Structure of the Oxygenated Condensation Product Between Copper(II) Ions, Oxalodihydrazide, and Acetaldehyde

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Summary We have determined the crystal structure of the compound which had been formulated as the first dioxygen complex of copper; our analysis shows this assignment to be incorrect.

Ammoniacal solutions containing copper(II) ions and oxalodihydrazide $(CONHNH_2)_2$ react with excess of acetaldehyde to form a green-brown solution. Oxygenation produces an intense purple coloration with one of the highest known molar extinction coefficients for a copper complex[1] and this reaction has therefore been extensively applied as a sensitive method for the microdetermination of copper.[2] The complex has been widely upheld as a dioxygen complex of copper serving as a model system for studying the oxygen-carrying mechanism of the blue copper proteins.[3]

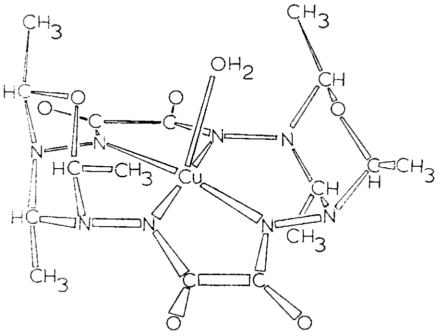

Figure. *The structure and geometry of the complex anion*

Because a variety of different structures have been proposed,[2a,c,4] we have isolated the purple complex and have determined its crystal structure.

The purple solution was prepared as previously described,[1] using copper perchlorate as source of cupric ions, and evaporated to dryness. Slow diffusion of CH_2Cl_2 vapour into a solution of the compound in propan-2-ol at -5 °C produced deep purple platelets, which are monoclinic, $a = 9{\cdot}373(2)$, $b = 14{\cdot}337(17)$, $c = 26{\cdot}129(4)$ Å, $\beta = 105{\cdot}25(1)°$ $Z = 4$, space group $P2_1/c$.

Intensity data were collected on a Hilger-Watts 4-circle diffractometer using Ni-filtered Cu-K_α X-radiation. A total of 1865 unique reflections with $I > 2{\cdot}5\sigma(I)$ were recorded. The structure was solved by Patterson and Fourier syntheses, and refined by least-squares techniques. The crystals contain many water molecules of crystallisation and, where appropriate, occupancy factors have also been refined. All other non-hydrogen atoms have been assigned anisotropic thermal parameters. The final residual, R, is 0·089.

The structure of the copper-containing species is illustrated in the Figure, electrophoresis and other experiments showing that it is, in fact, a dinegative anion. The crystals also contain a perchlorate ion, three ammonium ions, and six water molecules of crystallisation all linked by an extensive network of hydrogen bonds. The molecular formula is $[NH_4]_2[C_{16}H_{24}N_8O_6CuH_2O],NH_4ClO_4,6H_2O$. Within the complex ion the copper atom is co-ordinated, in a tetragonal pyramidal fashion, to four nitrogen atoms of the ligand and to an axial water molecule. The Cu–N distances average 1·86 Å; Cu–H_2O = 2·74 Å. The geometry of the oxalyl groups is consistent with their being present in the keto-form. Average distances are: C–O 1·24, C–C 1·51, and C–N (trigonal) 1·33 Å. The nature and magnitude of the anionic charge and the sp^2 hybridisation of the four donor nitrogen atoms indicate that co-ordination has occurred with loss of four protons. There is no evidence for molecular O_2 in the complex. The ligand itself has undergone a series of interligand condensations with acetaldehyde to produce the polycyclic ring systems in the Figure.

The analysis has thus shown that previous structural assignments are incorrect, and that the compound is not an oxygen carrier. It is, however, clear that oxygen is necessary to the reaction—possibly as an oxidiser for a copper(I) species initially formed by reduction. This problem is under further study.

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