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A Blue Copper(III) Complex

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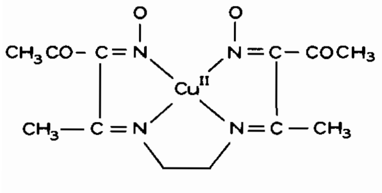
Interest in copper(II) complexes bound to four nitrogen atoms in a nearly square-planar structure has increased, as these may function as model systems for type 2 copper proteins [1]. In addition, this type of copper(II) complexes has been found to be readily oxidized to the corresponding copper(III) complexes [2–4].

Complex (I) has been prepared by the reaction of copper(II) acetate with N,N'-ethylenebis(isonitrosoacetylacetoneimine), and its composition verified by elemental analysis.



(I)

Complex (I) reacted readily with several oxidizing agents, $S_2O_8^{2-}$, IO_4^- and $IrCl_6^{2-}$, giving an intense blue product that decomposes slowly at room temperature. The blue product absorbs strongly at 581 ± 1 nm and has a molar absorption coefficient ≅6 × 10^3 M^{-1} cm^{-1}. The high absorption may be attributed to LTM charge transfer.

The blue product was confirmed to be a copper(III) complex by the loss of EPR signals of complex (I), in accordance with a low spin d^8 structure. Further support for the oxidation of complex (I) was obtained from cyclic voltammetry. Aqueous solutions of complex (I) exhibited quasi-reversible electrochemical behaviour with anodic and cathodic peak separations, $E_{Pa} - E_{Pc}$ = 140 mV at a scan rate of 20 mV sec^{-1}. A typical cyclic voltammogram is shown in Fig. 1.

The facile oxidation of copper(II) complexes with strong in-plane ligand donors is believed to be due to the gain in crystal field stabilization energy in the change of divalent d^9 to trivalent d^8. Trivalent copper has been suggested to be part of the active site of galactose oxidase, with two-electron transfer being operative in the redox process [6]. However, oxidation of various substrates by copper(III)–peptide complexes showed strong preference for one-electron transfer [7].

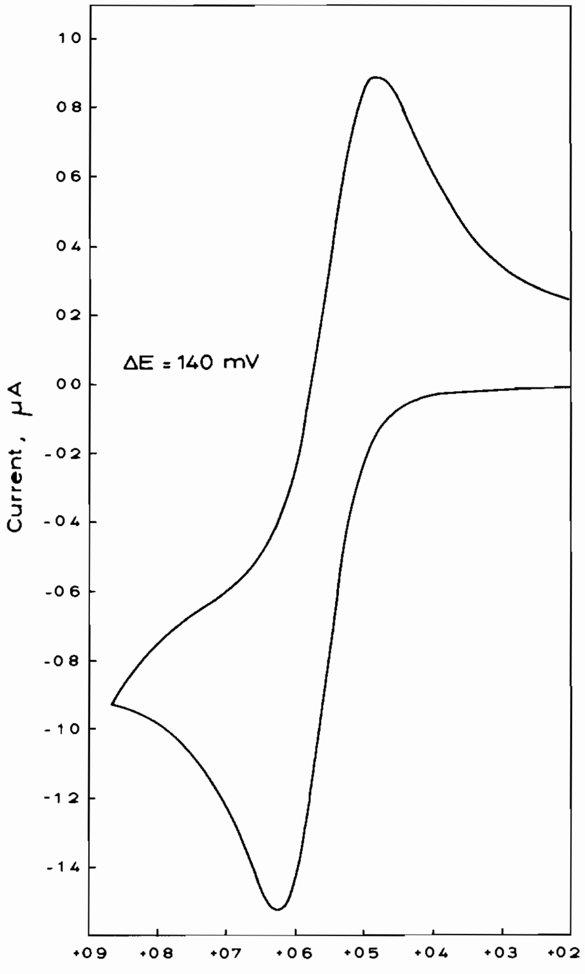


Fig. 1. Cyclic voltammogram of complex (I) in aqueous solution at a carbon paste electrode, $[Cu^{II}] = 2 \times 10^{-4}$ *M*, pH = 5.84 (phosphate), I = 0.15 *M*, 25° C at a scan rate 20 mV sec^{-1}. E^o = 0.80 V *vs.* NHE.

The blue copper(III) complex obtained from oxidation of complex (I) is, perhaps, the first copper(III) complex that absorbs strongly near 600 nm (where copper proteins normally absorb). This complex may act as a model for type 3 copper proteins. This type is characterized by being diamagnetic, which is met by the low-spin d^8 configuration of the copper(III) complex with a square planar structure.

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