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Novel One-electron Oxidation of a Trinuclear Copper(II) System

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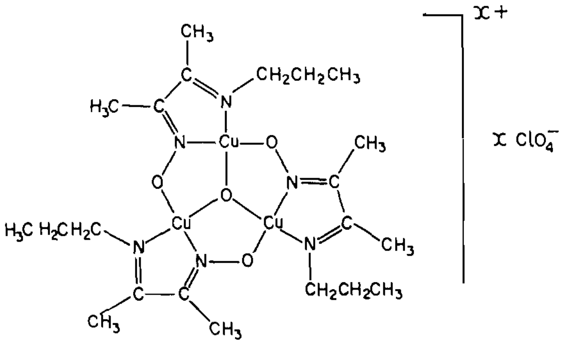
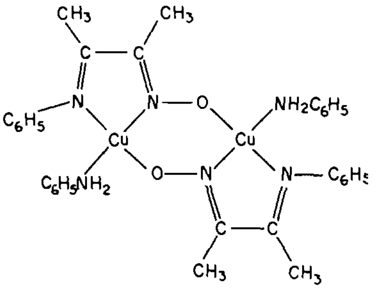
We wish to report an one-electron quasireversible redox reaction of the trinuclear copper(II) system *1* which has one unpaired electron (S = ½) over the temperature range 80–350 °K [1]. A molecular orbital calculation [2] indicates that the electron is located in a doubly degenerate antibonding orbital. This suggested that a one-electron oxidation of *1* may occur readily.



1 $X = 1$
2 $X = 2$



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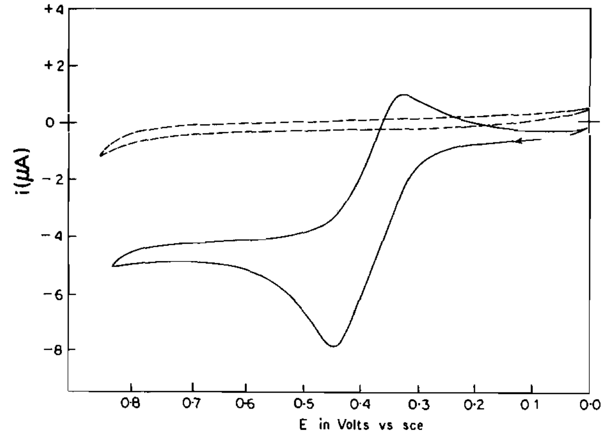

Figure 1. Cyclic voltammogram of *1* (2 × 10^{-3} *M 1*, 0.1 *M* TEAP in acetonitrile, 298 °K) at scan rate 0.0125 V sec^{-1} The pattern in broken line represents the non-electroactive behaviour of *3* under the same conditions as above.

The cyclic voltammogram [3, 4] (platinum wire electrode) of *1* in the potential range +0.80 to 0.00 V (*versus SCE, i.e.* saturated calomel electrode) in acetonitrile (0.1 *M* in TEAP *i.e.* tetraethylammonium perchlorate) is shown in Fig. 1. A redox cycle centered around 0.384 V is clearly observable. Peak positions of several scan rates are set out in Table I. Starting at 0.00 V, the initial process is anodic. The pattern does not change between the first and the few subsequent cycles. Evidently *1* undergoes an oxidation the product (*2*) of which is reduced back to the original species in the reverse scan. *2* is not very stable (see below). However, it evidently remains undecomposed on the cyclic voltammetric time scale. The electrode process is thus

$$2 + ne \rightleftharpoons 1 \qquad (1)$$

We have not yet been able to prove conclusively the value of n. However, exhaustive electrolysis (which is hampered to some extent by the decomposition of *2*) at potentials more positive than the anodic peak potential (E_{pa}) strongly suggests that n = 1. With n = 1, ΔE_p is ~60 mV for a reversible system. The observed ΔE_p is considerably larger even at the slowest scan rate available to use and it increases with increasing scan rate (Table I). The electrode process (1) is thus quasireversible.

There are examples in the literature [5] where dinuclear copper(II) species are reduced at the hanging mercury drop electrode (hmde) to mixed copper(II)–copper(I) system. However, in our system an *oxidation* process is identified – in the product *2* the formal average oxidation number of copper atoms is 7/3. In order to prove that the redox process does not arise primarily from the ligand fragment, we have studied the binuclear species *3* (containing ligands very similar to that in *1*). This is not

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TABLE I. Cyclic Voltammetric Data of *1* (2 × 10^{-3} *M 1*, 0.1 *M* TEAP in Acetonitrile, 298 °K.[a]

Scan Rate V sec^{-1}	E_{pa} (V)	E_{pc} (V)	ΔE_p (V)
0.0117	0.452	0.334	0.118
0.0243	0.464	0.326	0.138
0.0450	0.500	0.315	0.185
0.0720	0.510	0.305	0.205
0.1360	0.540	0.275	0.265

[a] E_{pa} = Anodic peak potential; E_{pc} = Cathodic peak potential; $\Delta E_p = |E_{pa} - E_{pc}|$.

electroactive in the potential range of interest here (Fig. 1). The novel redox process reported herein is a characteristic of the Cu_3 frame.

A thorough electrochemical study on binuclear and trinuclear copper(II) complexes of imine–oxime and related ligands [1, 2] in the potential range +1.0 to –1.0 V (combination of platinum wire electrode and hmde) is under progress.

Acknowledgment

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