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Synthesis and Characterization of an Imine–Oxime Copper(III) Complex

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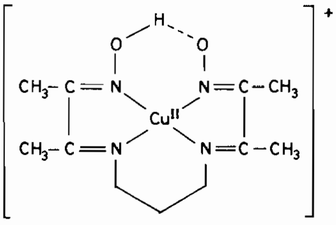
The trivalent oxidation state of copper has been shown to be stabilized in aqueous solutions and in the solid phase by many ligands [1, 2]. Several copper(III) peptide complexes display remarkable stability in aqueous solutions [2]. A recent report from this laboratory described the stabilization of this oxidation state of copper by the imine–oxime ligand N,N′-ethylenebis(isonitrosoacetylacetoneimine) [3]. The stabilization of the +3 oxidation of copper by imine–oxime ligands is not unexpected as these ligands are known to stabilize the +3 and +4 oxidation state of nickel [4].

The complex, 2-oximino-10-oximinato-3,9-dimethyl-4,8-diazaundeca-3,8-dienecopper(II) perchlorate dihydrate, $[Cu^{II}(PreH)]ClO_4 \cdot 2H_2O$ shown in (1) was found to be readily oxidized by PbO_2, $S_2O_8^{2-}$ and IO_4^- in aqueous acidic solutions to give an intensely red coloured product.



(1)

The red species has a molar absorptivity $\epsilon = 1.25 \times 10^4$ M^{-1} cm^{-1} at 515 nm. This high absorption may be attributed to ligand to metal (LTM) charge transfer. Aqueous solutions of this product were remarkably stable at pH 4 with a half-life >24 hours. Decomposition of the red species was observed to be catalyzed by both acid and base, as was observed with copper(III) peptide complexes [2].

Evidence that the red product is a copper(III) complex was obtained from the loss of the EPR signals of an aqueous solution of the copper(II) complex. In addition, cyclic voltammograms exhibited quasi-reversible electrochemical behaviour with peak-to-peak separation, $\Delta E \simeq 90$ mV, indicative of one-electron transfer (Fig. 1). The electrode potential, E, calculated at the mid-point between the anodic, E_a, and the cathodic, E_c, peaks was found to be pH-dependent. Thus at the pH values, 3.63, 4.00 and 4.59, E has the values 0.955 V, 0.933 V and 0.895 V respectively at 25 °C. A plot of E *vs.* pH is linear with a slope of $-(0.062 \pm 0.001)$ V consistent with eqns (1) and (2) (E° = standard potential).

$$[Cu^{III}(Pre)]^+ + e + H^+ \rightleftharpoons [Cu^{II}(PreH)]^+ \qquad (1)$$

$$E = E^\circ - 0.059\ pH \qquad (2)$$

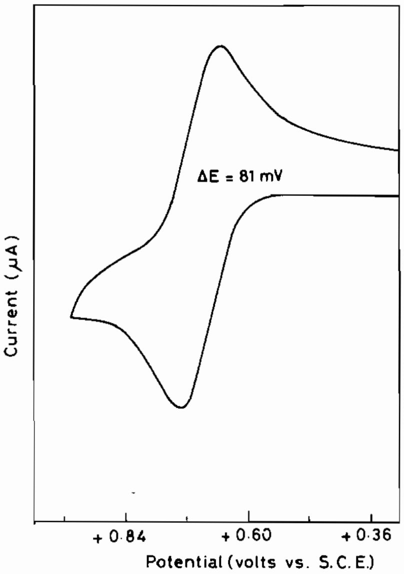


Fig. 1. Cyclic voltammogram of complex(I) in aqueous solution at a carbon paste electrode, $[Cu^{II}(PreH)^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, pH = 4.00 (sodium acetate/acetic acid), $\mu = 0.20$ mol dm^{-3} ($NaClO_4$ + $NaCH_3CO_2$), T = 25 °C at a scan rate of 100 mV s^{-1}.

The remarkable stability of this complex encouraged us to attempt its isolation. This was achieved by reacting 0.55 g of the copper(II) complex, prepared according to the method of Addison *et al.* [5], in 25 cm^3 of 0.05 *M* aqueous solution of acetic acid with a large excess of PbO_2. After about 20 min. the solution was filtered and solid $NaClO_4$ was added to the deep red filtrate. The solution was kept overnight in a refrigerator. Black shiny crystals were collected and air-dried. Elemental analysis, Found: C, 30.33; H, 4.86; N, 12.78; Cl, 8.11; Cu, 14.70. Calcd. for $[Cu^{III}(Pre)]ClO_4 \cdot 2H_2O$: C, 30.22; H, 5.07; N, 12.81; Cl, 8.11; Cu, 14.54. The isolated solid was shown by EPR to be diamagnetic (Fig. 2 (B)); this is consistent with the low spin d^8 electronic configuration

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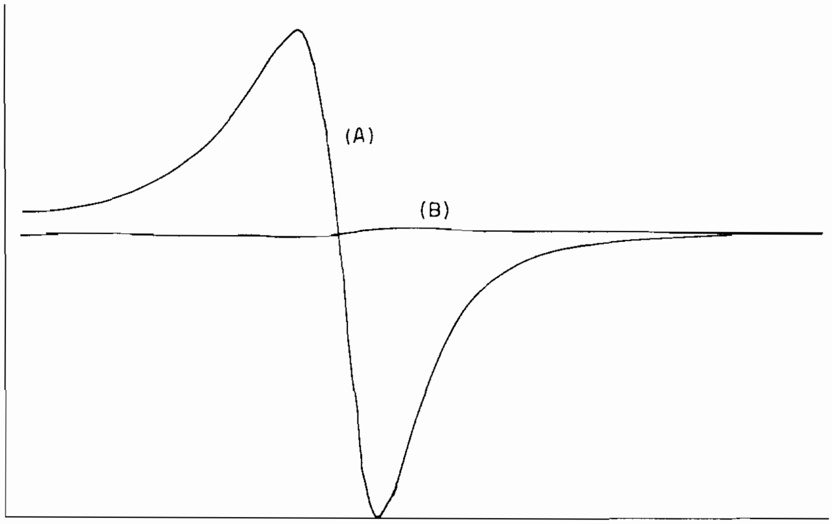

Fig. 2. EPR spectra of solid samples of (A) $[Cu^{II}(PreH)]ClO_4 \cdot 2H_2O$ and (B) $[Cu^{III}(Pre)]ClO_4 \cdot 2H_2O$.

proposed for copper(III) complexes. Solutions of this solid oxidized iodide, ascorbic acid and sulphite to give the corresponding copper(II) complex.

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