

Redox pattern in a group of copper(II) dimers : comments on equipotential $\text{Cu}_2^{\text{II}}-\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ and $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}-\text{Cu}_2^{\text{I}}$ couples

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Abstract. The redox activity of four oximato-bridged strongly exchange-coupled copper(II) dimers is examined using cyclic voltammetry and coulometry in acetonitrile solution. A well-defined quasi-reversible couple corresponding to the process $\text{Cu}_2^{\text{II}} + e \rightleftharpoons \text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ is observed in all cases. The couple corresponding to the next stage of reduction $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}} + e \rightleftharpoons \text{Cu}_2^{\text{I}}$ is identified in two complexes. The E_{298}^0 values for the various couples are reported with rationalisation of observed trends in terms of exchange interaction and ligand 10 Dq. The circumstances which may lead to superposition of the two successive one electron couples in copper(II) dimers are discussed.

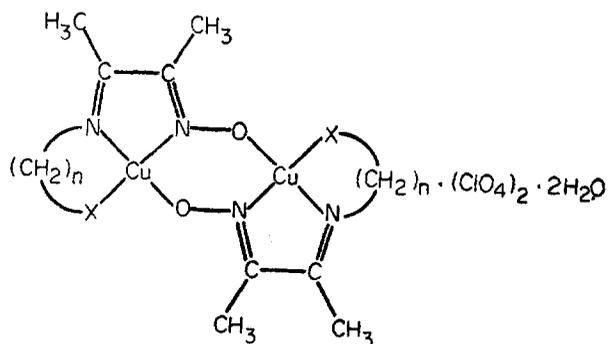
Keywords. Copper(II) dimers ; redox activity pattern ; $1e^-$ and $2e^-$ transfer.

1. Introduction

The electron transfer properties of strongly exchange-coupled binuclear copper(II) complexes of low molecular weight are of current interest as models of the ill-understood type 3 active site of copper oxidases (Fee 1975). Electrochemical techniques have been used in a limited number of cases (Patterson and Holm 1975; Hasty *et al* 1978; Addison 1976; Gagne *et al* 1977, 1979; Fenton and Lintvedt 1978) to assess such properties. We report in this paper the trends of electroactivity in four binuclear complexes (1)-(4).

2. Experimental

The complexes were prepared according to literature methods (1) and (2) (Baral and Chakravorty 1977), (3) (Ablow *et al* 1972) and (4) (Bertrand *et al* 1974). Cyclic voltammetry was performed by a PAR 174A polarographic analyzer and a PAR 175 universal programmer used in conjunction with a sensitive X-Y recorder. A hanging mercury drop working electrode (HMDE), a platinum wire auxiliary



- (1) $n = 2$, $X = \text{NH}_2$
 (2) $n = 2$, $X = \text{N}(\text{CH}_3)_2$
 (3) $n = 2$, $X = \text{OH}$
 (4) $n = 3$, $X = \text{OH}$

electrode and a saturated calomel reference electrode (SCE) constituted the three-electrode system. Purified acetonitrile was used as a solvent and tetraethylammonium perchlorate (TEAP) was the supporting electrolyte. Constant potential coulometry was performed at mercury pool electrode using PAR 173 potentiostat, PAR 179 digital coulometer and PAR 377A cell system. All electrochemical experiments were performed at 298 K under pure nitrogen atmosphere.

3. Results and discussion

From x-ray studies (Bertrand *et al* 1974) complex (3) is known to have a planar $\text{Cu}_2\text{N}_2\text{O}_2$ bridge system and the same is more or less likely to be true for the other complexes. While in (3) and (4) only the singlet state is populated (Bertrand *et al* 1974) at room temperature, (1) and (2) have the magnetic exchange coupling constant ($2J$) of -605 cm^{-1} , -815 cm^{-1} respectively (Baral and Chakravorty 1977). The relative magnitude of $2J$ is thus (1) < (2) < (3) and possibly (3) \sim (4).

The cyclic voltammetric response of (1)–(4) is collected in table 1. The voltammogram of (1) is displayed in figure 1. All potentials are referenced to SCE. Both (1) and (2) show the presence of two distinct couples *A* and *B*, *A* being the couple at higher potential. For complexes (3) and (4) only couple *A* could be detected since large currents flowed in these cases around -0.9 V due to some unknown process. Let E_{pa} and E_{pc} be the anodic and cathodic peak potentials and ΔE_p the magnitude of peak to peak separation. For a reversible one-electron process ΔE_p should be $\sim 60 \text{ mV}$. E_{298}^0 , the formal potential, is given by

$$E_{298}^0 = E_{pc} + 0.5 \Delta E_p \quad (1)$$

The results of table 1 show that all the couples are quasi-reversible. The reversibility character of *B* is better than that of *A* in (1) and (2). The *A* couple is more reversible in (3) and (4) than that in (1) and (2). Even in quasi-reversible cases equation (1) can be used to compute approximate E_{298}^0 values (table 1). Constant potential coulometry at potentials 200 mV more negative than E_{298}^0 of *A*, unequivocally established that it is an one-electron couple (table 1). Attempts

Table 1. Electrochemical data^a in acetonitrile (0.1 M TEAP) at 298 K.

Complex	Couple	E_{298}° (V)	ΔE_p (mV)
(1)	A	-0.44	175
	B	-0.80	102
(2)	A ^b	-0.48	210
	B	-0.88	68
(3)	A ^b	-0.37	87
(4)	A	-0.39	83

^a Symbols have the same meaning as in the text; scan rate 0.2 V s⁻¹.

^b Coulometric data: 4.25 mg of (2) electrolysed at -0.68 V, Q (Found) = 0.63, Q (Calc. for 1e) = 0.58; 4.41 mg of (3) electrolysed at -0.57 V, Q (Found) = 0.66, Q (Calc.) = 0.66.

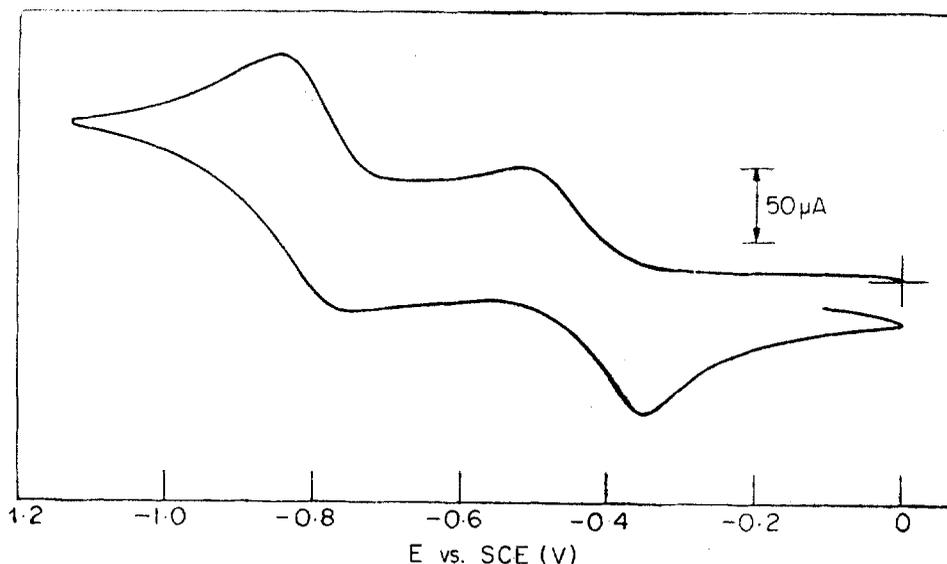


Figure 1. Cyclic voltammogram of (1) in acetonitrile (0.1 M TEAP) at 298 K; scan rate, 0.1 V s⁻¹.

to do coulometry at potentials more negative than E_{298}° of B led to continuous coulomb counts due to unknown reactions, thus vitiating direct determination of reaction stoichiometry. However, consideration of relative peak currents (figure 1) shows that both couples A and B involve the same number (one) of electrons. Thus we have schematically



The reduction potentials of copper(II) dimers will depend on factors like metal stereochemistry, ligand 10 Dq, 2J, etc. The various factors are usually interdependent and assessment of individual contribution by any one factor becomes

difficult. Even then certain observations are in order. In dimers with large $|2J|$, E_{298}^0 of couple *A* should decrease with increase in $|2J|$ (Hasty *et al* 1978). While this holds for (1) and (2), (3) and (4) with higher $|2J|$ is reduced at higher potentials. This may be due to the offsetting effect of ligand field order $10 Dq(NR_2) > 10 Dq(OH)$. Since $|2J| > 0$ means that the copper(II) atoms are orbitally interconnected, the transfer of the first electron is expected to affect the energetics of that of the second electron. There is, therefore, a difference ($\Delta\Delta G_{298}^0$) between the free energy changes of the two transfers and this results in a difference (ΔE_{298}^0) in the formal potentials of the two couples

$$\Delta\Delta G_{298}^0 = F \Delta E_{298}^0. \quad (4)$$

In a group of related complexes as $|2J|$ increases, ΔE_{298}^0 may also be expected (Hasty *et al* 1978) to increase. This is found to be true for (1) and (2).

If fast chemical and/or structural transformations are associated with the electron transfer steps and are such that they influence the two couples differently, equation (4) will still apply, but $\Delta\Delta G_{298}^0$ will now include a contribution from such transformations. If this contribution opposes that from the electron transfer step, a situation may arise where $\Delta\Delta G_{298}^0$ and hence ΔE_{298}^0 vanish. The transformation could be selective protonation (Mohanty and Chakravorty 1976, 1977) of the most reduced species (Cu_2^+), change in coordination number or geometry, change in conformation of ligand or protein (in enzymes), etc. The type 3 centre of copper oxidases contains a strongly coupled (S = O) dimer. Yet its function depends on couple *A* and *B* being equipotential or nearly so on the positive side of SCE (Farver *et al* 1978). Dynamic transformations of the kind indicated above may be of crucial importance in this regard. The complexes (1)-(4) are poor models of the type 3 centre in both E_{298}^0 and ΔE_{298}^0 values.

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