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A novel tricopper(II) complex of a polyamine alcohol†

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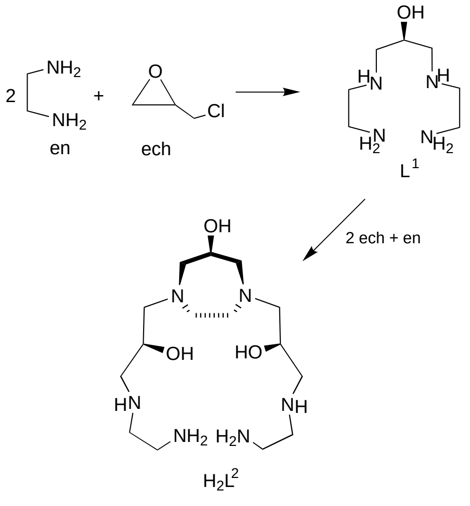
The trinuclear copper(II) complex of a new polyamino alcohol ligand has been isolated; it exhibits a structure similar to that found at the active site of ascorbate oxidase.

The four-electron reduction of oxygen to water is catalysed by several copper-containing enzymes. Laccase, ceruloplasmin and ascorbate oxidase are known to contain a trinuclear Cu site, with an additional Cu centre at a distance of approximately 12 Å from the active site. These multielectron reductions are associated with the one-electron oxidation of organic substrates such as ascorbate, polyphenols and polyamines.[1] The X-ray crystal-structure analyses of both the oxidised[2] (Cu^{II}) and reduced[3] (Cu^{I}) forms of ascorbate oxidase have been carried out. In the native oxidised form, three Cu^{II} ions of the trinuclear site comprise a pair of Type-III Cu ions and an adjacent Type-II centre, with Cu–Cu distances averaging 3.74(8) Å. There has been much interest in the synthesis of trinuclear Cu complexes as models for enzymes of this class.[4–7]

In this paper, we report the synthesis of the new ligand H_2L^2 and its trinuclear copper complex $[Cu_3(L^2)Cl_2][ClO_4]_2\cdot 2H_2O$, as a minor product from the reaction of epichlorohydrin (1-chloro-2,3-epoxypropane) with an excess of ethane-1,2-diamine.‡ The major product was, as expected, a Cu^{II} complex of the 2:1 ethane-1,2-diamine:epichlorohydrin addition product, which was crystallised as its perchlorate salt $[CuL^1][ClO_4]_2$ (Scheme 1). The crystal structure§ of $[CuL^1][ClO_4]_2$ comprises pairs of crystallographically independent $[CuL^1]^{2+}$ cations and perchlorate anions. There are no significant differences between the independent cations and the Cu–N bond lengths lie in the range 2.001–2.026 Å (Fig. 1). These dimensions are typical of Cu^{II} amines and the weak axial Cu–O contacts to perchlorate anions are in excess of 2.75 Å. The hydroxyl group is axially disposed with respect to the six-membered chelate ring, and is not co-ordinated.

The crystal structure¶ of the minor product of this reaction reveals a remarkable tricopper(II) complex of the doubly deprotonated ligand $(L^2)^{2-}$. The ligand H_2L^2 is an oligomeric 3:3 addition product of epichlorohydrin and ethane-1,2-diamine, probably involving L^1 as an intermediate (Scheme 1). Each of the three Cu^{II} ions exhibits a five-co-ordinate, distorted square-pyramidal geometry (Fig. 2). The central copper atom [Cu(2)]



Scheme 1

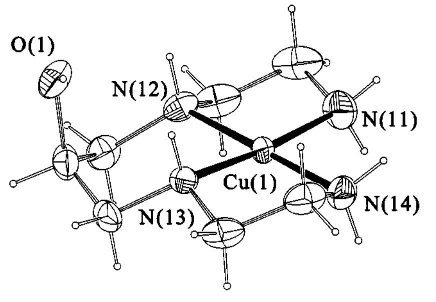


Fig. 1 View of one of the $[CuL^1]^{2+}$ cations showing 30% probability ellipsoids. Selected bond lengths (Å): Cu(1)–N(11) 2.026(5), Cu(1)–N(12) 2.017(5), Cu(1)–N(13) 2.008(4), Cu(1)–N(14) 2.001(5)

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† *Non-SI units employed*: mmHg = 133.322 Pa, $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

‡ To a solution of epichlorohydrin (15.7 g, 0.17 mol in 200 cm^3 water) was added ethane-1,2-diamine (30.1 g, 0.5 mol) and the solution was refluxed for 16 h then concentrated under vacuum. Anion exchange chromatography was employed to remove chloride ion and the eluent was concentrated on a rotary evaporator before vacuum distillation to remove excess ethane-1,2-diamine. The oil remaining after distillation (110°, 8 mmHg) was diluted to 5 dm^3 and an excess of $Cu(NO_3)_2\cdot 3H_2O$ was added. Column chromatography (0.2 mol dm^{-3} $NaClO_4$) eluted a major purple band $[CuL^1]^{2+}$ and (0.5 mol dm^{-3} NaCl) a minor blue band $[Cu_3(L^2)Cl_2]^{2+}$. X-Ray quality crystals of the perchlorate salts of both complexes were grown by slow evaporation of aqueous solutions of each complex in the presence of excess $NaClO_4$.

§ Crystal data for $\{[CuL^1][ClO_4]_2\}_2$: $C_{14}H_{40}Cl_4Cu_2N_8O_{18}$, $M = 877.4$, monoclinic, space group $P2_1/c$, $a = 15.215(4)$, $b = 14.914(1)$, $c = 15.528(3)$ Å, $\beta = 103.08(1)°$, $U = 3432(1)$ Å^3, $Z = 4$, D_c 1.698 g cm^{-3}, μ(Mo-Kα) = 16.32 cm^{-1}, $F(000) = 1800$, $T = 293$ K, final $R1 = 0.0458$, $wR2 = 0.1210$ for 3943 observed reflections $[|F_o| > 2\sigma|F_o|, 2\theta < 50°]$ and 0.1410 for all reflections, $w^{-1} = \sigma^2(F_o^2) + (0.0727P)^2 + 7.33P$, where $P = (F_o^2 + 2F_c^2)/3$.

¶ Crystal data for $[Cu_3(L^2)Cl_2][ClO_4]_2\cdot 2H_2O$: $C_{15}H_{38}Cl_4Cu_3N_6O_{13}$, $M = 842.93$, monoclinic, space group $C2/c$, $a = 21.48(1)$, $b = 11.710(3)$, $c = 25.59(1)$ Å, $\beta = 101.43(2)°$, $U = 6309(4)$ Å^3, $Z = 8$, D_c 1.775 g cm^{-3}, μ(Mo-Kα) = 24.08 cm^{-1}, $F(000) = 3232$, $T = 293$ K, final $R1 = 0.0678$, $wR2 = 0.1724$ for 3109 observed reflections $[|F_o| > 2\sigma|F_o|, 2\theta < 50°]$ and 0.2124 for all reflections, $w^{-1} = \sigma^2(F_o^2) + (0.1082P)^2 + 15.24P$, where $P = (F_o^2 + 2F_c^2)/3$. Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation and employing the ω–2θ scan method. Both structures were solved by direct methods with SHELXS 86[8] and refined by full-matrix least squares on F^2 with SHELXL 93.[9] Non-H atoms were refined with anisotropic thermal parameters, whereas H-atoms were constrained at estimated positions. CCDC reference number 186/912. See http://www.rsc.org/suppdata/dt/1998/1087/ for crystallographic files in .cif format.

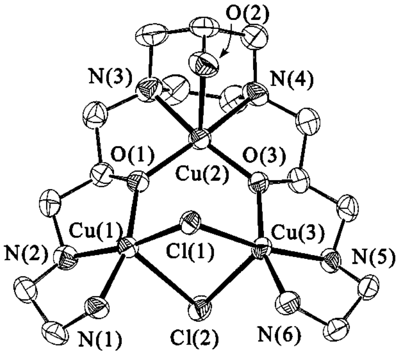

Fig. 2 View of the cation $[Cu_3(L^2)Cl_2]^{2+}$ showing 30% probability ellipsoids (H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 1.972(7), Cu(1)–N(2) 2.013(8), Cu(1)–O(1) 1.894(6), Cu(1)–Cl(1) 2.333(3), Cu(1)–Cl(2) 2.642(3), Cu(2)–N(3) 2.028(9), Cu(2)–N(4) 2.042(8), Cu(2)–O(1) 1.903(6), Cu(2)–O(2) 2.323(7), Cu(2)–O(3) 1.898(6); Cu(1)–O(1)–Cu(2) 132.5(3), Cu(2)–O(3)–Cu(3) 131.6(3), Cu(1)–Cl(1)–Cu(3) 91.48(9), Cu(3)–Cl(2)–Cu(1) 79.11(7)

possesses a N_2O_3 donor set whereas the other two terminal ions are found in N_2Cl_2O co-ordination environments, where chloro ligands bridge the terminal metal ions Cu(1) and Cu(3). The deprotonated alkoxo O-atoms [O(1) and O(3)] form bridges between the central and terminal Cu ions. Overall, the complex possesses an approximate mirror plane symmetry element passing through Cu(2) and bisecting the seven-membered ring of L^2. The co-ordination environments and metal ligand bond lengths of Cu(1) and Cu(3) are not markedly different. However, the two bridging chloro ligands exhibit distinctly different bond lengths depending on their axial or equatorial co-ordination site. The chloro ligand lying in the CuN_2O plane of each terminal ion displays a significantly shorter Cu(1,3)–Cl(1) bond length [2.333(3) Å] compared with the axially co-ordinated bridging ligand [Cu(1)–Cl(2) 2.642(3), Cu(3)–Cl(2) 2.606(3) Å]. Similarly, a relatively long axial Cu(2)–O(2) distance of 2.323(7) Å is found. Each of these axially elongated square-pyramidal geometries is expected for a Cu^{II} complex as a consequence of the pseudo-Jahn–Teller effect. The Cu–Cu distances are all similar, with both central–terminal distances being 3.48 Å and the terminal–terminal Cu–Cu distance being 3.34 Å. By comparison, the Cu–Cu distances within the trinuclear site of the oxidised form of ascorbate oxidase lie in the range 3.66 to 3.90 Å.[2]

The solution properties of the two complexes $[CuL^1]^{2+}$ and $[Cu_3(L^2)Cl_2]^{2+}$ are quite different. The purple mononuclear complex exhibits a single visible electronic maximum at 529 nm (ε 67.1 $dm^3\ mol^{-1}\ cm^{-1}$). Electrochemistry of $[CuL^1]^{2+}$ at a Hg working electrode identified a quasi-reversible $Cu^{II/0}$ redox couple at $E_{\frac{1}{2}}$ −0.59 V *vs.* Ag–AgCl, with the stoichiometry of the redox process being confirmed by waveheight comparisons with standards. This two-electron process is peculiar to reactions on mercury electrodes, whereas one-electron $Cu^{II/I}$ responses are typically observed on solid working electrodes (glassy carbon, Pt *etc.*).

The blue tricopper $[Cu_3(L^2)Cl_2]^{2+}$ complex displays a visible maximum at 620 nm [ε 302 $dm^3\ mol^{-1}\ cm^{-1}$ per tricopper(II) complex]. Electrochemistry of this complex on a Hg drop working electrode is quite complicated (Fig. 3). Two separate cathodic responses are seen at −0.16 and −0.56 V *vs.* Ag–AgCl, with the more negative wave being approximately twice the intensity of the other. Waveheights suggest that the first redox process is a single-electron reduction of the central Cu^{II} ion followed by a two-electron wave involving the terminal Cu^{II} sites. Three anodic peaks are found at −0.43, −0.28 and −0.03 V. The most positive of these anodic waves grows in intensity with deceasing scan rates; which is indicative of partial dissociation of the complex upon reduction. The solution magnetic moment of $[Cu_3(L^2)Cl_2]^{2+}$ (μ_{eff} 2.70 μ_B) points to significant antiferromagnetic coupling in the trinuclear complex. All these data are consistent with the integrity of the Cu^{II}_3 cluster being maintained in solution. It is not known whether the bridging chloro ligands are substituted by the solvent in aqueous solution, but the basic trinuclear framework remains intact as shown by the electrochemical, spectroscopic and magnetic data.

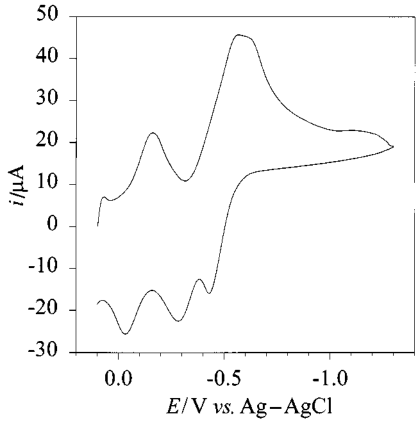

Fig. 3 Cyclic voltammogram of $[Cu_3(L^2)Cl_2]^{2+}$. Experimental conditions: Hg drop working, Pt counter and Ag–AgCl reference electrode, 0.1 mol dm^{-3} aqueous $NaClO_4$, scan rate 0.5 V s^{-1}

The co-ordination sites occupied by the bridging chloro ligands in $[Cu_3(L^2)Cl_2]^{2+}$ are predisposed to bind other guest ligands. There is very little conformational freedom in the tricopper complex, and this is a useful structural feature. The central Cu ion [Cu(2)] acts to force the two terminal Cu ions into close proximity and co-ordination of bridging ligands (in this case Cl^-) is clearly promoted by this cooperative arrangement. We are currently exploring the possibility of inserting other bridging ligands into this site.

Acknowledgements

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