Catalytic Activity of Copper(II) Complexes with a Flexible Polyatomic Bridging Group for the Oxidation of TMPD by O_2

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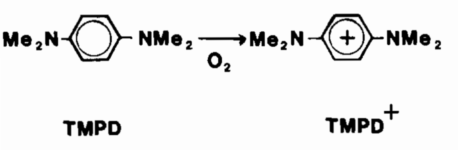
*The catalytic activities of copper(II) complexes with a flexible polyatomic bridging group were investigated on the oxidation of N,N,N′,N′-tetramethyl-*p*-phenylenediamine by dioxygen. The general trends revealed are: 1) the longer and more flexible the bridging chain, the higher the catalytic activity, and 2), flexibility is also required for chelating groups to manifest a high catalytic activity; complexes composed of chelating groups which form stable, rigid, square-planar coordination units would not be good catalysts.*

Introduction

In preceding papers [1, 2] we reported that planar binuclear copper(II) complexes with rigid bridging structure show much higher catalytic activity for the oxidation of TMPD (N,N,N′,N′-tetramethyl-*p*-phenylenediamine) by dioxygen (reaction (1)) than do the relevant mononuclear copper(II) complexes, and pointed out the importance of the structural factor rather than redox potentials for the emergence of catalytic function.



(1)

The remarkable catalytic activity of the binuclear copper(II) complexes should be closely related to the functions of Type-III copper in enzymes such as tyrosinase and laccase whose active center contains two copper ions. In such enzymes, however, it is unlikely that the two copper ions are linked by a rigid bridge, as was observed in the synthetic binuclear copper(II) complexes so far studied [1–4], but they are rather likely to be connected with a flexible polyatomic chain [5–7]. Thus we have in this study investigated the catalytic activity of binuclear copper(II) complexes with a flexible bridge. The binucleating ligands employed are grouped into three types, *i.e.*, those containing the tridentate

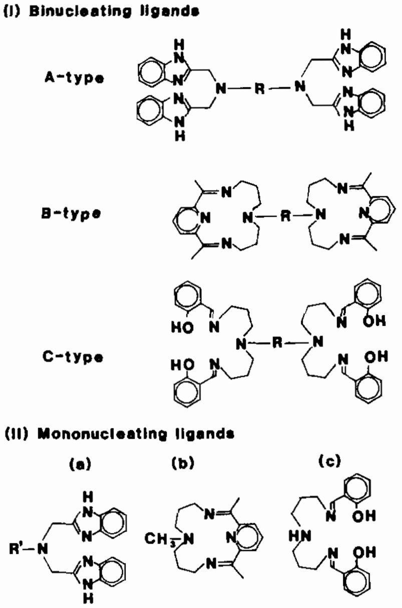


Fig. 1. The chemical structures of ligands cited in this paper, and their abbreviations. (I) binucleating ligands, A-type: R = $-(CH_2)_6-$ (L-6); R = $-(CH_2)_4-$ (L-4); R = $-(CH_2)_3-$ (L-3); R = *p*-xylyl($-CH_2C_6H_4CH_2-$) (L-px); R = *m*-xylyl (L-mx); B-type: R = $-(CH_2)_6-$ (cr-6); C-type: R = *p*-xylyl H_4(px-saldpt); R = *m*-xylyl H_4(mx-saldpt). (II) mononucleating ligands, (a), R′ = $C_6H_5CH_2-$ (babz); (b), (m-cr), and (c), H_2(saldpt).

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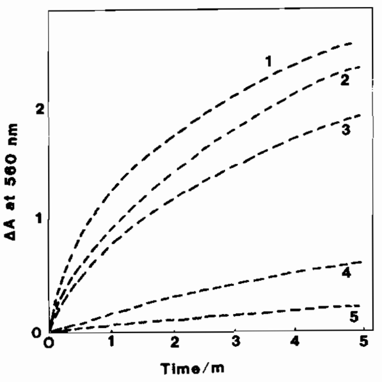

Fig. 2. Time course of the absorbance at 560 nm in the reaction mixture of TMPD and a copper(II) complex (in methanol at 300 K, methanol solutions of the tetrafluoroborate salts of complexes were used, [Cu^{2+}] = 2.5 × 10^{-5} mol dm^{-3}, [TMPD] = 4 × 10^{-4} mol dm^{-3}). 1: $Cu_2(L\text{-}6)^{4+}$; 2: $Cu_2(L\text{-}4)^{4+}$; 3: $Cu_2(L\text{-}mx)^{4+}$; 4: $Cu_2(L\text{-}3)^{4+}$; 5: $Cu(babz)^{2+}$.

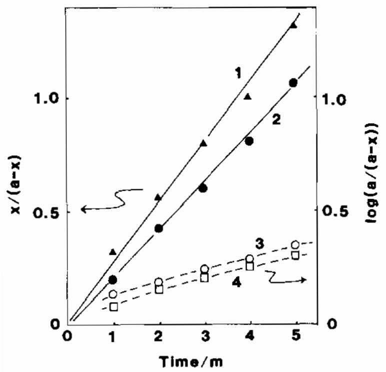

Fig. 3. The plots of $x/(a - x)$ for 1: $Cu_2(L\text{-}4)^{4+}$–TMPD and 2: $Cu_2(L\text{-}6)^{4+}$–TMPD systems. The $\log(a/(a - x))$ plots are for 3: $Cu_2(L\text{-}4)^{4+}$–TMPD and 4: $Cu_2(L\text{-}6)^{4+}$–TMPD systems.

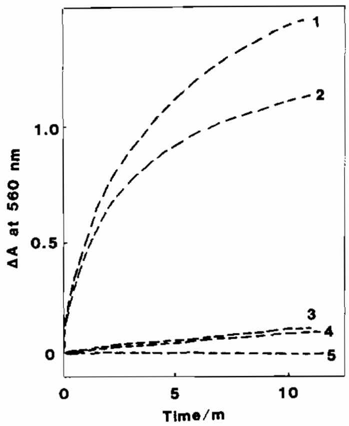

Fig. 4. Time course of the absorbance at 560 nm in the reaction mixture of TMPD and a copper(II) complex (in dmf/methanol = 1/7 solution at 298 K, [Cu^{2+}] = [TMPD] = 2.5 × 10^{-4} mol dm^{-3}. 1: A-type, $Cu_2(L\text{-}mx)(NO_3)_4$; 2: A-type, $Cu_2(L\text{-}px)(NO_3)_4$; 3: C-type, $Cu_2(mx\text{-}saldpt)$; 4: C-type, $Cu_2(px\text{-}saldpt)$; 5: B-type, $Cu_2(cr\text{-}6)(ClO_4)_4$.

(A-type), macrocyclic quadridentate (B-type) and quinquedentate (C-type) chelating groups, as illustrated in Fig. 1.

Experimental

The binuclear copper(II) complexes (A-type [6, 7] and C-type [5]) were prepared according to published methods. The complex (B-type [8]) was a kind gift from Prof. I. Murase.

The measurements of the catalytic activities for the reaction (1) were performed according to the reported method [2]. The measurements were carried out with a Shimadzu model MPS-5000 spectrophotometer.

Results and Discussion

The effect of bridging group on the catalytic activity was investigated for the series of the A-type complexes (*cf.* Fig. 1). The reaction (1) was run in the presence of a copper(II) complex in methanol solution at 300 K. The reaction was monitored by the absorption at 560 nm of TMPD$^+$ formed [1, 2]. The result was shown in Fig. 2. As obvious from Fig. 2, the catalytic activity is dependent on the bridging group. Among the complexes so far utilized here the larger and the more flexible the bridging group, the higher the catalytic activity exhibited. The component mononuclear complex, $Cu(babz)^{2+}$ (*cf.* Fig. 1) showed the weakest catalytic activity. These facts imply that in order to achieve the catalytic reaction, the two coordination units must approach each other and assume the favorable form for the formation of an intermediate complex with O_2 and TMPD.

In order to gain further insight into the reaction mechanism, $\log[a/(a - x)]$ (first-order plot) and $x/(a - x)$ (second-order plot) were plotted *versus* time (Fig. 3), where a and x represent the initial and the reacted quantities (mol dm^{-3}) of TMPD, respectively. The results showed that only the second-order rate plots gave straight lines intersecting the zero point. Thus, the reaction rate is second-order with respect to TMPD.

The relative initial reaction velocities $V_0 = -(d[TMPD]/dt)_{t=0}$ were determined from the

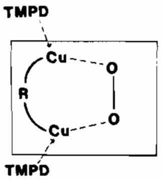

Fig. 5. Assumed intermediate complex in the oxidation reaction of TMPD catalyzed by the copper(II) complex with a flexible polyatomic bridge (R).

plots of absorbance at 560 nm *versus* time as reported in the literature [1]. The Cu^{2+}–TMPD continuous variation plots for V_0 revealed a maximum at $[Cu^{2+}]/[TMPD] = 1$. These results are quite consistent with the assumption proposed in the preceding papers [1, 2] for the catalytic function of binuclear copper(II) complexes with rigid bridge; that is, in the rate determining step two molecules of TMPD react with one binuclear complex.

The catalytic activities of A-, B- and C-type complexes were compared, as illustrated in Fig. 4. In contrast to the remarkable catalytic activity of A-type complexes, C-type complexes showed lower activities, and the B-type complex no activity. As already pointed out in the preceding paper [2], the reduction potentials of the complexes cannot be the main factor to determine the catalytic activities of copper(II) complexes. In fact, the polarographic halfwave potentials of the mononuclear complexes, $Cu(babz)(NO_3)_2$, $[Cu(m\text{-}cr)](ClO_4)_2$ and [Cu(saldpt)], corresponding to A-, B- and C-types, are –0.05, –0.40 and –1.12 V (*vs.* SCE) [9], an order which does not agree with that of the catalytic activity.

According to the results of the preceding papers [1, 2] and those obtained in this study, the reaction (1) is assumed to proceed via an intermediate complex formation as shown in Fig. 5; that is, the first step is the association of an O_2 molecule with two copper ions (intermediate complex enclosed by a rectangle in Fig. 5), the second step is the approaching of two molecules of TMPD to the copper ions from the other side of the coordination plane, and the third is the two-electron transfer from TMPD to dioxygen through the copper ions. In the case of binuclear complexes with a flexible polyatomic bridge, the structure of the intermediate complex would be considerably different from those [2] of the rigid-bridged binuclear complexes. Such a structure should depend on the bridging group and the coordination structure. In the case of A-type complexes the coordination manner is the most flexible among the three types, since they contain open chain tridentate chelating groups. Hence, A-type complexes can easily assume a favorable conformation for the formation of an intermediate complex to achieve the two-electron transfer from TMPD to O_2. Thus, the A-type complexes exhibit the highest catalytic activities. In the case of B-type complexes the chelating groups are the 14-membered N_4-macrocycles which are only suitable for square planar coordination so that only weak axial coordination is possible for the fifth coordination. This makes it difficult to form an intermediate complex favorable to mediate the two-electron transfer from TMPD to O_2. The C-type complexes contain open-chain quinquedentate chelating groups, whose coordination flexibility is between A- and B-type complexes. Accordingly, the C-type complexes bear some catalytic activities lower than those of A-type complexes.

In conclusion, in order to display a high catalytic activity the copper(II) complexes must assume a conformation which is favorable for forming an intermediate complex with O_2 and TMPD to perform the facile two-electron transfer from TMPD to O_2. Therefore, the catalytic activity of binuclear copper(II) complexes with a flexible bridge is highly dependent on the length and flexibility of the bridging groups and also on the flexibility of the chelating group.

References

1 Y. Nishida, N. Oishi and S. Kida, *Inorg. Chim. Acta, 46,* L69 (1980).
2 Y. Nishida, N. Oishi, H. Kuramoto and S. Kida, *Inorg. Chim. Acta, 57,* 253 (1982).
3 N. Oishi, Y. Nishida, K. Ida and S. Kida, *Bull. Chem. Soc. Jpn., 53,* 2847 (1980).
4 N. Oishi, M. Takeuchi, Y. Nishida and S. Kida, *Bull. Chem. Soc. Jpn., 55,* 3747 (1982).
5 N. Oishi, Y. Nishida and S. Kida, *Chem. Lett.,* 1031 (1981).
6 Y. Nishida, K. Takahashi, H. Kuramoto and S. Kida, *Inorg. Chim. Acta, 54,* L103 (1981).
7 K. Takahashi, Y. Nishida and S. Kida, *Bull. Chem. Soc. Jpn., 56,* 339 (1983).
8 I. Murase, K. Hamada and S. Kida, *Inorg. Chim. Acta, 54,* L171 (1981).
9 M. Takeuchi, N. Oishi, Y. Nishida and S. Kida, unpublished works.