Synthesis, *X*-Ray Crystal Structure, and Properties of a Tetranuclear Complex formed by Oxidation of Copper(I) Chloride with Molecular Dioxygen in *N*-methylpyrrolidin-2-one. Isolation of a Catalyst for the Oxidative Coupling of Phenols by Dioxygen

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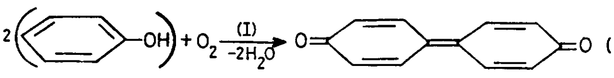
Summary The *X*-ray crystal structure and properties of a tetranuclear, catalytically active derivative of the product of oxidation of copper(I) chloride with dioxygen in *N*-methylpyrrolidin-2-one are reported.

Studies of the products of oxidation of copper(I) chloride by molecular dioxygen in aprotic media are of interest in two respects. Firstly, the products are useful catalysts for the oxidative coupling of acetylenes, aromatic amines, and phenols by O_2.[1] Secondly, the structure and properties of such species may improve our understanding of those multi-centred copper oxidases which catalyse the same reactions.[2]

Oxidation of a slurry of copper(I) chloride with dioxygen in anhydrous *N*-methylpyrrolidin-2-one (L) obeys equation (1) and yields a brown solution [λ_{max} 820nm, ϵ = 100 l (g atom Cu)$^{-1}$ cm^{-1}; shoulder at 875 nm] which catalyses reaction (2). The formation of a single product in equation

$$4CuCl + O_2 \xrightarrow{L} \underset{(I)}{L_3Cu_4Cl_4O_2} \qquad (1)$$

(1) is strongly indicated by chromatography of the brown product solution on Biobeads SX-12 resin with L as eluant.[3]



(2)

Cryoscopic measurements in L as solvent (f.p. −22·8 °C, K_{fp} 7·2 °C mol^{-1} with *o*-dichlorobenzene as a standard) indicate that (I) is a tetranuclear copper(II) complex.

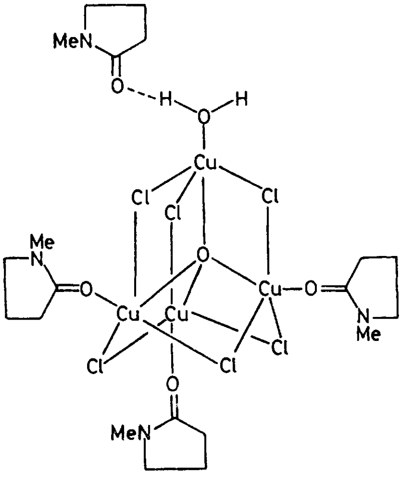
Attempts to crystallize (I) from L as solvent have been unsuccessful. However, we have recently obtained a catalytically active derivative of (I) after precipitation with anhydrous 1,2-dimethoxyethane (DME), as follows.

Addition of DME to a solution of (I) in L yields an unstable amorphous yellow-green solid with an e.s.r. spectrum (at −50 °C) identical to that of the original solution. If this solid is immediately washed with DME and kept under DME for 2—3 weeks in a loosely closed container, orange-brown crystals (λ_{max} 822 and 915 nm, both ϵ 926 l mol^{-1} cm^{-1} in CH_2Cl_2) of catalytically active $L_3Cu_4OCl_6(OH_2).L$ (II) are formed.

If (I) is only partially precipitated with DME, catalytically inactive orange-brown crystals of the complex $L_4Cu_4OCl_6$ (III) can be grown from the supernatant solution. The species (III) is presumably formed as in reaction (3) and can be synthesized independently by rational procedures.[4]

$$\underset{\text{(II)}}{L_3Cu_4OCl_6(OH_2).L} \longrightarrow \underset{\text{(III)}}{L_4Cu_4OCl_6} + H_2O \qquad (3)$$

A single crystal X-ray structural analysis of (II) has been carried out in order to determine unambiguously its molecular geometry.



(II)

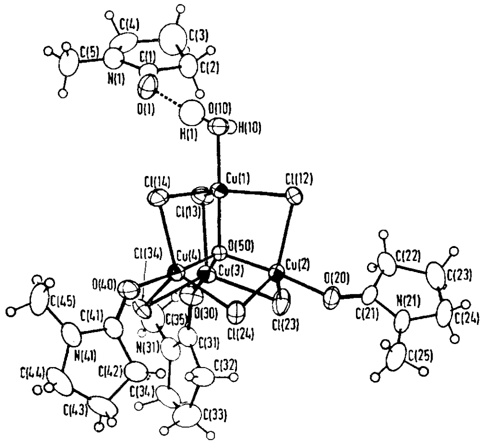


FIGURE. An ORTEP-II diagram of the molecular geometry of $L_3Cu_4OCl_6(OH_2).L$ (II) (L = N-methylpyrrolidin-2-one). The 30% probability contours of the thermal vibration ellipsoids are shown for all atoms other than hydrogen atoms of the L ligands.

The complex (II) crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 9{\cdot}062(2)$, $b = 22{\cdot}051(5)$, $c = 17{\cdot}278(3)$ Å, $\beta = 96{\cdot}65(1)°$, $U = 3429{\cdot}4(11)$ Å^3, $Z = 4$, $D_c = 1{\cdot}738$ and $D_m = 1{\cdot}733(5)$ g cm^{-3}. Intensity data were collected *via* the θ–2θ scan technique on a Syntex $P2_1$ automated diffractometer[5] and were corrected for absorption ($\mu = 29{\cdot}72$ cm^{-1}) by an empirical method.[6] The structure was solved by direct methods (using MULTAN)[7] and was refined by difference-Fourier and least-squares refinement (370 variables) techniques to final discrepancy indices of $R_F = 5{\cdot}65\%$ and $R_{WF} = 4{\cdot}70\%$ for the 3203 reflections with $4{\cdot}5° < 2\theta < 40°$ (Mo-K_α radiation). The geometry of the molecule is shown in the Figure. There is a central Cu_4OCl_6 core (of approximate T_d symmetry) to the molecule, in which Cu $\cdots$ Cu distances range from 3·0752(13) to 3·1374(14) Å (average = 3·095 ± 0·024 Å) and Cu–Cl (bridging) distances range from 2·344(2) to 2·502(2) Å (average = 2·406 ± 0·041 Å). The copper–(μ^4-oxide) linkages are equivalent, with Cu(1)–O(50) = 1·897(4), Cu(2)–O(50) = 1·895(4), Cu(3)–O(50) = 1·889(4), and Cu(4)–O(50) = 1·902(4) Å. Three of the copper atoms are bonded to the oxygen atoms of the N-methylpyrrolidin-2-one ligands [Cu(2)–O(20) = 1·913(5), Cu(3)–O(30) = 1·919(5), and Cu(4)–O(40) = 1·923(5) Å], while the fourth copper atom is linked to an aquo ligand [Cu(1)–O(10) = 1·936(6) Å]. We emphasize that the hydrogen atoms in this latter fragment were both located and refined; resulting distances and angles are O(10)–H(1) = 0·95(8), O(10)–H(10) = 0·81(5) Å, $\angle$Cu(1)–O(10)–H(1) = 114(5), $\angle$Cu(1)–O(10)–H(10) = 84(4), and $\angle$H(1)–O(10)–H(10) = 93(6)°. This aquo-ligand is involved in hydrogen bonding to the oxygen atom of an otherwise 'free' N-methylpyrrolidin-2-one molecule in the crystal lattice [$\angle$O(10)–H(1) $\cdots$ O(1) = 176(5)°, O(10)–H(1) = 0·95(8) Å, H(1) $\cdots$ O(1) = 1·62(8) Å]. (See Addendum on p. 1080 regarding availability of atomic co-ordinates).

The solid state structure of copper(I) chloride (zinc blende, $a_0 = 5{\cdot}406$ Å)[8] is compatible with the formation of a clustered product in reaction (1). The cluster (I) is evidently stabilized[1,3] by the amide L, which may serve as a crude model for the peptide environments of the active sites of copper oxidases.[9] It is noteworthy that the terminal oxygen atom in (I) is very basic; the fact that (III) is not a catalyst for reaction (2) indicates that the presence of a basic, terminal oxygen group is a requirement for phenolic oxidative coupling by such copper complexes.

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[4] H. T. Dieck, *Inorg. Chim. Acta*, 1973, **7**, 397; We are currently investigating the structure of (III). The near-i.r. spectrum of (III) is virtually identical to that of (II) in CH_2Cl_2.

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[9] Studies (refs. 1 and 3) with other ligand systems (pyridines and amines) indicate that amides are particularly effective as $Cu_4Cl_4O_2$ stabilizers. It should be noted that treatment of (I) with pyridine leads to the same products as formed by the oxidation of copper(I) chloride in pyridine; G. Davies, M. F. El-Shazly, D. R. Kozlowski, C. E. Kramer, W. M. Rupich, and R. W. Slaven, *Adv. Chem.*, in the press.