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Effect of Coordination Structure on the Redox Reactions of Mononuclear Copper(II) Complexes

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Abstract

Catalytic activities of mononuclear copper(II) complexes were studied for the reactions, 1) O_2 oxidation of N,N,N′,N′-tetramethyl-1,4-diaminobenzene, and 2) decomposition of hydrogen peroxide. For both reactions, distorted tetrahedral complexes showed much higher reactivities than the complexes of other coordination geometries such as plane, square pyramid and trigonal bipyramid. This could not be explained in terms of the reduction potentials of the complexes only, but the governing factor for this fact was attributed to the ease of the fifth coordination of tetrahedral complexes caused by the spacial distribution of the electron hole of copper(II) ion.

Introduction

In previous papers Nishida *et al.* reported the reactivities of square planar coordinated copper(II) complexes in some redox reactions, and revealed that binuclear complexes with appropriate Cu–Cu distances are much more reactive than mononuclear ones, irrespective of their reduction potentials [1–4]. Reactivities of mononuclear copper(II) complexes of various coordination geometries were also studied [2, 3], *e.g.* square planar complexes such as [Cu(salen)], [Cu(J-en)] and $[Cu(m\text{-}cr)]^{2+}$ (for the abbreviations of the complexes, see Fig. 1) were not reduced by ascorbic acid and/or 3,5-di-tert-butylcatechol, whereas the distorted tetrahedral complexes such as $[Cu(sal\text{-}tbu)_2]$ and $[Cu(p\text{-}ip)_2]$ (see also Fig. 1) were readily reduced to copper(I) complexes which are oxidized by molecular oxygen to the original copper(II) complexes.

Reactivities of metal complexes in redox reactions have been considered to depend mainly on the redox potentials. However, our experimental results have clearly shown that this is not true *i.e.* the reduction potentials of some square planar complexes are higher than those of the tetrahedral complexes, such as $[Cu(sal\text{-}tbu)_2]$, as shown in the Table I. Thus, in

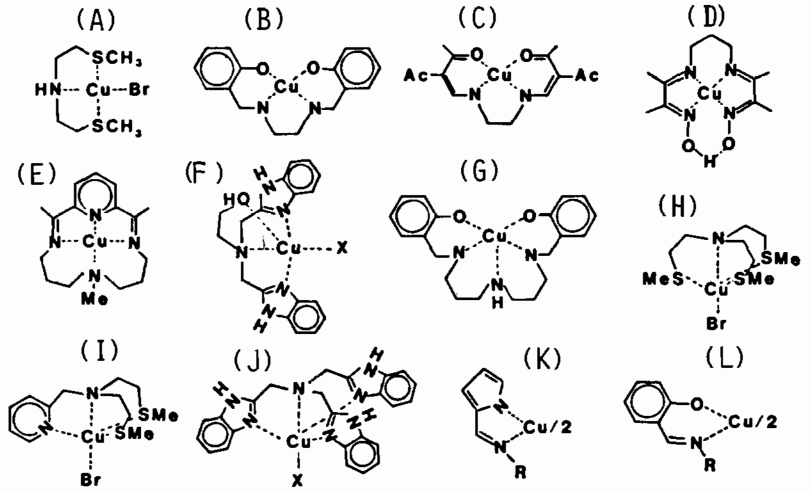

Fig. 1. The copper(II) complexes used in this study and their abbreviations. These complexes are classified into four groups. (1) square planar complexes, (A) $[Cu(ns_2)Br]ClO_4$, (B) [Cu(salen)], (C) [Cu(J-en)], (D) $[Cu(dopn)]ClO_4$, (E) $[Cu(m\text{-}cr)](ClO_4)_2$; (2) square pyramidal complexes, (F) $[Cu(n_3O)X]ClO_4$ (X = Cl, Br), (G) [Cu(saldpt)]; (3) trigonal bipyramidal complexes, (H) $[Cu(ns_3)Br]ClO_4$, (I) $[Cu(n_2s_2)Br]ClO_4$, (J) $[Cu(ntb)X]PF_6$ (X = Cl, Br); and (4) tetrahedral complexes, (K) $[Cu(p\text{-}R)_2]$ (R = me, CH_3; = ip, i-C_3H_7), (L) $[Cu(sal\text{-}R)_2]$ (R = ip, i-C_3H_7; = tbu, t-C_4H_9).

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TABLE I. Electrochemical Data of the Compounds.

Compound	$E'_{1/2}$ (V *vs.* SCE)	Compound	$E'_{1/2}$ (V *vs.* SCE)
[Cu(ns$_2$)Br]ClO$_4$	+0.19	[Cu(ns$_3$)Br]ClO$_4$	+0.34
[Cu(m-cr)](ClO$_4$)$_2$	−0.40	[Cu(n$_2$s$_2$)Br]ClO$_4$	+0.13
[Cu(dopn)]ClO$_4$	−0.64	[Cu(ntb)Br]PF$_6$	−0.14
[Cu(J-en)]	−1.09	[Cu(ntb)Cl]PF$_6$	−0.20
[Cu(salen)]	−1.21*	[Cu(p-ip)$_2$]	−0.53*
[Cu(n$_3$O)Br]ClO$_4$	−0.12	[Cu(p-me)$_2$]	−0.61*
[Cu(n$_3$O)Cl]ClO$_4$	−0.18	[Cu(sal-tbu)$_2$]	−0.66*
[Cu(saldpt)]	−1.08	[Cu(sal-ip)$_2$]	−0.74*

*Electrochemical data of these complexes were reported earlier by Holm and Patterson [17].

order to elucidate the relation between the coordination structure and the reactivity of copper(II) complexes in redox reactions, we have in this study examined reactivities or catalytic activities of copper(II) complexes of various coordination geometries for the following reactions,

reaction (1) $\mathrm{TMPD} + \mathrm{Cu(II)} \xrightarrow[\text{under } N_2]{} \mathrm{TMPD}^+ + \mathrm{Cu(I)}$

reaction (2) $\mathrm{TMPD} \xrightarrow[\mathrm{Cu(II)}, O_2]{} \mathrm{TMPD}^+$

reaction (3) $2H_2O_2 \xrightarrow[\mathrm{Cu(II)}]{} 2H_2O + O_2$

where TMPD denotes N,N,N′,N′-tetramethyl-1,4-diaminobenzene, and Cu(II) and Cu(I) represent mononuclear copper(II) and copper(I) complexes respectively.

Experimental

Materials

Copper(II) complexes used in this study were prepared by the published methods. [Cu(ns$_2$)Br]-ClO$_4$ [5], [Cu(m-cr)](ClO$_4$)$_2$ [6], [Cu(dopn)]-ClO$_4$ [7], [Cu(n$_3$O)X]ClO$_4$ (X = Cl, Br) [8], [Cu-(ns$_3$)Br]ClO$_4$ [9], [Cu(n$_2$s$_2$)Br]ClO$_4$ [10, 11], [Cu(ntb)X]PF$_6$ (X = Cl, Br) [12], and [Cu(p-R)$_2$] [13]. TMPD·2HCl and H_2O_2 (guaranteed grade, 30%, Nakarai Chemicals) were obtained commercially.

Evaluations of Reactivities

Reaction (1)

The reaction was run by mixing methanol (dmf in the case of [Cu(salen)]) solutions of a copper(II) complex ([Cu^{2+}] = 2.5 × 10^{-4} mol dm^{-3}) and TMPD (2.5 × 10^{-4} mol dm^{-3}) in (1:1) ratio at room temperature under nitrogen atmosphere. The reaction was monitored by measuring at 565 nm the absorbance of the resulted solution, since TMPD$^+$ shows a strong absorption band at this wavelength.

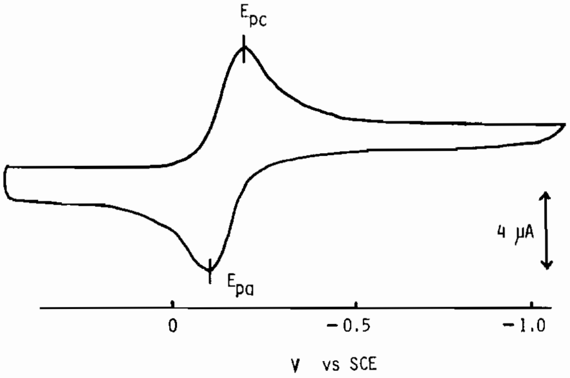

Fig. 2. Cyclic voltammogram of [Cu(n$_3$O)Cl]ClO$_4$ (in dmf, scan rate 40 mV/sec).

Reaction (2)

The methanol solutions of copper(II) complex and TMPD were mixed in a 10 × 10 × 40 mm glass cell to make a solution of 2.5 × 10^{-4} mol dm^{-3} TMPD and 2.5 × 10^{-5} mol dm^{-3} copper(II) complex under an atmospheric condition at 25 °C. The absorbance at 565 nm of the resulted solution gradually increased with the formation of TMPD$^+$, and this was recorded for a range of time intervals.

Reaction (3)

The methanol solution (2 cm^3) of the copper(II) complex (2 × 10^{-3} mol dm^{-3}) was mixed with 2 cm^3 of H_2O_2 solution (2 × 10^{-2} mol dm^{-3}) at 25 °C, and the content of H_2O_2 in the reaction mixture was determined by the Fe^{2+}–NH$_4$NCS method [14].

Measurement

The cyclic voltammograms were obtained by the published procedure [15] in N,N-dimethylformamide solutions at 20 °C, a typical example being shown in Fig. 2. The $E'_{1/2}$ values in Table I were calculated by the equation, $E'_{1/2} = \frac{1}{2}(E_{pa} + E_{pc})$, and referenced to the saturated calomel electrode (SCE) corrected by the use of the $E_{1/2}$ value of ferrocene [16] and [Cu-

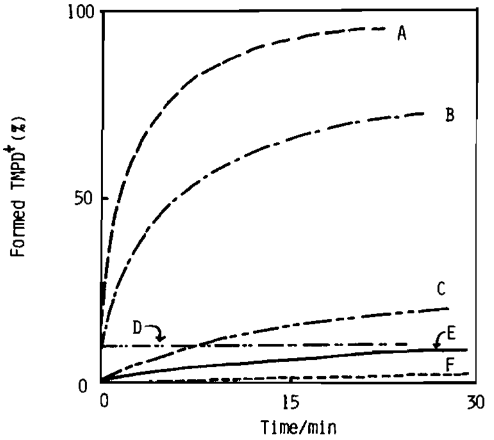

Fig. 3. Time course of $TMPD^+$ formation in the presence of a copper(II) complex. The percentage of the $TMPD^+$ formed was calculated by the use of the absorbance at 565 nm; (A) (– – –) $[Cu(sal\text{-}ip)_2]$, (B) (—-–) $[Cu(p\text{-}ip)_2]$, (C) (–··–) $[Cu(ntb)Br]PF_6$, (D) (–··—) $[Cu(ns_3)Br]ClO_4$, (E) (———) $[Cu(n_3O)Cl]ClO_4$ and (F) (------) $[Cu(J\text{-}en)]$.

(salen)] ($E'_{1/2}$ =–1.21 V *vs.* SCE) [17] as an internal standard. The obtained data were summarized in Table I, in which the values with an asterisk were already reported by Patterson and Holm [17]. Absorption spectra were measured with a Shimadzu spectrophotometer MPS-5000 or UV–240.

Results

In nitrogen atmosphere the only complexes ($[Cu(ns_2)Br]ClO_4$, $[Cu(ns_3)Br]ClO_4$ and $[Cu(n_2s_2)Br]ClO_4$) incorporating sulfur as donor atoms readily reacted with TMPD to give $TMPD^+$ in 100% yield (with respect to copper(II)), whereas the other complexes were inactive toward TMPD. However, these three complexes, once reduced to copper(I) no longer showed any change upon exposure to the open atmosphere *i.e.*, they have no catalytic activity for the O_2 oxidation of TMPD (reaction 2)). For reaction (2), [Cu(salen)] and all the square planar complexes (except for $[Cu(ns_2)Br]ClO_4$) were inert, whereas complexes other than the square planar type catalyzed the reaction similarly, except for $[Cu(ns_3)Br]ClO_4$ and $[Cu(n_2s_2)Br]ClO_4$. It is noteworthy that the tetrahedral complexes show distinctly high activities. The above results are illustrated for some complexes in Fig. 3, where relative quantity (absorbance at 565 nm of $TMPD^+$ yielded) is shown as a function of time.

The general trend of the complexes for the reaction (3) was very similar to that for the reaction (2) in that the square planar complexes are inert, and the tetrahedral complexes are very active catalysts. Square pyramidal and trigonal bipyramidal complexes are practically inactive for reaction (3), except for $[Cu(ns_3)Br]ClO_4$ which showed a slight activity as seen in Fig. 4 where the content of residual H_2O_2 in the reaction mixture is plotted as a function of time.

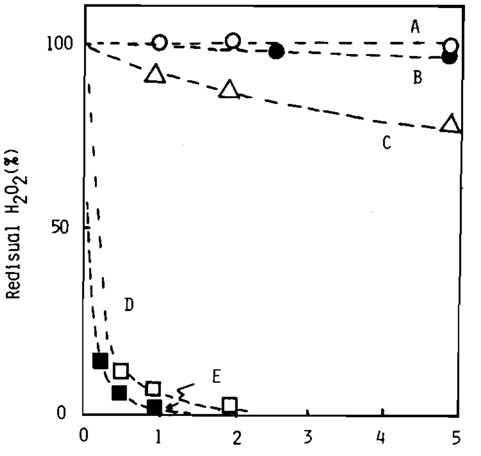

Fig. 4. Time course of the decomposition of H_2O_2; A (○) [Cu(salen)], B (●) [Cu(saldpt)], C (△) $[Cu(ns_3)Br]ClO_4$, D (□) $[Cu(sal\text{-}ip)_2]$, and E (■) $[Cu(p\text{-}ip)_2]$.

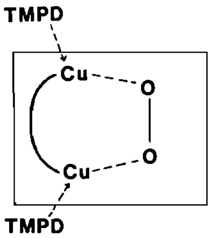

Fig. 5. Assumed structure for intermediate complex formation among TMPD, copper complex and O_2 molecule [20].

Discussion

Since TMPD cannot coordinate to metal ions (due to the steric hindrance) the redox reactions of TMPD with metal complexes should proceed through the outer-sphere mechanism [18]. Therefore, reaction (1) should depend on the redox potentials of the reactants. In fact, the complexes which reacted with TMPD under nitrogen atmosphere were limited to $[Cu(ns_2)Br]ClO_4$, $[Cu(n_2s_2)Br]ClO_4$ and $[Cu(ns_3)Br]ClO_4$ whose $E'_{1/2}$ are higher than that (+0.12 V *vs.* SCE in dmf) of TMPD. In contrast, the reactions (2) and (3) depend strongly on the structural factors rather than the redox potentials, suggesting that the inner-sphere mechanism is involved in these reactions [19].

In previous papers Nishida *et al.* have reported that some binuclear copper(II) complexes with appropriate Cu–Cu distances (~3 Å) show high reactivity for reaction (2) [1, 3], and they have assumed that electrons would be transferred from two molecules of TMPD to an O_2 molecule forming the intermediate complex illustrated in Fig. 5 [3, 20], since two-electron transfer process is much more favored for reduction of O_2 than one-electron transfer process from the thermodynamic point of view. Thus, the binuclear complexes sterically favorable for such intermediate O_2 complex in Fig. 5 can easily catalyze the O_2 oxidation of TMPD, even though the complexes are square planary coordinated as reported in the preceding papers [1, 3]. This mechanism predicts for (2) a second-order reaction with respect to TMPD and also to Cu, or first-order with respect to the binuclear complex,

$$dx/dt = (a - x)^2 m^2 k \quad \text{for mononuclear complex} \tag{i}$$

$$dx/dt = (a - x)^2 b k' \quad \text{for binuclear complex} \tag{ii}$$

where a represents the initial concentration of TMPD, and m, b, and x the concentrations of mononuclear copper(II) complex, binuclear copper(II) complex, and $TMPD^+$, respectively. From (i) and (ii) the following relations are derived,

$$a m^2 k t = x/(a - x) \tag{iii}$$

$$a b k' t = x/(a - x) \tag{iv}$$

predicting that the $x/(a - x)$ *vs.* t. plots make a straight line passing through the origin. This was already verified experimentally for the binuclear copper(II) complexes [20]. In this latter study the same relation was also verified for mononuclear complexes (*cf.* Fig. 6), and furthermore the experiments verified that the inclination of the $x/(a - x)$ *vs.* time plots is proportional to the square of the copper(II) concentration, as expected from equation (iii). Figure 6 shows a typical example of the results. These data clearly imply that the O_2 oxidation of TMPD by the tetrahedral complexes may proceed via the intermediate complex formation, which should be similar to that assumed for the cases of the binuclear complexes, and the electron transfer from copper to O_2 molecule must involve the inner-sphere mechanism.

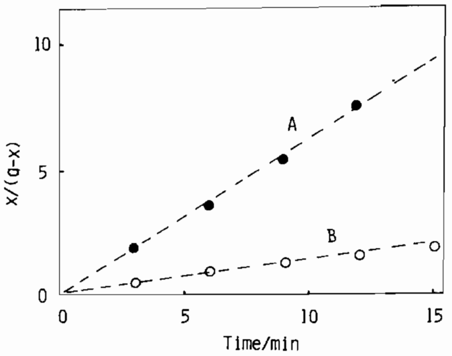

Fig. 6. The $x/(a - x)$ *vs.* time plots in the TMPD–[Cu(sal-tbu)$_2$] system ([TMPD] = 2.5×10^{-3} mol dm^{-3} in dmf/methanol = 1/7 solution, 290 K). A: [Cu^{2+}] = 2.5×10^{-4} mol dm^{-3}; B: [Cu^{2+}] = 1.25×10^{-4} mol dm^{-3}.

On this basis, it is natural that the rates of reaction (2) depend strongly on the ease of O_2 coordination in the intermediate complex in Fig. 5. The most easily accessible part of the copper(II) ion for an approaching ligand should be where the electron hole localizes. In the case of square planar and square pyramidal complexes, the electron hole localizes in the $d_{x^2-y^2}$ orbital which is already occupied by the ligands in the plane, hence the fifth or sixth coordination is generally very weak. In the case of the distorted tetrahedral coordination, however, the electron hole hauses in one of the dϵ orbitals, whose robes are not exactly directed toward the coordination bonds but rather toward the space between the bonds [21, 22], so that the fifth coordination may be nearly comparable to the first ~ fourth ones. This view is in good harmony with the Flias' result that a tetrahedral complex, [Cu(sal-tbu)$_2$] forms (1:1) adducts with a weak ligand such as methanol [23]. Accordingly, the distorted tetrahedral copper(II) complexes can form O_2 adduct (Fig. 5) much easier than can the square planar, square pyramidal and trigonal bipyramidal complexes. This must be the main reason for the high reactivity of the distorted tetrahedral complexes in reaction (2).

In view of the above discussion, the high reactivity of tetrahedral copper(II) complexes for the oxidation of ascorbic acid can also be explained in terms of their ease of coordination. In this case, the electron transfer would occur from ascorbic acid to the d-orbital of copper(II) ion through the inner-sphere mechanism. Similar mechanisms can be assumed for reaction (3) *e.g.*, the facile coordination of H_2O_2 to the copper(II) ion would lead to rapid decomposition of H_2O_2, which seems to be consistent with the results reported by Sigel *et al.* [24].

In conclusion, we emphasize the importance of the coordination structure for the redox reactions of copper(II) complexes. The remarkable difference of the reactivities in the redox reactions between planar and tetrahedral copper(II) complexes is attributed to the difference of the fifth-coordination ability.

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