

## An Unusual Bi-Tri-Binuclear Sandwich Complex formed in the Reaction of $\text{CuCl}_2$ with the $\text{Et}_2\text{N}-\text{N}_2\text{O}_2^-$ Ion

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Reaction of the  $\text{Et}_2\text{N}-\text{N}_2\text{O}_2^-$  ligand with  $\text{Cu}^{\text{II}}$  ions in methanol produces a mixed complex, shown by X-ray crystallography to consist of simple, alkoxo-bridged bi- and tri-nuclear units held together in a discrete triple-decker array.

The  $\text{Et}_2\text{N}-\text{N}_2\text{O}_2^-$  ion **1** is of current interest as a vehicle for the controlled biological delivery of nitric oxide, with demonstrated activity as a vasorelaxant,<sup>1</sup> mutagen<sup>2</sup> and antiplatelet agent.<sup>3</sup> We are examining the coordination chemistry of this and related  $\text{R}_2\text{N}-\text{N}_2\text{O}_2^-$  ions which, aside from an early report by Longhi and Drago,<sup>4</sup> is virtually unexplored.

In investigating the ligand properties of these ions, we have now isolated a mixed complex, **3**, from the reaction of  $\text{CuCl}_2$  with the  $\text{Et}_2\text{N}-\text{N}_2\text{O}_2^-$  ion in methanol. Compound **3** is a novel stacked array of linear  $[(\mu\text{-OR})_n\text{M}_m]$  units, the trinuclear portion of which is sandwiched between two binuclear molecules. We report here the synthesis and crystallographic characterisation of this aggregate in view of its possible significance in the areas of biomedical<sup>1-3</sup> and materials<sup>5</sup> science, molecular recognition and self-assembly,<sup>6</sup> and mechanisms of enzyme action.<sup>7</sup>

Compound **3** was synthesised by two different methods, as outlined in Scheme 1. In a stepwise procedure, the sodium salt of **1** was prepared as previously described<sup>1,8</sup> and treated under an inert atmosphere in ROH (R = Me, Et) with  $\text{CuCl}_2$  to produce a blue solid. When this product was crystallised from ethanol, the binuclear complex, **2**,<sup>†</sup> was obtained in good yield.<sup>‡</sup> By allowing **2** to stand in methanol at  $-30^\circ\text{C}$ , a new complex was crystallised which was not the mononuclear  $[\text{Cu}(\text{MeOH})(\text{Et}_2\text{N}-\text{N}_2\text{O}_2)_2]$  reported previously.<sup>4</sup> Instead, the elemental analysis<sup>§</sup> indicated a much higher metal:ligand ratio consistent with formula **3**. An alternative route to the mixed complex, **3**, was effected *via* a spontaneous self-assembly reaction involving ligand **1**, copper(II) chloride and sodium methoxide in the appropriate stoichiometry, as also shown in Scheme 1.

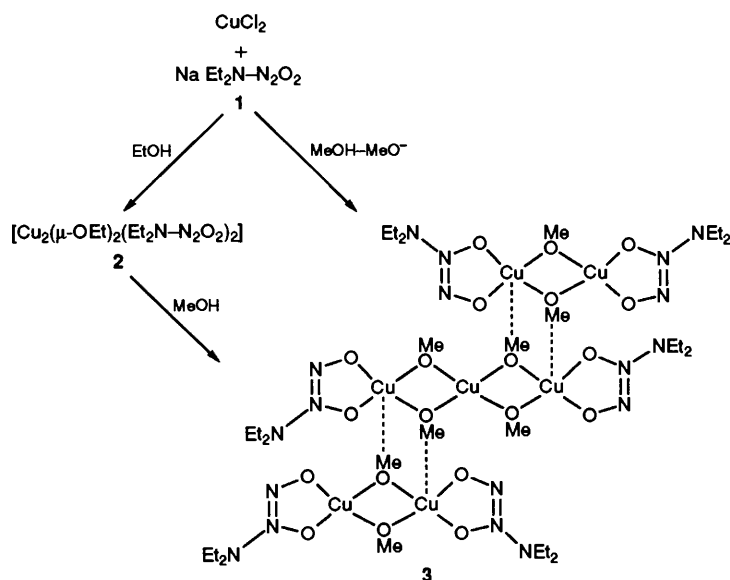
<sup>†</sup> *Crystal data*: This molecule is chemically analogous to the binuclear component of **3** shown in Fig. 1. Blue prismatic crystals of  $\text{C}_{12}\text{H}_{30}\text{Cu}_2\text{N}_6\text{O}_6$  are monoclinic, space group  $C2/c$ ,  $a = 22.944(15)$ ,  $b = 11.575(6)$ ,  $c = 34.57(2)$  Å,  $\beta = 103.78(4)^\circ$ ,  $V = 8916(9)$  Å<sup>3</sup>,  $Z = 16$ ,  $D_c = 1.435$  g cm<sup>-3</sup>,  $F(000) = 481.5$ ,  $T = 223$  K. Single crystal X-ray diffraction data were collected on a Siemens R3m/V automated diffractometer using an incident beam graphite monochromator,  $\lambda(\text{Mo-K}\alpha) = 0.71073$  Å in the  $\theta$ - $2\theta$  scan mode,  $2\theta_{\text{max}} = 40^\circ$ . The structure was determined by direct methods (Siemens SHELXTL Plus)<sup>9</sup> and refined by full-matrix least-squares methods on the basis of 4167 unique reflections, 2540 with  $F > 3.0\sigma(F_o)$ ; 469 parameters were refined, including the atomic coordinates and anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were included with a riding model [coordinate shifts of C applied to attached H-atoms, C-H set to 0.96 Å, angles idealised, and  $U_{\text{iso}}(\text{H})$  fixed]. Final  $R = 0.067$  and  $R_w = 0.057$  [ $W^{-1} = \sigma^2(F) + 0.0002F^2$ ]; residual electron density 0.60 e Å<sup>-3</sup>.

<sup>‡</sup> The yield was 57%. Satisfactory C, H, N and Cu analyses were obtained for  $\text{C}_{12}\text{H}_{30}\text{Cu}_2\text{N}_6\text{O}_6$ .

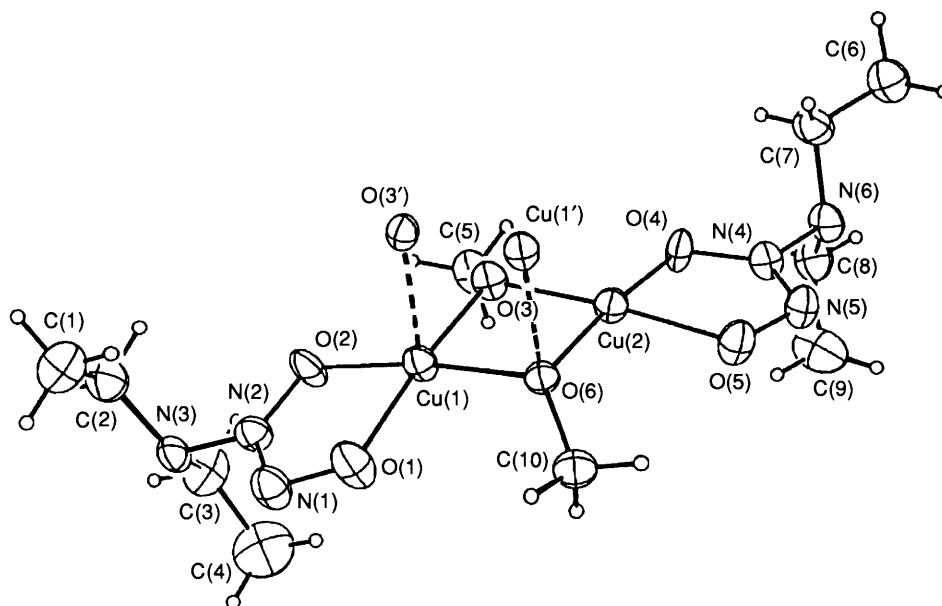
<sup>§</sup> Satisfactory C, H, N and Cu analyses were obtained for  $\text{C}_{32}\text{H}_{84}\text{Cu}_7\text{N}_{18}\text{O}_{20}$ . The magnetic, spectroscopic and electrochemical data are also consistent with the structural assignment, as will be detailed in the full report.

The unusual structure of this material, established by X-ray diffraction analysis,<sup>¶</sup> is shown in Figs. 1 and 2. The unit cell ( $P\bar{1}$ ,  $Z = 1$ ) is composed of a linear trinuclear  $[\text{Cu}_3(\text{OMe})_4(\text{Et}_2\text{N}-\text{N}_2\text{O}_2)_2]$  molecule with its central Cu atom located on the centre of symmetry, held between two centrosymmetrically related binuclear  $[\text{Cu}_2(\text{OMe})_2(\text{Et}_2\text{N}-\text{N}_2\text{O}_2)_2]$  molecules. The intermolecular interactions involve a copper atom and an associated bridging alkoxide of one molecular layer with its counterparts on the next layer. Only one copper atom of each binuclear entity is thus engaged, while both peripheral metal centres of the trinuclear molecule are involved, holding the array in a three-layered configuration. Cu(2') of the trinuclear molecule is in a square planar environment, with  $\text{O}(3')-\text{Cu}(2')-\text{O}(3'A)$  ( $-x, 1.0 - y, 1.0 - z$ ) angles of  $180^\circ$  in the central  $[\text{CuO}_4]$  unit. The peripheral Cu atoms are in a trigonally distorted square pyramidal environment. The intermolecular Cu-O distances at 2.393(4) and 2.437(5) Å [ $\text{Cu}(1)\cdots\text{O}(3')$  and  $\text{Cu}(1')\cdots\text{O}(6)$ , respectively] resemble those observed in other  $\text{Cu}^{\text{II}}$  complexes<sup>10a</sup> that favour five-coordination *via* axial interactions. The intramolecular Cu-O (ligand **1**) distances, ranging from 1.917(4) to 1.944(3) Å, are similar to terminal copper-oxygen bonds found in  $\beta$ -polyketonate complexes.<sup>10</sup> The Cu-O(bridge) distances, ranging from 1.931(3) to 1.978(3) Å, resemble the copper-alkoxo bridging distances observed in  $[\text{Cu}_4\text{Zr}_4\text{O}_3(\mu\text{-OPr})_{18}]$ ,<sup>5a</sup>  $[\text{Cu}_2(\mu\text{-OMe})_2(\mu\text{-3-methylpyrrolidono-N,O})_4\text{Hg}_2(\text{NO}_3)_2]$ <sup>11</sup> and  $[\text{Cu}_3(\mu\text{-OCMe}_3)_4\{\text{OC}(\text{CF}_3)_3\}_2]$ .<sup>12</sup> As a result of the bridging alkoxides, the intramolecular Cu $\cdots$ Cu distances are quite short [binuclear, 2.910(1); trinuclear, 2.946(1) Å], but do not represent bonding distances. The closest intermolecular Cu $\cdots$ Cu distances are 3.286(2) and 3.288(2) Å [ $\text{Cu}(1)\cdots\text{Cu}(1')$  and  $\text{Cu}(1')\cdots\text{Cu}(2)$ , respectively]. The  $\text{Et}_2\text{N}-\text{N}_2\text{O}_2^-$  anions coordinate to the copper atoms *via* the oxygens of the bidentate chelate  $\text{N}_2\text{O}_2^-$  group. The N-O distances in these groups, averaging 1.317(4) Å, have equivalent, single bond character similar to that in  $\text{Na}_2\text{N}_2\text{O}_3\cdot\text{H}_2\text{O}$ .<sup>13</sup> The two nitrogens in each  $\text{N}_2\text{O}_2^-$  group are doubly bound, with N-N distances averaging 1.278(6) Å; this is considerably shorter than the typical single bond length of the  $(\text{Et}_2\text{N})-\text{N}$  linkages, which average 1.409(6) Å. The *trans* arrangement of the diethylamino moieties on the trinuclear complex in **3**, imposed by the crystallographic centre of symmetry, contrasts with the *cis* geometry of these moieties in the binuclear molecules.

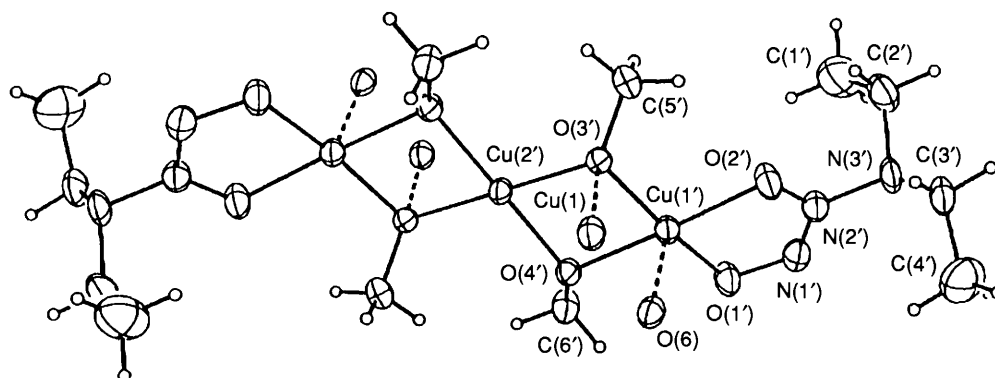
<sup>¶</sup> *Crystal data*:  $\text{C}_{32}\text{H}_{84}\text{Cu}_7\text{N}_{18}\text{O}_{20}$ , triclinic,  $P\bar{1}$ ,  $a = 10.886(3)$ ,  $b = 11.946(3)$ ,  $c = 13.845(3)$  Å,  $\alpha = 76.04(2)$ ,  $\beta = 66.54(2)$ ,  $\gamma = 70.26(2)^\circ$ ,  $V = 1542.6(7)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.599$  g cm<sup>-3</sup>,  $F(000) = 765$ ,  $T = 223$  K. In the range of  $4.0 < 2\theta < 45.0^\circ$  a total of 4288 reflections were collected as described in footnote †. 4056 unique reflections, 3151 with  $F > 3.0\sigma(F_o)$  were used for all calculations. The structure was determined by direct methods<sup>9</sup> and refined by full-matrix least-squares methods; 349 final parameters included atomic coordinates and anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were calculated with a riding model, fixed isotropic U. Final  $R = 0.0389$  and  $R_w = 0.0378$ ; residual electron density 0.49 e Å<sup>-3</sup>. Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



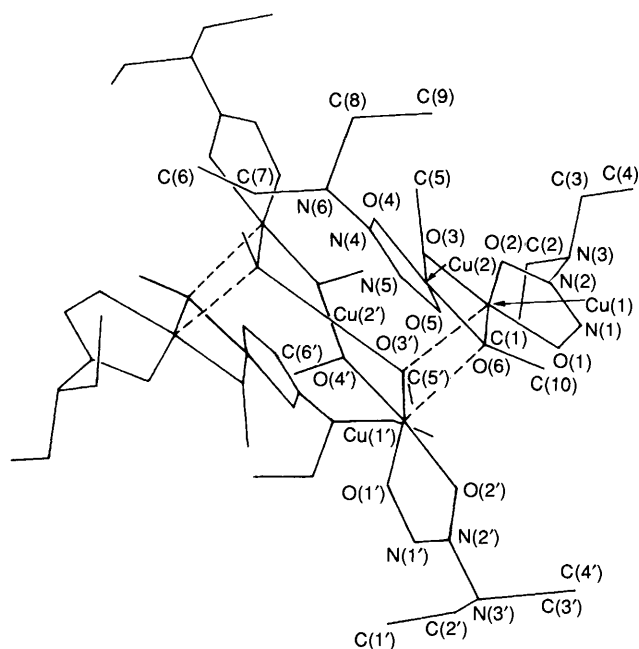
Scheme 1



**Fig. 1** Structure and labelling of the binuclear component of molecular aggregate **3**, drawn by ORTEP, including hydrogen atoms. Selected bond distances (Å) and angles (°): Cu(1)-O(1) 1.928(3), Cu(1)-O(2) 1.926(3), Cu(1)-O(3) 1.944(3), Cu(1)-O(6) 1.936(3), Cu(2)-O(3) 1.939(4), Cu(2)-O(4) 1.927(3), Cu(2)-O(5) 1.917(4), Cu(2)-O(6) 1.943(3); Cu(1)-O(3)-Cu(2) 97.1(1), Cu(1)-O(6)-Cu(2) 97.2(1), O(3)-Cu(1)-O(6) 82.4(1), O(3)-Cu(2)-O(6) 82.4(1).



**Fig. 2** Structure and labelling of the trinuclear component of **3**, drawn by ORTEP, including hydrogen atoms. Selected bond distances (Å) and angles (°): Cu(1')-O(1') 1.926(3), Cu(1')-O(2') 1.944(3), Cu(1')-O(3') 1.942(3), Cu(1')-O(4') 1.931(3), Cu(2')-O(3') 1.978(3), Cu(2')-O(4') 1.973(3), Cu(1')-O(3')-Cu(2') 97.4(1), Cu(1')-O(4')-Cu(2') 98.0(2), O(3')-Cu(2')-O(4') 80.0(1), O(3')-Cu(2')-O(3'a) 180.0(1), O(3')-Cu(2')-O(4'a) 100.0(1), O(3')-Cu(1')-O(4') 82.0(1), O(1')-Cu(1')-O(2') 80.5(1).



**Fig. 3** Bonding diagram for **3**, drawn from experimental coordinates, showing intermolecular interactions between the trinuclear and binuclear molecules. Average bond distances (Å) and angles (°) for  $\text{Et}_2\text{N}-\text{N}_2\text{O}_2^-$  ligands: O(1)–N(1) 1.312(6), O(2)–N(2) 1.319(5), N(1)–N(2) 1.275(6), N(2)–N(3) 1.411(6); N(1)–N(2)–N(3) 116.7(4), O(2)–N(2)–N(1) 123.3(4), O(1)–N(1)–N(2) 112.1(4), O(2)–N(2)–N(3) 119.9(4).

The magnetic moment of  $4.69 \mu_{\text{B}}$  at 300 K,  $\mu_{\text{eff}} = 0.67 \mu_{\text{B}}$  per  $\text{Cu}^{\text{II}}$  ion, suggests strong antiferromagnetic coupling for the Cu–OR–Cu units in **3**, as also reflected in the variable temperature magnetic susceptibility data to be published in the full report. Consistent with this finding is the temperature dependence of the isotropically shifted resonances of the  $\text{Et}_2\text{N}-\text{N}_2\text{O}_2^-$  ligand protons in the NMR spectra of the complexes in solvents of varying polarity.

The crystallographic results demonstrate the ligand properties of ion **1**, which contains the planar, bidentate  $\text{N}_2\text{O}_2^-$  group, and provide the first examples of structurally characterised metal complexes of the  $\text{R}_2\text{N}-\text{N}_2\text{O}_2^-$  ligand. Compound **3** is unusual in that it is composed of discrete alkoxy-bridged units of relatively low molecular mass; such materials are uncommon<sup>5a,12,14</sup> except when the bridge is part of a polydentate ligand,<sup>15</sup> and they could prove useful in the synthesis of larger aggregates or in studies of intermetallic magnetic interactions. The intermolecular interactions present in the solid state (Fig. 3) and the labile nature of the

ligands suggest a variety of reactivity possibilities for the species in solution. Nitric oxide release from anion **1** is spontaneous<sup>1</sup> in aqueous media; as non-nitrosyl metal complexes capable of generating several molecules of the multifaceted bioregulatory agent, nitric oxide,<sup>16</sup> **2** and **3** might be expected to display an interesting variety of pharmacological activities. The potential utility of these and related species in a diversity of applications is currently under investigation.

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