Reaction between Various Copper(II) Complexes and Ascorbic Acid or 3,5-Di-*t*-butylcatechol

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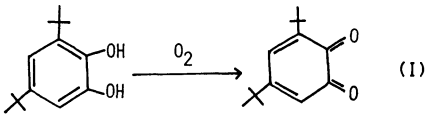
The electron transfer reactions between various copper(II) complexes and two-electron donors, such as ascorbic acid and 3,5-di-*t*-butylcatechol, were investigated. Mononuclear copper(II) complexes with a distorted tetrahedral and a trigonal bipyramidal structure, and some binuclear complexes were readily reduced to copper(I) complexes by the two-electron donors, but not mononuclear planar copper(II) complexes. The catalytic activities of these copper(II) complexes for the oxidation of 3,5-di-*t*-butylcatechol by O_2 were studied in relation to the above reactions.

Copper(II) ion in proteins are classified into three types, Type I, Type II, and Type III, Type I and Type II copper ions being isolated from other copper ions and functioning as mononuclear complexes, while a binuclear structure has been proposed for Type III because of its ESR-nondetectable nature.[1,2] The structures of two proteins containing a copper(II) ion in Type I form (plastocyanin and azurin)[3] have been determined by X-ray analysis, but the geometries around copper(II) ions are still unclarified for other copper proteins.

All the copper(II) ions have relatively high redox potentials, being readily reduced to copper(I) by ascorbic acid, hydroquinones and catechols.[1,2] We have investigated the reaction of various copper(II) complexes with two-electron donors, such as ascorbic acid and 3,5-di-*t*-butylcatechol (hereafter abbreviated as 3,5-DTBC) in order to elucidate the relationship between 1) the structure and reactivity of copper(II) complexes in the reduction to copper(I) complexes by two-electron donors, and 2) the catalytic activity for the oxidation of 3,5-DTBC by O_2 (corresponding quinone formed according to reaction (I)) and the structure of copper(II) complexes.



(I)

3,5-DTBC 3,5-DTBCQ

Experimental

Copper(II) Complexes. The copper(II) complexes we used are shown in Fig. 1, **5** being a new complex.

Preparation of **5**, $[Cu_2(me\text{-}ox)]X_2(X=ClO_4, PF_6)$. An ethanol solution of *N*-[2-(dimethylamino)ethyl]-1,3-propanediamine(0.01 mol) and diethyloxalate(0.005 mol) was refluxed for 1 h, and resulting solution was mixed with an aqueous solution of $Cu(H_2O)_6(ClO_4)_2$(0.01 mol). Violet prisms separated immediately were recrystallized from hot water. Found: C, 28.96; H, 5.23; N, 12.70%. Calcd for $[Cu_2(me\text{-}ox)](ClO_4)_2$: C, 28.74; H, 5.12; N, 12.56%. The magnetic moment of the perchlorate complex is 1.16 BM at 295 K. Its magnetic property can be explained in terms of the Bleaney-Bowers equation[4] (temperature range, 80—295 K, $2J=-440$ cm^{-1}, and $N\alpha=60\times10^{-6}$ cgs). By adding NH_4PF_6 to a hot water solution of the perchlorate, $[Cu_2(me\text{-}ox)](PF_6)_2$ was obtained as red needles.

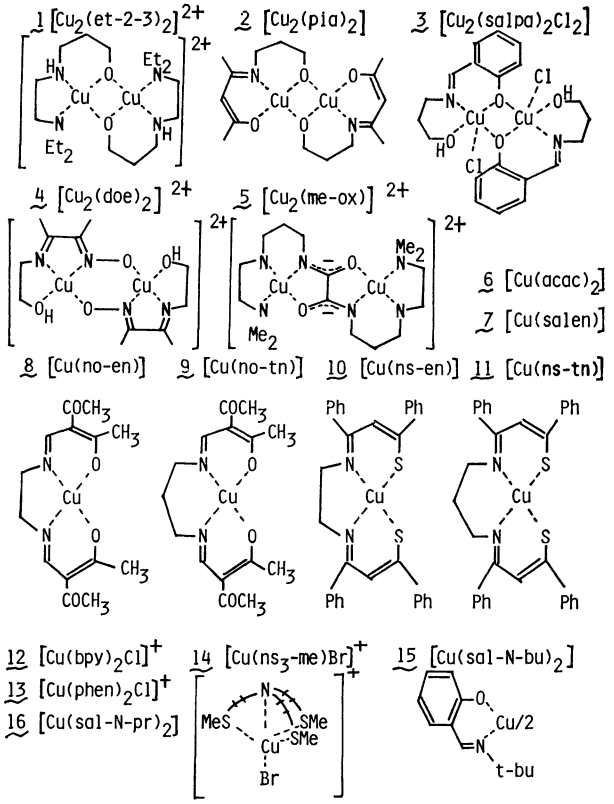


Fig. 1. Copper(II) complexes used in this study.
The abbreviations of ligands are: **6**; H(acac), acetylacetone, **7**; H_2(salen), *N,N'*-disalicylideneethylenediamine, **12**; bpy, 2,2'-bipyridine, **13**; phen, 1,10-phenanthroline, **16**; H(sal-N-pr), *N*-salicylideneisopropylamine.

Complexes **1**—**5** are binuclear, the structural and magnetic properties of **1**—**4** being reported (**1**,[5,6] **2**,[7] **3**,[8] and **4**[9]). In these binuclear copper(II) complexes, the strong antiferromagnetic interaction was found to be operative between two copper atoms. Complexes **6**—**11** are of four-coordinated planar structure, **6**, **7**—**9**[10], and **10**—**11**[11] having $[CuO_4]$-, $[CuN_2O_2]$- and $[CuN_2S_2]$-type coordinations, respectively. Complexes **12**—**14**[12] and **15**—**16** are of trigonal bipyramidal and distorted tetrahedral structures, respectively.

Reaction with Ascorbic Acid or Catechol. A methanol solution containing stoichiometric amount of ascorbic acid was added to a methanol solution of copper(II) complexes at 20 °C under nitrogen atmosphere and the absorption spectra of the resulting solutions were measured in the visible

region. When 3,5-DTBC was used instead of ascorbic acid, the same procedure was applied except for the addition of triethylamine[13] (3,5-DTBC: base=2: 1).

Catalytic Activity for the Oxidation of 3,5-DTBC by O_2. Oxidation was carried out according to the method of Tsuruya and Linvedt.[13] A methanol solution(20 cm^3) of 3,5-DTBC(0.1 mol/dm^3), triethylamine(0.015 mol/dm^3) and copper(II) complex (0.002 and 0.001 mol/dm^3 for mononuclear and binuclear complexes, respectively) was kept at 15 °C (in a thermostat) in a 12 mm diam. necked flask for 6—7 h. The yield of quinone(3,5-DTBCQ) formed was determined by the measurements of absorption spectra of the resulting solutions. 3,5-DTBCQ shows a characteristic absorption band at 400 nm (ε/mol^{-1} dm^3 cm^{-1}=1900 in methanol[14]).

Measurements. Absorption spectra were obtained with a Shimadzu Multipurpose spectrometer model MPS-5000.

Results and Discussion

Electron-transfer Reaction between Two-electron Donors and Various Copper(II) Complexes. Compounds **12**, $[Cu(bpy)_2Cl]Cl$ and **13**, $[Cu(phen)_2Cl]Cl$ are easily reduced to copper(I) complexes by ascorbic acid, where bpy and phen denote 2,2′-bipyridine and 1,10-phenanthroline, respectively. The green color of **14**, $[Cu(ns_3\text{-}me)Br]^+$ disappeared immediately upon addition of ascorbic acid (or 3,5-DTBC), indicating that the complex is reduced to copper(I) complex by two-electron donors.

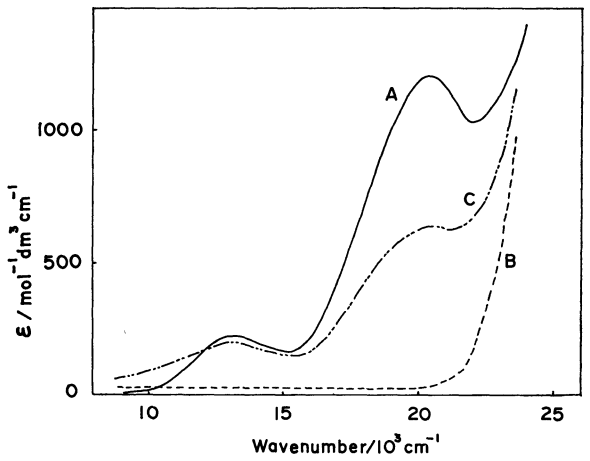


Fig. 2. Absorption spectra of **15** $[Cu(sal\text{-}N\text{-}bu)_2]$ (in methanol, 15 °C).
A: $[Cu(sal\text{-}N\text{-}bu)_2]$, B: $[Cu(sal\text{-}N\text{-}bu)_2]$+ascorbic acid (in N_2), C: solution (B) + O_2(in air).

Figure 2 shows that the spectral change of **15**, $[Cu(sal\text{-}N\text{-}bu)_2]$, caused by the addition of ascorbic acid. The d-d band (*ca.* 13000 cm^{-1}) due to copper(II) ion disappears immediately upon the addition of ascorbic acid under nitrogen atmosphere, reappearing when the solution was exposed to the air. This indicates that the copper(II) complexes with a distorted tetrahedral structure are reduced to copper(I) by ascorbic acid (or 3,5-DTBC). On the other hand, planar mononuclear copper(II) complexes such as **6**, $[Cu(acac)_2]$ and **7**, [Cu(salen)] are not reduced by these two-electron donors at room temperature.

Patterson and Holm[15] measured the reduction potentials of various copper(II) complexes by polarography, and concluded that mononuclear copper(II) complexes with nonplanar structure (*e.g.*, distorted tetrahedron and trigonal bipyramid) are readily reduced as compared with their planar analogs. Our results seem to be in line with their conclusion. This indicates that nonplanar mononuclear copper(II) complexes can be a good model for Types I and II in biological systems.

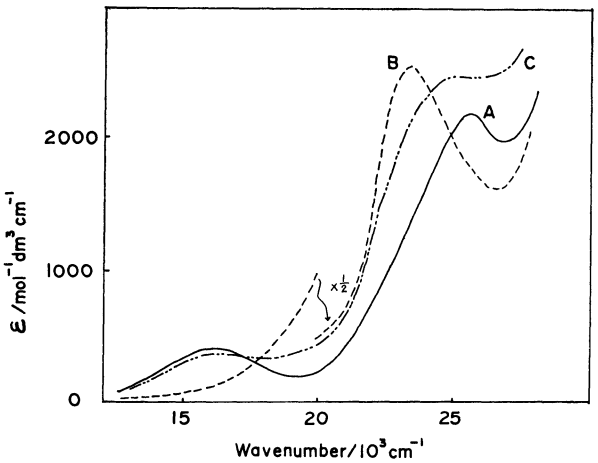


Fig. 3. Absorption spectra of **4** $[Cu_2(doe)_2](NO_3)_2$(in methanol, 15 °C).
A: $[Cu_2(doe)_2](NO_3)_2$, B: $[Cu_2(doe)_2](NO_3)_2$+ascorbic acid(in N_2), C: solution (B)+O_2(in air).

Binuclear copper(II) complexes (Fig. 1) except for **5** were also found to be readily reduced to copper(I) complexes by ascorbic acid and/or 3,5-DTBC. The spectral change of **4**, $[Cu_2(doe)_2]^{2+}$ in the reaction with ascorbic acid is shown as an example in Fig. 3. The d-d band at 16000 cm^{-1} disappears upon addition of ascorbic acid under nitrogen atmosphere, appearing again when the solution is exposed to air. It is noteworthy that planar mononuclear copper(II) complexes such as **6** and **7** are not reduced by ascorbic acid, while binuclear copper(II) complexes with planar structure such as **2**, **3**, and **4**, are readily reduced to copper(I) by ascorbic acid.

Catalytic Activity for the Oxidation of 3,5-DTBC. Since 3,5-DTBCQ shows a characteristic absorption band at 400 nm and the content of copper(II) complex is very small, the absorbance at 400 nm can be a good measure for the catalytic activity of copper(II) complexes to the oxidation of 3,5-DTBC. Examples are given in Figs. 4 and 5. Square planar mononuclear complexes (**6** and **7**) have little catalytic activity, while nonplanar copper(II) complexes (such as **12**, **14**, and **15**) and binuclear complexes (except for **5**) act as a good catalyzer for the oxidation of 3,5-DTBC. In the cases of **14** and **4**, 100% formation of 3,5-DTBCQ was observed within 6 hours. The results obtained for binuclear complexes (**1**—**4**) are in line with that of Tsuruya and Lintvedt,[13] who first pointed out the high catalytic activity of a binuclear complex, **17**, relative

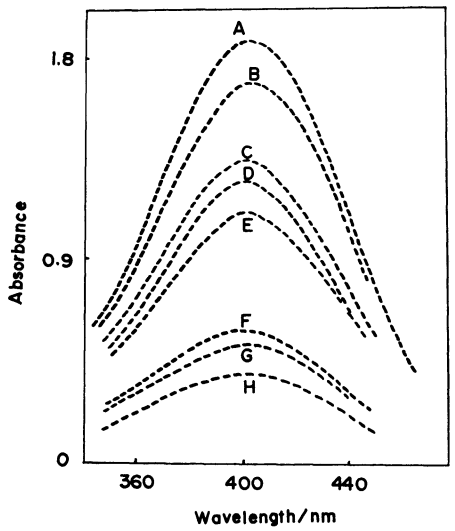


Fig. 4. Absorbance at 400 nm of the solution containing a copper (II) complex and 3,5-DTBC(in methanol, 15 °C, after 6 h).
A: **12** $[Cu(bpy)_2Cl]Cl$, B: **4** $[Cu_2(doe)_2](NO_3)_2$, C: **15** $[Cu(sal\text{-}N\text{-}bu)_2]$, D: **14** $[Cu(ns_3\text{-}me)Br]ClO_4$, E: **2** $[Cu_2(pia)_2]$, F: **6** $[Cu(acac)_2]$, G: **8** [Cu(no-en), H: no copper(II) complex.

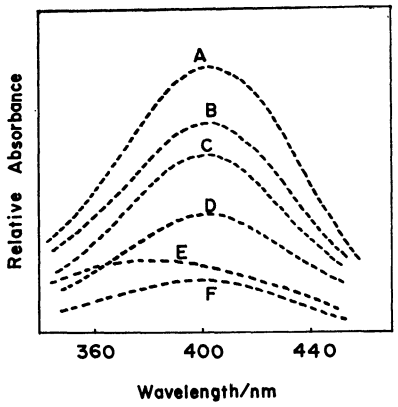
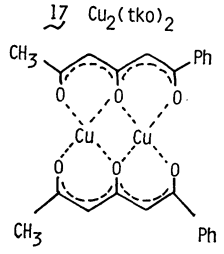


Fig. 5. Absorbance at 400 nm of the solution containing a copper (II) complex and 3,5-DTBC(in $CHCl_3$, 15 °C, after 10 h).
A: **11** [Cu(ns-tn)], B: **10** [Cu(ns-en)], C: **9** [Cu(no-tn)], D: **8** [Cu(no-en)], E: **7** [Cu(salen)], F: no copper(II) complex.

to that of a mononuclear complex, **6**, for the oxidation of 3,5-DTBC by O_2.



Since **10** and **11** are insoluble in methanol, the result in Fig. 5 was obtained in a $CHCl_3$ solution. Thus the catalytic activity of **11** and **10** cannot be compared directly with that of **14** and **15**. The order of catalytic activity is as follows: **12**~**13**>**14**; **15**>**16**; **11**>**10**>**9**>**8**>**7**~**6** and **4**>**1**~**2**~**3**≫**5**. Although **8** has a $[CuN_2O_2]$-type coordination similar to that of **7**, **8** is more reducible than **7** because of the presence of electron-withdrawing group in the chelate ring.[16,17] Copper(II) complexes with a $[CuN_2S_2]$-type coordination are more reducible than those with a $[CuN_2O_2]$-type coordination.[15] Complexes with 6-membered chelate ring (such as **11** and **9**) are more reducible than the corresponding complexes with 5-membered chelate ring (such as **10** and **8**).[15,16] Thus, the results indicate that more reducible mononuclear copper(II) complexes can be a better catalyzer for the oxidation of 3,5-DTBC by O_2, suggesting that the reversible change of oxidation state, *i.e.*, Cu(II)⇄Cu(I), plays an important role in the catalytic function of mononuclear copper(II) complexes. Since binuclear complexes, **1**—**4**, are reduced by 3,5-DTBC and readily oxidized by O_2 again, these binuclear copper(II) complexes act as a good catalyzer for the oxidation of 3,5-DTBC by O_2.

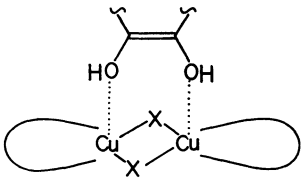


Fig. 6. "Steric match" proposed for electron transfer reaction between ascorbic acid and a binuclear copper (II) complex. This situation is impossible for ascorbic acid and a mononuclear planar copper(II) complex.

The reduction potentials of the two copper(II) complexes, **6** and **17**, are almost the same (**6**; −0.50 V, **17**; −0.48 V), **6** and **17** undergoing two-electron reduction to Cu^0 and Cu^I–Cu^I, respectively at the electrode.[18] However, the difference of reactivity between the two complexes in the electron transfer reaction with 3,5-DTBC (and/or ascorbic acid) cannot be explained by the electrochemical data. Accordingly we propose that a "steric match" between a donor and an acceptor (Fig. 6) is important in the electron transfer reaction between planar copper(II) complexes and two-electron donors, such as ascorbic acid and 3,5-DTBC. Thus on this basis the very low catalytic activity of **5** can be explained; *i.e.*, the distance between two copper atoms is estimated to be larger than 5 Å from the X-ray analysis of anologous complexes,[19] so that the "steric match" is impossible between **5** and two-electron donors.

References

1) R. Malkin and B. G. Malmstrom, *Adv. Enzymol.*, **33**, 177 (1970).
2) J. A. Fee, *Struct. Bonding*, **23**, 1 (1975).
3) P. M. Colman, H. C. Freemen, J. M. Guss, M. Murata, V. A. Morris, J. A. M. Ramshaw, and M. P. Venkatappa, *Nature(London)*, **272**, 319 (1978).
4) B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).

5) Y. Nishida, F. Numata, and S. Kida, *Inorg. Chim. Acta*, **11**, 189 (1974).
6) A. C. Villa, L. Coghi, A. G. Manfredotti, and C. Guastini, *Cryst. Struct. Commun.*, **1974**, 543.
7) J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, **4**, 203 (1974).
8) J. A. Bertrand, J. A. Kelley, and J. L. Breece, *Inorg. Chim. Acta*, **4**, 247 (1974).
9) J. A. Bertrand, J. H. Smith, and P. Garyeller, *Inorg. Chem.*, **13**, 1649 (1974).
10) L. Wolf and E-G. Jager, *Z. Anorg. Allg. Chem.*, **346**, 76 (1966).
11) E. Uhlemann, *Z. Naturforsch., Teil B*, **21**, 592 (1966).
12) M. Suzuki, H. Kanatomi, H. Koyama, and I. Murase, in press.
13) S. Tsuruya and R. L. Lintvedt, Abstracts, 176th National Meeting of the American Chemical Society, Miami Beach, FL. Sep. 1978, No. Inorg. 70.
14) W. Flaig, Th. Ploetz, and A. Kullmer, *Z. Naturforsch., Teil B*, **10**, 668 (1955).
15) G. S. Patterson and R. H. Holm, *Bioinorg. Chem.*, **4**, 257 (1975).
16) E-G. Jager, *Z. Chem.*, **18**, 229 (1978).
17) D. G. Pillsbury and D. H. Busch, *J. Am. Chem. Soc.*, **98**, 7836 (1976).
18) D. E. Fenton and R. L. Lintvedt, *J. Am. Chem. Soc.*, **100**, 6367 (1978).
19) C. Chavel, J. J. Gierd, Y. Jeannin, O. Kahn, and G. Lavigne, *Inorg. Chem.*, **18**, 3015 (1979); J. J. Gierd, O. Kahn, and M. Verdagure, *ibid.*, **19**, 274 (1979).