

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

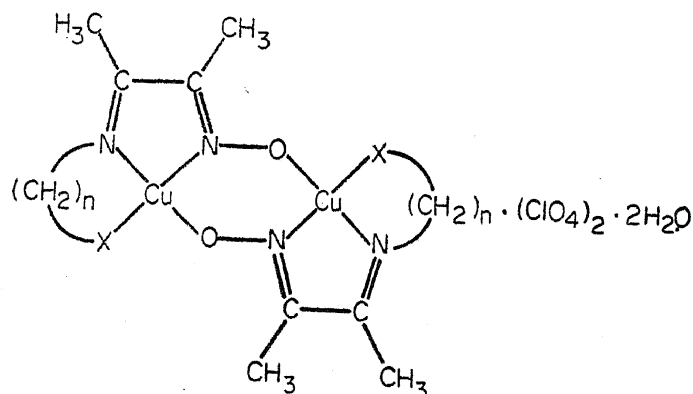
**Keywords.** Copper(II) dimers ; redox activity pattern ;  $1 e^-$  and  $2e^-$  transfer.

### 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) (Ablov *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  $-605 \text{ cm}^{-1}$ ,  $-815 \text{ cm}^{-1}$  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  $-0.9 \text{ V}$  due to some unknown process. Let  $E_{pa}$  and  $E_{pc}$  be the anodic and cathodic peak potentials and  $\Delta E_p$  the magnitude of peak to peak separation. For a reversible one-electron process  $\Delta E_p$  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<sup>a</sup> in acetonitrile (0.1 M TEAP) at 298 K.

Complex	Couple	$E_{298}^0$ (V)	$\Delta E_p$ (mV)
(1)	A	-0.44	175
	B	-0.80	102
(2)	A <sup>b</sup>	-0.48	210
	B	-0.88	68
(3)	A <sup>b</sup>	-0.37	87
(4)	A	-0.39	83

<sup>a</sup> Symbols have the same meaning as in the text; scan rate 0.2 V s<sup>-1</sup>.

<sup>b</sup> 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.

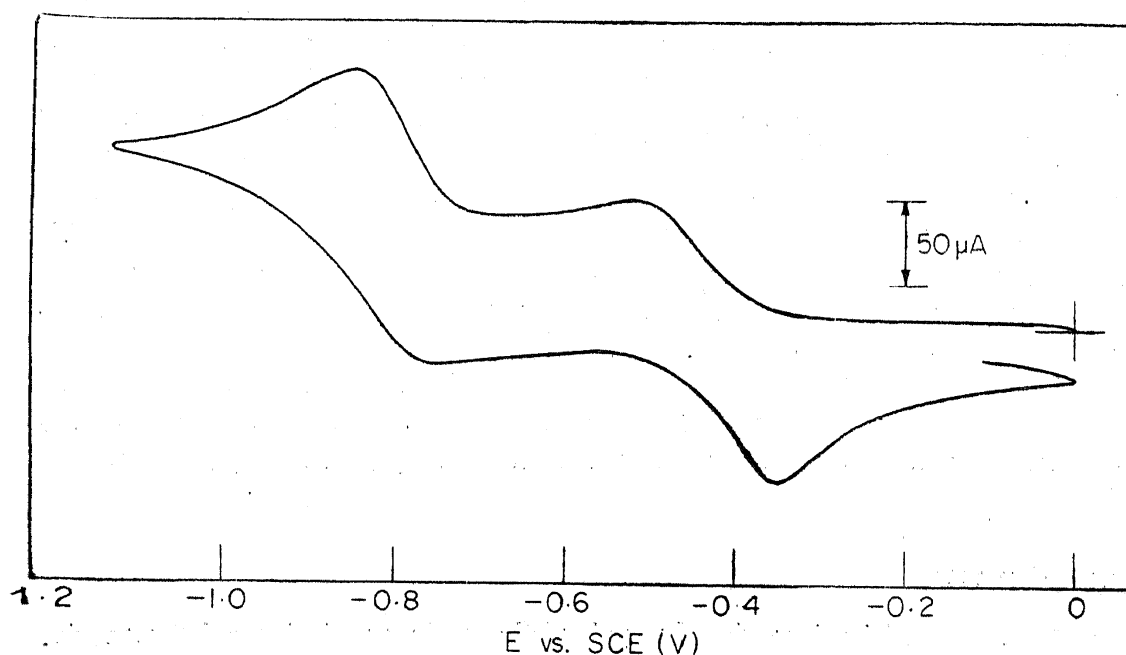
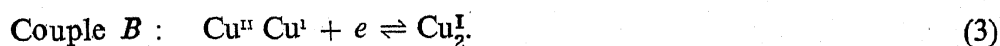


Figure 1. Cyclic voltammogram of (1) in acetonitrile (0.1 M TEAP) at 298 K; scan rate, 0.1 V s<sup>-1</sup>.

to do coulometry at potentials more negative than  $E_{298}^0$  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 ( $\Delta E_{298}^0$ ) 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,  $\Delta E_{298}^0$  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  $\Delta E_{298}^0$  vanish. The transformation could be selective protonation (Mohanty and Chakravorty 1976, 1977) of the most reduced species ( $Cu_2^I$ ), 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  $\Delta E_{298}^0$  values.

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### References

- Ablov A V, Belichuk N I and Pereligina M S 1972 *Russ. J. Inorg. Chem.* **17** 534  
 Addison A W 1976 *Inorg. Nucl. Chem. Lett.* **12** 899  
 Baral S and Chakravorty A 1977 *Proc. Indian Acad. Sci.* **A86** 45  
 Bertrand J A, Smith J H and Eller P G 1974 *Inorg. Chem.* **13** 1949  
 Farver O, Goldberg M, Wherland S and Pecht I 1978 *Proc. Natl. Acad. Sci.* **75** 5245  
 Fee J A 1975 *Struct. Bonding (Berlin)* **23** 1  
 Fenton D E and Lintvedt R L 1978 *J. Am. Chem. Soc.* **100** 6367  
 Gagne R R, Koval C A and Smith T J 1977 *J. Am. Chem. Soc.* **99** 8367  
 Gagne R R, Kreh R P and Dodge J A 1979 *J. Am. Chem. Soc.* **101** 6917  
 Hasty E H, Wilson L J and Hendrickson D N 1978 *Inorg. Chem.* **17** 1834  
 Mohanty J G and Chakravorty A 1976 *Inorg. Chem.* **15** 2912  
 Mohanty J G and Chakravorty A 1977 *Inorg. Chem.* **16** 1561  
 Patterson G H and Holm R H 1975 *Bioinorg. Chem.* **4** 257