH})_2$  **1** separated out; their nature was fully elucidated by an X-ray study.<sup>†</sup>

In the crystals of **1**, dimeric copper complexes, having an imposed  $C_i$  symmetry, and ethane-1,2-diol molecules of solvation are present. The structure of the dimer is shown in Fig. 1, together with the most significant bond distances and angles. The doubly deprotonated hydroxyethanoic acid is bound to the copper atoms through the two O(1) and O(2) atoms, the former almost symmetrically bridging the two metal atoms [ $\text{Cu}-\text{O}(1)$  1.936(2) and  $\text{Cu}'-\text{O}(1)$  1.971(3) Å] and both chelating a copper atom [ $\text{Cu}-\text{O}(2)$  1.956(3) Å]. Square pyramidal coordination around each copper atom is achieved by two N atoms from pyridine ligands [ $\text{Cu}-\text{N}(1)$  1.995(3) and  $\text{Cu}-\text{N}(2)$  2.277(4) Å], the longer bond distance involving the

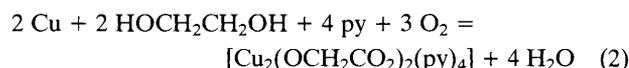
N in the apical position. The O(3) atom from the carboxylate group, not involved in coordination, forms a hydrogen bond with the hydroxy group of the ethane-1,2-diol molecule of solvation that lies on an inversion centre; thus chains of alternating dimers and solvation molecules, running among the inversion centres, can be envisaged within the crystal structure.

Under the same experimental conditions leading to **1**,  $\text{Cu}_2\text{O}$ ,  $\text{CuCl}$  and  $\text{CuCl}_2$  failed to produce the oxidation of the glycol, as shown by the dioxygen absorption reported in Table 1.

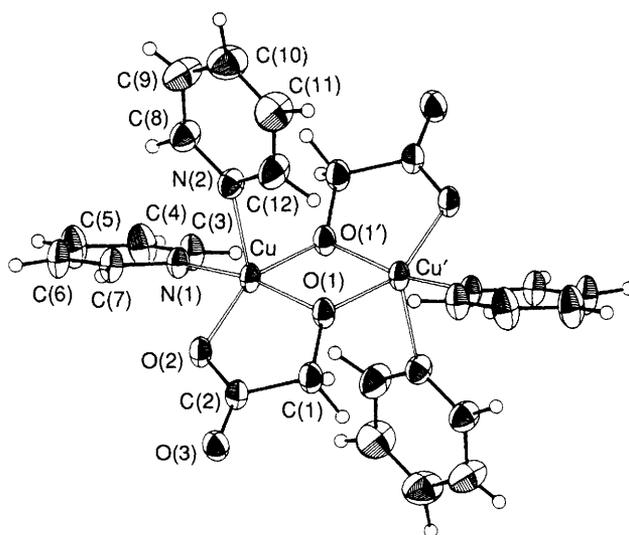
The low  $\text{O}_2$  uptake observed for  $\text{CuCl}$ , which also occurs in the absence of ethane-1,2-diol, may be accounted for by the known oxidation of  $\text{Cu}^I$  to  $\text{Cu}^{II}$  [eqn. (1)].<sup>4</sup> The  $\text{O}_2/\text{Cu}$  ratio



found for Cu approaches the values required for the stoichiometry of reaction (2).



The reaction of Cu,  $\text{C}_2\text{H}_6\text{O}_2$ , py and  $\text{O}_2$  at 298 K and 310 kPa for a longer time (24 h) led to a blue solution, and crystals of  $[\text{Cu}(\text{HCO}_2)_2(\text{py})_2] \cdot \text{H}_2\text{O}$  **2** separated out on addition of ethyl acetate. The formate complex **2** was identified by its known crystal structure;<sup>5</sup> the crystals of both **1** and **2** were found to be unstable in the absence of the mother liquor. In particular, complex **1** loses pyridine and produces a material sparingly soluble in pyridine.



**Fig. 1** View of the structure of **1**. Selected bond distances (Å) and angles (°):  $\text{Cu}-\text{O}(1)$  1.936(2),  $\text{Cu}-\text{O}(2)$  1.956(3),  $\text{Cu}-\text{O}(1')$  1.971(3),  $\text{Cu}-\text{N}(1)$  1.995(3),  $\text{Cu}-\text{N}(2)$  2.277(4),  $\text{C}(1)-\text{O}(1)$  1.405(6),  $\text{C}(2)-\text{O}(2)$  1.271(5),  $\text{C}(2)-\text{O}(3)$  1.242(6),  $\text{C}(1)-\text{C}(2)$  1.517(6);  $\text{O}(1)-\text{Cu}-\text{O}(2)$  83.7(1),  $\text{Cu}-\text{O}(1)-\text{Cu}'$  99.4(1),  $\text{O}(2)-\text{C}(2)-\text{O}(3)$  124.0(4),  $\text{C}(1)-\text{C}(2)-\text{O}(2)$  117.1(3),  $\text{O}(1)-\text{C}(1)-\text{C}(2)$  110.4(4). The primed atoms are related to the unprimed ones by the transformation:  $1-x, -y, -z$ .

<sup>†</sup> *Crystal data* for  $[\text{Cu}_2(\text{py})_4(\text{OCH}_2\text{CO}_2)_2] \cdot (\text{CH}_2\text{OH})_2$  **1**:  $\text{C}_{24}\text{H}_{24}\text{Cu}_2\text{N}_4\text{O}_6$ ,  $\text{C}_2\text{H}_6\text{O}_2$ ,  $M = 653.64$ , triclinic, space group  $P\bar{1}$ ,  $a = 9.606(5)$ ,  $b = 8.759(3)$ ,  $c = 8.980(3)$  Å,  $\alpha = 89.16(2)$ ,  $\beta = 87.30(2)$ ,  $\gamma = 73.59(2)^\circ$ ,  $U = 724.0(5)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.499$  g cm<sup>-3</sup>,  $F(000) = 336$ , nickel-filtered Cu-K $\alpha$  radiation,  $\lambda = 1.54178$  Å,  $\mu = 22.22$  cm<sup>-1</sup>.

The intensity data for the compounds were collected on a Siemens AED diffractometer, using the  $\theta$ - $2\theta$  scan technique at room temperature. 2750 unique reflections were measured with  $\theta$  in the range 3–70°; 2443, having  $I > 2\sigma(I)$ , were used in the refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures, with anisotropic thermal parameters in the last cycles of refinement for all nonhydrogen atoms. All hydrogen atoms were clearly localized in the final  $\Delta F$  map and refined isotropically. The  $R$  and  $R_w$  values were 0.0547 and 0.0537. Atomic coordinates, thermal parameters, and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

**Table 1** Oxygen consumption

Reagent <sup>a</sup>	Molar O <sub>2</sub> /Cu uptake	Blank <sup>b</sup>
Cu	1.4	0
Cu <sub>2</sub> O	0	0
CuCl	0.3	0.3
CuCl <sub>2</sub>	0	0

<sup>a</sup> Reagent (10 mmol), ethane-1,2-diol (100 mmol), pyridine (10 ml),  $T = 298\text{ K}$ ,  $P(\text{O}_2) = 310\text{ kPa}$ , reaction time 4 h. <sup>b</sup> In the absence of ethane-1,2-diol.

The results reported here indicate that the ethane-1,2-diol oxidation promoted by copper metal involves a stepwise mechanism where the fast formation of an oxoethanoate complex precedes the slower carbon-carbon bond fission which leads to the formate complex.

The presence of only hydroxyethanoic and formic acids in the hydrolysed reaction mixtures, and the absence of carbon dioxide in the gas phase, indicate the selectivity of these steps. The outstanding feature of this reaction system lies in the modulated oxygen addition that leads to the oxidation of only one carbon atom of the glycol to the carboxylate.

Although recent studies on models of the enzyme galactose oxidase have reported new examples of copper complexes able to catalyse primary alcohol conversion to aldehydes or acids,<sup>6,7</sup> these complexes suffer the limitation of being active only in the presence of strong bases. To the best of our knowledge, there has been no report dealing with the selective mono-oxidation of 1,2-diols promoted by transition metals. Moreover bond fission between aliphatic carbon atoms, leading to coordinated formate, is also peculiar to the ethane-1,2-diol oxidation, and can be compared with the C-C

bond cleavage of activated or secondary diols<sup>3,8</sup> in different chemical and enzymatic systems. As already reported, the interaction of O<sub>2</sub> with metal copper forms a layer of atomic oxygen which can interact with proton donor molecules such as glycols.<sup>1</sup> Thus, an hydroxylated Cu<sup>II</sup> derivative of formula Cu(OH)(OCH<sub>2</sub>CH<sub>2</sub>OH) can be considered as an intermediate which may be compared with copper species present in biological systems.

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