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SYNTHESIS OF A NEW BINUCLEAR COPPER(II) COMPLEX WITH 1,4-BIS[N,N-BIS(3-SALICYLIDENEAMINOPROPYL)AMINOMETHYL]BENZENE AND ITS CATALYTIC ACTIVITY FOR THE OXIDATION OF N,N,N',N'-TETRAMETHYL-1,4-DIAMINOBENZENE BY DIOXYGEN

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A new binuclear copper(II) complex with 1,4-bis[N,N-bis(3-salicylideneaminopropyl)aminomethyl]benzene was prepared and characterized. This complex showed catalytic activity for the oxidation of N,N,N',N'-tetramethyl-1,4-diaminobenzene by dioxygen in contrast to the inertness of the component mononuclear complex.

In the previous paper,[1)] we have shown that some binuclear copper(II) complexes with appropriate Cu-Cu distance(for example, [$Cu_2(pia)_2$], ref. Fig. 1) exhibit high catalytic activity for the oxidation of TMPD(N,N,N',N'-tetramethyl-1,4-diaminobenzene) by dioxygen(reaction (1)),

$$\mathrm{TMPD} \xrightarrow[\mathrm{Cu(II)}]{O_2} \mathrm{TMPD}^{+} \qquad (1)$$

whereas planar mononuclear complexes(for example, [Cu(salen)], ref. Fig. 1) have practically no catalytic activity for the reaction (1). This result seems to be very important for the understanding of the functions and the structures of Type-III copper in the biological system.[2)]

All the binuclear copper(II) complexes used in our previous papers,[1,3)] have a rigid binuclear structure with one or two bridging atoms, such as [$Cu_2(pia)_2$]. However, it seems to be more likely that Type-III copper proteins in the biological system consist of a rather flexible binuclear unit, as pointed out for Hemocyanin.[4)] Recently several binuclear copper(II) complexes bridged by a flexible chain(or chains) have been reported, however no report has appeared

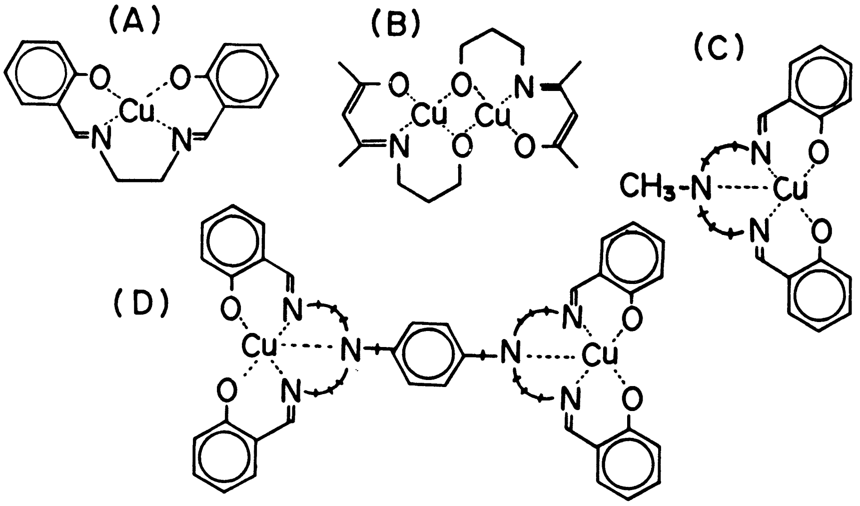

Fig. 1 Copper(II) complexes cited in this paper

(A) [Cu(salen)] (B) $[Cu_2(pia)_2]$

(C) [Cu(sal-medpt)] (D) $[Cu_2(px\text{-}saldpt)]$

on the reactivity of such binuclear copper(II) complexes with a flexible chain. Thus, in this study we have prepared a nobel type binuclear copper(II) complex with a flexible chain, $[Cu_2(px\text{-}saldpt)]$(ref. Fig. 1), and investigated the catalytic activity of this complex for the reaction (1).

The ligand and the copper(II) complex were prepared as follows. 1,4-bis[N,N-bis(3-aminopropyl)aminomethyl]benzene hexahydrobromide was prepared according to a similar method to that for 1,4-bis[N,N-bis(2-aminoethyl)aminomethyl]benzene.$^{5)}$ Found: C, 28.13%; H, 5.43%; N, 9.61%. Calcd. for $C_{20}H_{46}N_6Br_6$, C, 28.26%; H, 5.45%; N, 9.89%. The ligand, 1,4-bis[N,N-bis(3-salicylideneaminopropyl)aminomethyl]benzene, H_4(px-saldpt), was prepared by adding the calculated amount of triethylamine and salicylaldehyde to the suspension of the amine hydrobromide in methanol. Found: C, 71.89%; H, 7.29%; N, 10.42%. Calcd. for H_4(px-saldpt)$\cdot H_2O$, C, 72.15%; H, 7.32%; N, 10.52%. Copper(II) complex was obtained from the reaction mixture of $CuCl_2\cdot 2H_2O$, the ligand and triethylamine. Green crystals yielded were recrystallized from a dmf-CH_3OH solution. Found: C, 62.71%; H, 5.96%; N, 9.13%; Cu, 13.50%. Calcd. for $[Cu_2(px\text{-}saldpt)]$ H_2O, C, 62.52%; H, 5.90%; N, 9.11%; Cu, 13.78%.

In Fig. 2, the ESR spectra of [Cu(sal-medpt)] and $[Cu_2(px\text{-}saldpt)]$ are shown. These were obtained at 77 K using an X-band for the dmf-CH_3OH frozen

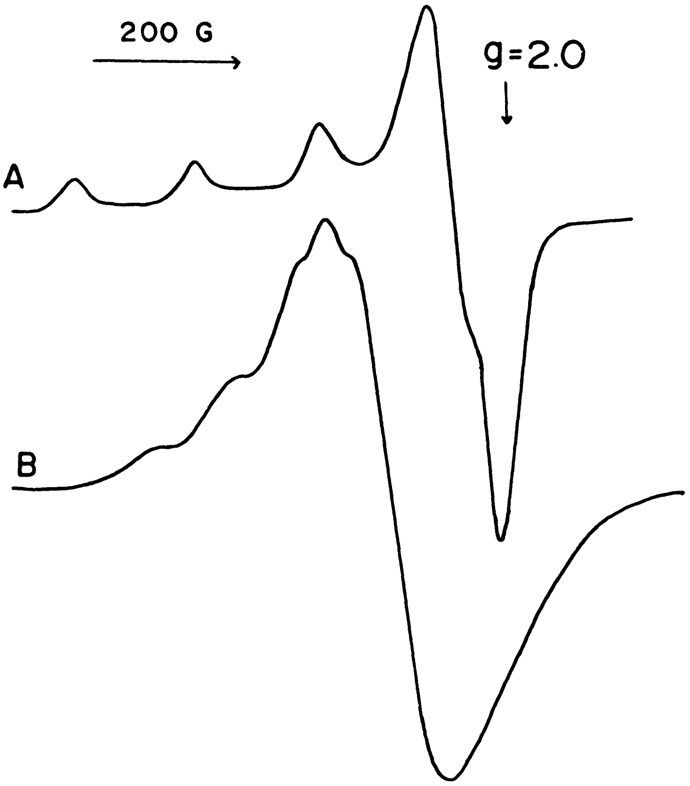

Fig. 2 ESR spectra of the copper(II) complexes (obtained at 77K, X-band dmf-CH_3OH frozen solution)
(A) [Cu(sal-medpt)]
(B) [Cu_2(px-saldpt)]

solutions of 10^{-3} mol dm^{-3} for copper(II) ion. The spectrum of [Cu(sal-medpt)] is of an axial symmetry which are generally observed for the mononuclear copper(II) complexes. On the other hand, the spectrum of [Cu_2(px-saldpt)] is different from that of [Cu(sal-medpt)] in the spectral pattern and A value. The $|A|$ value of [Cu_2(px-saldpt)](~85 G, G=10^{-4} T) is roughly as half as that of [Cu(sal-medpt)](~180 G), suggesting that two copper(II) ions in [Cu_2(px-saldpt)] are interacting with each other.[6)] Examination of Dreding model shows that two copper(II) ions in [Cu_2(px-saldpt)] can approach each other, the shortest distance being 5 Å.

Measurements of the catalytic activity of the copper(II) complexes for the reaction (1) was performed in a similar manner to that described in the previous paper.[1)] The methanol solution of TMPD and the dmf solution of the copper(II) complex were mixed at 25 °C, and the $TMPD^+$ formation was followed by measuring the absorbance at 560 nm. The concentrations of TMPD and copper(II) ion were fixed at 2.5×10^{-5} mol dm^{-3}. As shown in Fig. 3, no formation of $TMPD^+$ was observed when [Cu(sal-medpt)] was mixed with TMPD, indicating that the monomeric

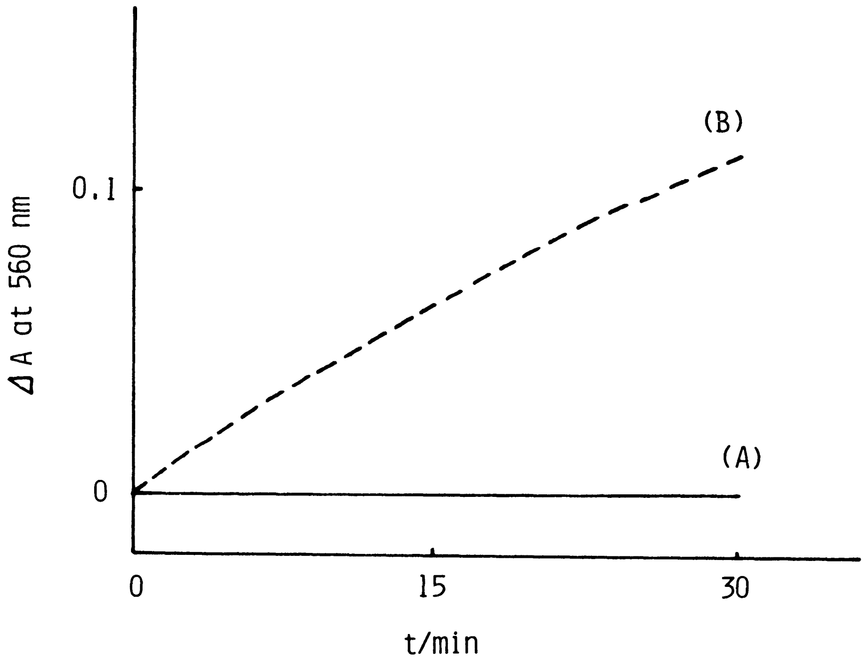

Fig. 3 Time course of $TMPD^+$ formation at the presence of (A) [Cu(sal-medpt)] and (B) $[Cu_2(px\text{-}saldpt)]$

complex, [Cu(sal-medpt)] has no catalytic activity for the reaction (1). On the other hand, the formation of $TMPD^+$ was revealed by the increase of absoprtion at 560 nm when the binuclear complex, $[Cu_2(px\text{-}saldpt)]$ was mixed with TMPD. These results clearly indicate that the catalytic activity of copper(II) complexes for the reaction (1) is closely related to the presence of two adjacent copper(II) ions of appropriate Cu-Cu distance. More detailed investigation on the catalytic functions of binuclear copper(II) complexes similar to the present complex is now in progress.

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