

## Importance of Structural Factor in the Catalytic Activity of Copper(II) Complexes for the Oxidation of TMPD by Dioxygen

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*Binuclear copper(II) complexes with appropriate Cu–Cu distance (3.0 ~ 3.5 Å) exhibited high catalytic activity, except for some binuclear complexes with non-equivalent coordination sites, whereas planar mononuclear copper(II) complexes have practically no catalytic activity for the oxidation of TMPD (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine) by dioxygen. Measurements of polarographic half-wave potentials of copper(II) complexes have revealed that the catalytic activity of binuclear complexes largely depends on molecular structure as well as reduction potential. An intermediate complex formed by O<sub>2</sub>, two molecules of TMPD and a binuclear complex were proposed at which two-electron transfer proceeds easily as a 'concerted reaction' of the three reaction components.*

### Introduction

In the previous paper [1], we have shown that some binuclear copper(II) complexes (e.g., [Cu<sub>2</sub>(pia)<sub>2</sub>] and [Cu<sub>2</sub>(et-2-3)<sub>2</sub>]<sup>2+</sup>, etc.; for the abbreviations of the complexes, see Fig. 1) show high catalytic activity for the oxidation of TMPD (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine) by O<sub>2</sub> (eqn. (1)),



whereas planar mononuclear copper(II) complexes (e.g., [Cu(salen)] and [Cu(acac)<sub>2</sub>], etc.) show practically no catalytic activity. This result seems to be very important for the understanding of the functions and structures of Type-III copper in the biological system [2–4].

In order to elucidate the mechanism of the catalytic function of copper(II) complexes for the reaction (1) in more detail, in this report we have investigated the catalytic activities of various copper(II) complexes for the reaction (1), and discussed the results in relation to the structural and electrochemical properties of the copper(II) complexes.

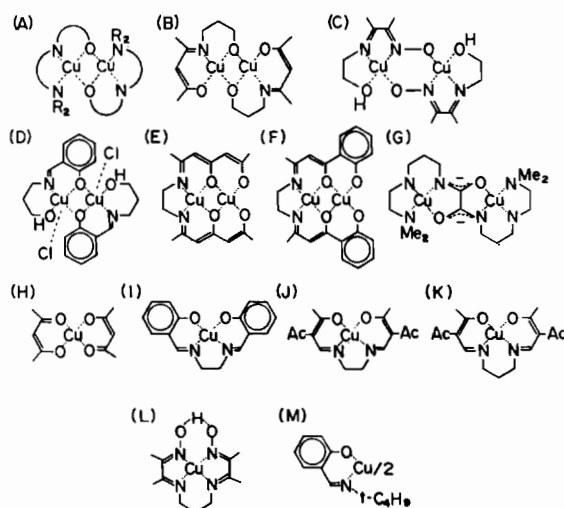


Fig. 1. Copper(II) complexes used in this study. (X denotes several anions, such as ClO<sub>4</sub>, NO<sub>3</sub> and PF<sub>6</sub>, etc.) (A) [Cu<sub>2</sub>(R<sub>2</sub>N–(CH<sub>2</sub>)<sub>m</sub>NH(CH<sub>2</sub>)<sub>n</sub>O)<sub>2</sub>]X<sub>2</sub>. (These complexes are abbreviated as [Cu<sub>2</sub>(R-m-n)<sub>2</sub>]X<sub>2</sub> [14]). (B) [Cu<sub>2</sub>(pia)<sub>2</sub>] [9-a]; (C) [Cu<sub>2</sub>(doe)<sub>2</sub>]X<sub>2</sub> [9-b]; (D) [Cu<sub>2</sub>(salpr)<sub>2</sub>Cl<sub>2</sub>]; (E) [Cu<sub>2</sub>(entko)<sub>2</sub>] [15]; (F) [Cu<sub>2</sub>(aapen)<sub>2</sub>] [10]; (G) [Cu<sub>2</sub>(me-ox)]X<sub>2</sub> [8]; (H) [Cu(acac)<sub>2</sub>]; (I) [Cu(salen)]; (J) [Cu(J-en)]; (K) [Cu(J-tn)] (L) [Cu(dopn)]X [17]; (M) [Cu(sal-t-bu)<sub>2</sub>].

### Experimental

#### Copper(II) Complexes

The copper(II) complexes used in this study are shown in Fig. 1 with their abbreviations.

#### Measurements of Catalytic Activity

Under an atmosphere of nitrogen, methanol solutions of TMPD and copper(II) complex were mixed in a 10 × 10 × 40 mm glass cell to make a solution of 2.25 × 10<sup>-4</sup> mol dm<sup>-3</sup> TMPD and 2.5 × 10<sup>-5</sup> mol dm<sup>-3</sup> copper(II) ion. When the solution was exposed to the air, the absorbance at 560 nm gradually increased due to the formation of TMPD<sup>+</sup>. This was recorded at 25 °C for a range of time. In the cases

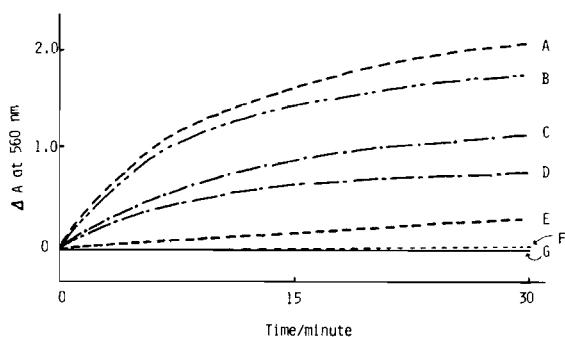


Fig. 2. Time course of  $\text{TMPD}^+$  formation at the presence of copper(II) complexes. (A)  $[\text{Cu}_2(\text{me-3-2})_2](\text{ClO}_4)_2$ ; (B)  $[\text{Cu}_2(\text{et-2-3})_2](\text{ClO}_4)_2$ ; (C)  $[\text{Cu}_2(\text{H-3-3})_2](\text{NO}_3)_2$ ; (D)  $[\text{Cu}_2(\text{pia})_2]$ ; (E)  $[\text{Cu}_2(\text{doe})_2](\text{NO}_3)_2$ ; (F)  $[\text{Cu}_2(\text{entko})_2]$ ; (G)  $[\text{Cu}_2(\text{me-ox})](\text{PF}_6)_2$ .

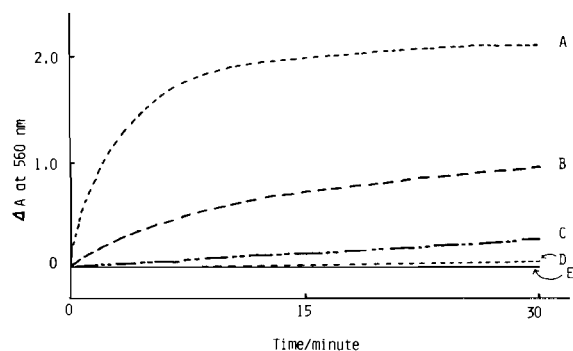


Fig. 3. Time course of  $\text{TMPD}^+$  formation at the presence of copper(II) complexes: (A)  $[\text{Cu}(\text{sal-t-bu})_2]$ ; (B)  $[\text{Cu}_2(\text{salpr})_2\text{-Cl}_2]$ ; (C)  $[\text{Cu}(\text{en})_2](\text{ClO}_4)_2$  and  $[\text{Cu}(\text{J-tn})]$ ; (D)  $[\text{Cu}(\text{acac})_2]$  and  $[\text{Cu}(\text{J-en})]$ ; (E)  $[\text{Cu}(\text{dopn})]\text{ClO}_4$ .

of  $[\text{Cu}_2(\text{entko})_2]$  and  $[\text{Cu}_2(\text{aapen})_2]$ , DMF was used for the solvent of the complexes.

#### Polarograms of Copper(II) Complexes

A Yanagimoto electrochemical system was employed for polarographic experiments. The measurements were performed at  $20^\circ\text{C}$ , a dropping mercury electrode being employed. The concentrations of complexes and the supporting electrolyte, tetraethylammonium perchlorate were about  $0.001$  and  $0.1 \text{ mol dm}^{-3}$ , respectively. Slopes and half-wave potentials were evaluated from plots of  $\log[i/(i_d - i)]$  vs.  $E$ .  $E_{1/2}$  values are referenced to a saturated calomel electrode.

### Results and Discussion

#### Catalytic Activity of Planar Copper(II) Complexes

The time courses of the  $\text{TMPD}^+$  formation at the presence of a copper(II) complex are shown in Figs.

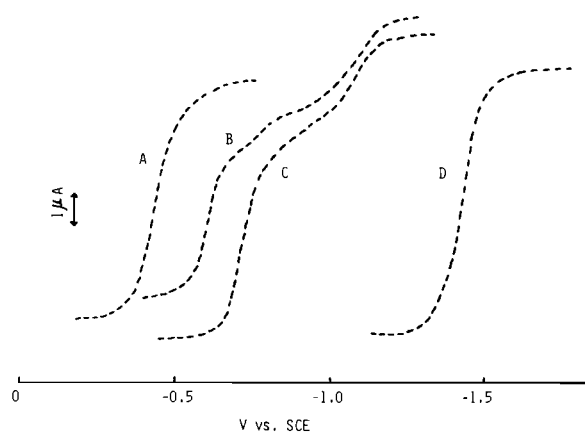


Fig. 4. Polarograms of some binuclear copper(II) complexes: (A)  $[\text{Cu}_2(\text{me-3-2})_2](\text{ClO}_4)_2$ ; (B)  $[\text{Cu}_2(\text{H-3-3})_2](\text{NO}_3)_2$ ; (C)  $[\text{Cu}_2(\text{me-ox})](\text{PF}_6)_2$ ; (D)  $[\text{Cu}_2(\text{pia})_2]$ .

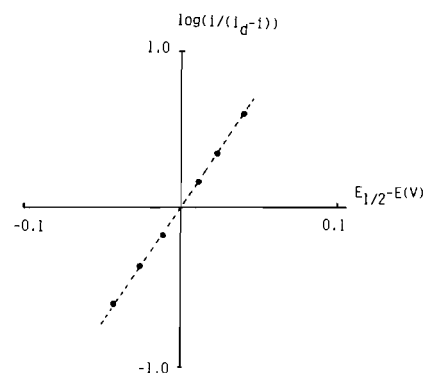


Fig. 5. Plot of  $\log[i/(i_d - i)]$  vs.  $(E_{1/2} - E)$  from the polarographic reduction of  $[\text{Cu}_2(\text{pia})_2]$ . The dots are experimental points.

2 and 3. Since  $\text{TMPD}$  is not oxidized by  $\text{O}_2$  alone, the amount of  $\text{TMPD}^+$  formed reflects the catalytic activity of the copper(II) complex used. The results revealed that some binuclear complexes exhibit high catalytic activities, whereas other binuclear complexes,  $[\text{Cu}_2(\text{me-ox})]^{2+}$ ,  $[\text{Cu}_2(\text{entko})_2]$  and  $[\text{Cu}_2(\text{aapen})_2]$ , and planar mononuclear complexes have little or practically no catalytic activities.

Some of polarograms obtained in this study are shown in Fig. 4. The half-wave potentials and the slopes evaluated from the plots of  $\log[i/(i_d - i)]$  vs.  $E$  are listed in Table I, an example of the plots of  $\log[i/(i_d - i)]$  being shown in Fig. 5. The values in Table I reveal that these polarographic waves are reversible. According to Aihara and Kubo [5],  $[\text{Cu}_2(\text{me-3-2})_2]^{2+}$  and  $[\text{Cu}_2(\text{et-2-3})_2]^{2+}$  are reduced in one two-electron step, i.e.,  $\text{Cu(II)-Cu(II)} + 2e^- \rightarrow \text{Cu(I)-Cu(I)}$ . However, the values in Table I suggest that  $[\text{Cu}_2(\text{H-3-3})_2]^{2+}$  and  $[\text{Cu}_2(\text{me-ox})]^{2+}$  are reduced in two one-electron steps [6], i.e.,  $\text{Cu(II)-Cu(II)} + e^- \rightarrow \text{Cu(II)-Cu(I)}$  and  $\text{Cu(II)-Cu(I)} + e^- \rightarrow \text{Cu(I)-Cu(I)}$ .

TABLE I. Polarographic Data.

Complex	$E_{1/2}/V(\text{slope}/mV)$	Ref.
$[\text{Cu}_2(\text{me-3-2})_2]^{2+}$	-0.39(53)	5
$[\text{Cu}_2(\text{H-3-3})_2]^{2+}$	-0.65(54), -1.16(65)	a
$[\text{Cu}_2(\text{et-2-3})_2]^{2+}$	-0.53	5
$[\text{Cu}_2(\text{pia})_2]$	-1.42(62)	a
$[\text{Cu}_2(\text{me-ox})]^{2+}$	-0.69(58), -1.06(62)	a
$[\text{Cu}_2(\text{entko})_2]$	-1.02(58), -1.90(64)	a
$[\text{Cu}(\text{salen})]$	-1.21	16
$[\text{Cu}(\text{J-en})]$	-1.09(58)	a
$[\text{Cu}(\text{J-tn})]$	-0.98(56)	a
$[\text{Cu}(\text{dopn})]^+$	-0.56	17

<sup>a</sup>This work.

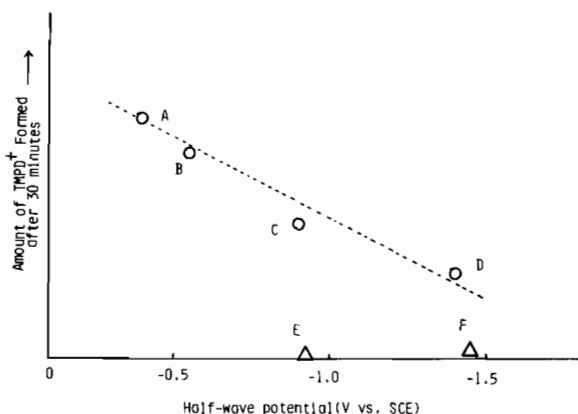


Fig. 6. Relationship between the catalytic activity and half-wave potentials of some binuclear copper(II) complexes: (A)  $[\text{Cu}_2(\text{me-3-2})_2](\text{ClO}_4)_2$ ; (B)  $[\text{Cu}_2(\text{et-2-3})_2](\text{ClO}_4)_2$ ; (C)  $[\text{Cu}_2(\text{H-3-3})_2](\text{NO}_3)_2$ ; (D)  $[\text{Cu}_2(\text{pia})_2]$ ; (E)  $[\text{Cu}_2(\text{me-ox})](\text{PF}_6)_2$ ; (F)  $[\text{Cu}_2(\text{entko})_2]$ .

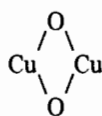
Cu(I). In the cases of  $[\text{Cu}_2(\text{doe})_2]^{2+}$ ,  $[\text{Cu}_2(\text{salpr})_2\text{Cl}_2]$  and  $[\text{Cu}_2(\text{aapen})_2]$ , distinct half-wave potentials for  $\text{Cu(II)} \rightarrow \text{Cu(I)}$  could not be obtained because of overlapping of reduction waves in the 0.0 ~ -1.5 V region. This is probably due to the presence of the reduction waves of the ligands in this region [7].

It appeared that the extensive variety of catalytic activity of the copper(II) complexes is mainly attributable to their reduction potentials, e.g., the more positive the reduction potential is, the higher the catalytic activity becomes. In Fig. 6, the catalytic activities of the binuclear complexes are plotted against half-wave potentials. In the cases of  $[\text{Cu}_2(\text{me-ox})]^{2+}$ ,  $[\text{Cu}_2(\text{H-3-3})_2]^{2+}$  and  $[\text{Cu}_2(\text{entko})_2]$ , the average values of two half-wave potentials were used. Figure 6 revealed that the above view is not always

correct though the general trend is nearly in line with the relation as supposed above. As obviously seen in Fig. 6,  $[\text{Cu}_2(\text{me-ox})]^{2+}$  and  $[\text{Cu}_2(\text{entko})_2]$  largely deviate from the general trend. Thus, the catalytic activity of copper(II) complex depends on not only reduction potential but also other factors, among which the most important one would be the structural factor.

The remarkable structural difference of  $[\text{Cu}_2(\text{me-ox})]^{2+}$  from those of  $[\text{Cu}_2(\text{H-3-3})_2]^{2+}$  and  $[\text{Cu}_2(\text{pia})_2]$  is found in the Cu—Cu distance; that of the former (>5 Å) [8] is much larger than those of the latter (3.0 ~ 3.5 Å) [9]. Accordingly, the inertness of the catalytic activity of  $[\text{Cu}_2(\text{me-ox})]^{2+}$  may be explained in terms of the long Cu—Cu distance.

As shown in Fig. 2,  $[\text{Cu}_2(\text{entko})_2]$  and  $[\text{Cu}_2(\text{aapen})_2]$  have practically no catalytic activity. However, their Cu—Cu distances are normal (about 3.0 Å) [10] as complexes having

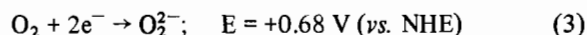
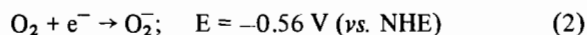


bridging system. The obvious characteristics of their complexes is that each molecule has two different coordination sites, the  $\text{N}_2\text{O}_2$  and the  $\text{O}_4$  donor sets. This appears to relate to the reason for the poor catalytic activity of these complexes, but final conclusion cannot be drawn at present.

#### Origin of the Catalytic Activity of Binuclear Complexes

As already mentioned [1], the electron of TMPD is transferred to  $\text{O}_2$  when TMPD, a copper(II) complex and  $\text{O}_2$  are present in a solution. In the absence of  $\text{O}_2$ , copper(II) complexes are not reduced by TMPD (except for the cases of non-planar copper(II) complexes, such as  $[\text{Cu}(\text{bip})_2\text{Cl}]^+$ , where bip represents 2,2'-bipyridine). The largest initial velocity of the reaction (1) is attained when the ratio of TMPD to a binuclear complex is 2:1.

It is well known that  $\text{O}_2$  receives electrons in the following ways [11],



The standard electrode potentials predict that two-electron reaction (3) is much more facile than the one-electron reaction (2).

On the basis of the above discussion, we propose that the formation of an intermediate complex formed with TMPD, copper complex and  $\text{O}_2$  (as illustrated in Fig. 7) plays a key role in the catalytic

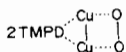


Fig. 7. An 'Intermediate Complex' formed by two molecules of TMPD, a binuclear copper(II) complex and dioxygen.

reaction of planar binuclear copper(II) complexes. Thus, the two-electron transfer proceeds easily via the intermediate complex as a 'concerted reaction' of two molecules of TMPD,  $O_2$  and a binuclear complex. This model well explain the fact that binuclear copper complexes with Cu—Cu distance in the range 3.0 ~ 3.5 Å have high catalytic activity for the reaction (1).

It is to be noted that the roles of binuclear copper complexes in two-electron transfer reactions were already shown in the reaction with ascorbic acid [8], and catalytic activity for the degradation of  $H_2O_2$  [12], where intermediate complexes similar to that of Fig. 7 were also supposed to be important for a facile reaction.

#### Catalytic Activity of Non-planar Mononuclear Complexes

In contrast to the very poor catalytic activity of planar mononuclear copper(II) complexes, some non-planar copper(II) complexes (such as  $[Cu(\text{sal-t-bu})_2]$  [13], as shown in Fig. 1) show high catalytic activity for the reaction (1). The mechanism of this reaction seems to be entirely different from that of the binuclear complexes. Detailed study on the reactions of this type is in progress, and the results will be reported shortly.

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