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Reaction between Several Binuclear Copper(II) Complexes and One-electron Donors, such as TMPD and $[Cu(bip)_2]^+$

YUZO NISHIDA, NAOYASU OISHI and SIGEO KIDA

Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812, Japan

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Recently we have reported [1] that some binuclear copper(II) complexes of planar structure (for exmaple, [Cu(pia)] and $[Cu(doe)]^+$, see Fig. 1) are easily reduced to copper(I) complexes by two-electron donors, such as ascorbic acid and 3,5-di-t-butylcatechol, whereas such a redox reaction does not occur between a two-electron donor and a mononuclear square planar copper(II) complex, such as $[Cu(acac)_2]$ and [Cu(salen)]. In this paper, we report that planar binuclear copper(II) complexes show quite different behaviour from planar mononuclear copper(II) complexes in the reaction with one-electron donors, such as TMPD and $[Cu(bip)_2]^+$, where TMPD and bip represent N,N,N′,N′-tetramethyl-p-phenylenediamine and 2,2′-bipyridine, respectively.

TMPD is a colorless compound, but its oxidized form, $TMPD^+$ is blue, showing strong absorption bands at 560 and 608 nm in alcohol [2]. No remarkable color change was observed when TMPD was mixed with a planar mononuclear complex in methanol and left to stand at 20 °C in an aerobic condition for several hours. This indicates that no $TMPD^+$ is formed under such conditions. However, a remarkable blue color developed immediately when a binuclear copper(II) complex was added to a methanol solution of TMPD in an aerobic atmosphere. Figure 2 shows absorbance at 560 nm (due to $TMPD^+$) as a function of time obtained for the methanol solution of TMPD and $[Cu(Et\text{-}2\text{-}3)]^+$ (*cf.* Fig. 1). Similar results were also observed for the mixed solution of TMPD and $[Cu(doe)]^+$ and/or [Cu(pia)]. However, very little formation of $TMPD^+$ was detected in a solution containing a binuclear copper(II) complex and TMPD under a nitrogen atmosphere. These results indicate that the oxidation of TMPD occurs only when both binuclear complex and O_2 molecule are present in a solution.

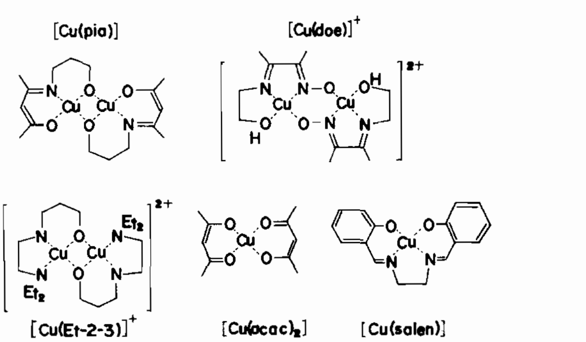

Fig. 1. Copper(II) complexes cited in this paper. For the properties of binuclear complexes, see references: [Cu(pia)] [8], $[Cu(doe)]^+$ [9] and $[Cu(Et\text{-}2\text{-}3)]^+$ [10].

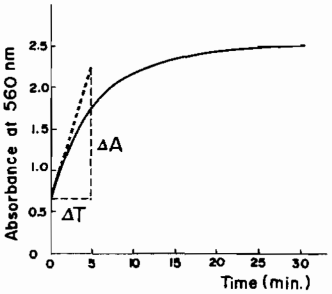

Fig. 2. Change of absorbance at 560 nm (——) in the system of TMPD (2.25×10^{-4} mol/l) and $[Cu(Et\text{-}2\text{-}3)]^+$ (2.5×10^{-5} mol/l) at 15 °C. Measurement was initiated 10 seconds after the solution was exposed to air.

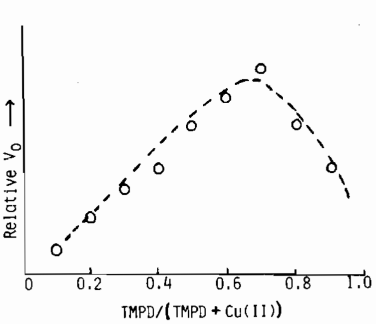

Fig. 3. Relative V_0 (○) at various ratios of TMPD to $[Cu(Et\text{-}2\text{-}3)]^+$ in methanol at 15 °C. Total concentration of (TMPD + $[Cu(Et\text{-}2\text{-}3)]^+$) was fixed at 2.5×10^{-4} mol/l.

According to a conventional method [3], we can evaluate the relative velocity of $TMPD^+$ formation at $t = 0$, V_0 ($= \Delta A/\Delta T$, *cf.* Fig. 2). It was found that V_0 is dependent on the binuclear complex used and also on the ratio of TMPD to binuclear complex. The latter relation was exemplified by the system of TMPD and $[Cu(Et\text{-}2\text{-}3)]^+$ in Fig. 3. Similar curves were also obtained for the [Cu(pia)]– and $[Cu(doe)]^+$–TMPD systems. These results indicate that the largest V_0 is attained at the ratio of 2:1 of TMPD to the binuclear complex. Thus, we propose that the oxidation of TMPD by binuclear copper(II) complex and O_2 proceeds by the following mechanism.

$$2\ \mathrm{TMPD} + \mathrm{Cu(II)\text{–}Cu(II)} \rightarrow \{(\mathrm{TMPD})_2\cdot(\mathrm{Cu(II)\text{–}Cu(II)})\}$$

$$\{(\mathrm{TMPD})_2\cdot(\mathrm{Cu(II)\text{–}Cu(II)})\} + \mathrm{O_2} \rightarrow 2\ \mathrm{TMPD}^+ + \mathrm{Cu(II)\text{–}Cu(II)} + \mathrm{O_2^{2-}}$$

It is known that $[\mathrm{Cu(bip)_2}]^+$ is slowly oxidized by O_2 in the air [4]. We have found in this study that the oxidation of $[\mathrm{Cu(bip)_2}]^+$ is greatly promoted by the presence of a binuclear copper(II) complex in the air. The methanol solution of $[\mathrm{Cu(bip)_2}]^+$ was prepared by adding a stoichiometric amount of ascorbic acid to $[\mathrm{Cu(bip)_2Cl}]^+$ under an atmosphere of nitrogen. In our experimental conditions, it took about 45 minutes for the oxidation of the half amount of $[\mathrm{Cu(bip)_2}]^+$ in an aerobic condition, whereas the oxidation of $[\mathrm{Cu(bip)_2}]^+$ was accelerated by about seven times in the presence of a binuclear copper(II) complex.

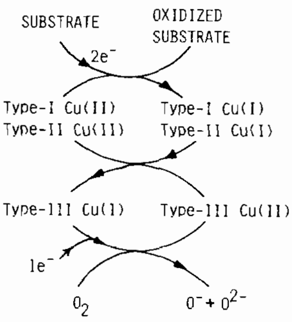

Fig. 4. Proposed cycle of electron-transfer reactions in laccase [7]. Substrates are ascorbic acid, catechols and hydroquinones.

Our present results seem to be very important in elucidating the function of copper proteins in the biological systems. For example, the following cycle of electron-transfer reactions was proposed for an enzymatic reaction of laccase [5] (*cf.* Fig. 4). The so-called Type-I and Type-II copper are incorporated in protein as mononuclear copper(II) complexes, but for Type-III copper, a binuclear structure has been proposed because of its ESR non-detectable nature [6]. In the above mechanism, it is noteworthy that reduced Type-I and Type-II copper are oxidized simultaneously by O_2 only in the presence of Type-III copper(II) complex. Thus, our present reaction (the oxidation of TMPD (or $[\mathrm{Cu(bip)_2}]^+$) by O_2 and a binuclear copper(II) complex) may provide a model for a part reaction of laccase, the so-called 'concerted electron-transfer reaction' [7].

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