X-Ray Crystal Structure of a Stable Complex of Copper(III); the Use of Deprotonated Nitrogen Atoms as Donors

Kenneth J. Oliver and T. Neil Waters

Department of Chemistry, University of Auckland, New Zealand

The stable blue compounds arising from the reaction of aldehydes or ketones with oxalodihydrazide in the presence of Cu^{2+} ions and molecular oxygen have been characterised by *X*-ray diffraction and e.s.r. studies and are proposed as oxidase models.

The reactions of oxalodihydrazide in the presence of copper(II) ions, simple aldehydes or ketones, and molecular oxygen, long known to produce strongly coloured solutions[1,2] useful for colorimetric analyses,[3–5] have been the subject of considerable disagreement.[6–9] A number of investigations have been made and the role of molecular oxygen has been studied[10] leading to a suggestion that it occurs as dioxygen,[11] *i.e.* that an oxygen carrier is present. When acetaldehyde is used as a source of carbonyl groups the colour passes through a deep-blue stage (ϵ 16 000 at 600 nm) which can be retained if excess of aldehyde is avoided. Otherwise the more usual purple colour (ϵ 29 000 at 515 nm) develops. The latter species has been isolated and crystallised and shown by *X*-ray investigation[12] and e.s.r. measurements[13] to be an anionic five-co-ordinate Cu^{III} complex in which a macrocyclic ligand has been formed by the condensation reaction of six acetaldehyde molecules with oxalodihydrazide.

We have now determined that the reaction to the blue stage is not only reversible on pumping or flushing with nitrogen[10] but that the colour also disappears on the addition of acid, being restored by base followed by molecular oxygen, one mole of gas being required per mole of copper(II) initially present. With excess of acetaldehyde and the addition of further molecular oxygen the purple colour develops and at this point the reaction is irreversible. An *X*-ray structural analysis of crystals of the blue product from acetaldehyde and acetone shows that two carbonyl species have condensed to form a ligand and that this time the product is planar, *i.e.* only four-co-ordinate. E.s.r. measurements of both solid and solution gave no signals, a result compatible with the view that this is again a copper(III) species. Although containing solvent of crystallisation, and therefore sensitive to the atmosphere, both blue and purple species are relatively stable. *X*-Ray data on some blue compounds were collected with crystals protected only by lacquer spraying. An outline of the *X*-ray analysis of the ethylammonium salt of the blue species from acetaldehyde is given here.

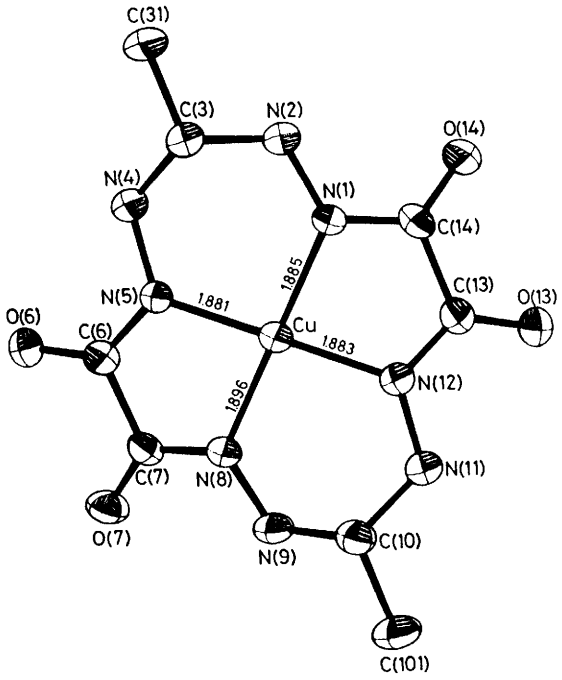

Figure 1. The structure of the complex anion, found to be based on 1,2,4,5,8,9,11,12-octa-aza-3,10-dimethyltetradecane-6,7,13,14-tetrone. Important bond lengths (Å) are shown.

Crystal data: $C_{10}H_{30}CuN_9O_9$, M = 484.0, monoclinic, space group $P2_1/c$, a = 12.825(1), b = 15.561(1), c = 11.289(1) Å, β = 111.18(1)°, U = 2101 Å^3, Z = 4, D_c = 1.53 g cm^{-3}, D_m = 1.50 g cm^{-3}, λ = 1.5418 Å, μ(Cu-K_α) = 20.6 cm^{-1}. The structure was solved and refined conventionally to an R

factor of 0.047 for 3031 reflexions, $F_0 > 3\sigma(F_0)$, collected on an Enraf-Nonius CAD-4 diffractometer.†

The complex anion, found to be based on 1,2,4,5,8,9,11,12-octa-aza-3,10-dimethyltetradecane-6,7,13,14-tetrone, is shown in Figure 1. It contains short Cu–N bonds corresponding to the high oxidation state of the metal but otherwise geometric details appear normal. The ethylammonium cation and the five water molecules complete a hydrogen-bonding network.

It is clear that the deep colours of these compounds arise from the presence of complexed copper(III). Within the pH range 8.0—9.0 aqueous solutions can be kept for long periods and, as noted, the solids are also very stable. This we ascribe mainly to the presence of deprotonated nitrogen atoms as donors confirming earlier indications of this requirement.[14,15] The presence of 6-membered rings does not appear to be detrimental, contrary to other suggestions.[16]

Finally we report that, judged by criteria applied elsewhere,[18] the blue compound based on acetaldehyde appears to be a good model for a copper oxidase.[15,17] Following the procedures of Yano *et al.*[18] we have established that it reacts with ascorbic acid in aqueous solutions, the blue colour then being restored by reaction with molecular oxygen, a recovery of the oxidant not previously observed.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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