The Interaction of Substituted Catechols with some Binuclear Copper(II) Compounds

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Four dicopper(II) complexes were tested as catalysts for the air oxidation of several substituted o-diphenols. The oxidation reactions were followed by measuring the change in the optical spectra and by measuring the oxygen uptake. The oxidase activities decreased with a decrease in pH and increased for o-diphenols with good electron donating substituents in the para position. Because of their complexity, the oxidation products were not identified and characterized. Lack of characterized products prevented an analysis of the reaction mechanism.

Introduction

The role of copper as catalysts in the oxidizing systems of plant and animal life has long been of interest [1]. They catalyze the oxidation of numerous organic substrates such as mono and polyphenols, amines, *etc.* These metalloenzymes of copper were often found to contain at least one pair of antiferromagnetically spin coupled Cu(II) ions per molecule [2–6]. A mechanism proposed for the dioxygen oxidation of phenols and *o*-diphenols catalyzed by the dicopper metalloenzyme tyrosinase is given by Ochiai [7]. The mechanism exploits the need for the two contiguous copper ions as coordination sites for the hydroxyl oxygens of *o*-diphenyls and the binding of dioxygen (Figs. 1a and 1b).

The site of the dicopper enzymes not only provides a pathway for the electron transfer between *o*-diphenol (and other organic substrates) but, arguments can be made for the role dicopper plays in the mediation of the forbidden reaction between the triplet oxygen and singlet organic substrates [6–8]. Simple binuclear copper complexes may serve as models for the study of such dicopper enzymes as tyrosinase, laccase, hemocyanin and others. Recently dicopper complexes have been used in the investigation of new synthetic organic procedures for ring opening reactions of phenols and *o*-diphenols [9], for prepararing alkaloids [10] and for preparing phenol coupled polymers [11]. Studies are presently being undertaken in this laboratory to investigate their potential in the treatment of organic materials in waste water. Each of the above areas involve the interaction of *o*-diphenols and binuclear copper complexes.

This study proposes to investigate the interaction of several substituted *o*-diphenols with the binuclear copper complexes of the type shown in Fig. 2.

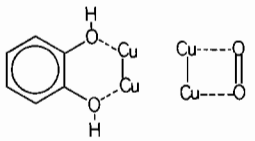

Fig. 1. The coordination of the hydroxyl oxygens of *o*-diphenols and the binding of dioxygen.

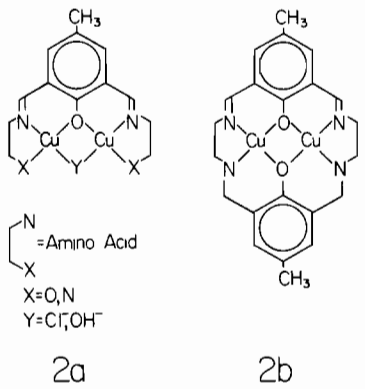

Fig. 2. Interaction of substituted *o*-diphenols with binuclear copper complexes.

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Experimental

Synthesis

The synthesis of the 2,6-diformyl-4-methylphenol was prepared using a procedure similar to that of Okawa [12]. A mixture of 136 g concentrated H_3PO_4 (70%) and 114 g P_4H_{10} were used in the place of 250 g of polycyclic phosphoric acid. The complexes $MCu_2Cl_2 \cdot 6H_2O$ [13], $Fsal(=gly)_2Cu_2Cl$ [12], $[(Cu_2(HA)_2IPA)OH](ClO_4)_2$ [14] and $[(Cu_2(H_2HA)_2IPA)OH](ClO_4)_2 \cdot H_2O$ [14], hereafter called Fsal Pn, Fsal Gly, Fsal His and Fsal His-red, were prepared by literature procedures.

PH Profile

The pH profile for the oxidation reaction of 4-methylcatechol by the four dicopper complexes was collected at minute intervals by mixing an aqueous solution of 4-methylcatechol and the dicopper complexes to give initial concentrations (before oxidation) of 10^{-2} *M* and 10^{-4} *M* respectively. The starting pH for the solution of the Fsal Gly catalyzed oxidation was 6.457 and decreased to 6.347 after 10 minutes and then to 5.950 after 2 hours. The three other dicopper complexes gave similar results.

Oxidation of O-Diphenols

A final mixture of 10^{-4} *M* Fsal Gly and 10^{-2} 4-methylcatechol in a buffered solution of pH-7 was placed in a 1 cm optical cell in a Cary 17 spectrophotometer. The change in absorbance was observed with time at 495 nm. An irregular trace at this concentration was observed (Fig. 3).

A similar run was made in a cell prepared so that the cell was completely filled and closed (no ullage above the solution). The oxygen content of the solution was measured with an Orion oxygen probe prior to the mixing of 4-methylcatechol and each of the dicopper complexes. Upon mixing, the solution contained 10^{-4} *M* dicopper complex and 10^{-3} *M* 4-methylcatechol The cell was maintained at 25 °C. The change in absorbance was observed with time at $\lambda = 495$ nm.

The oxygen uptake for the catalytic reaction of 4-methylcatechol by each of the dicopper catalyst under the same closed condition described in the paragraph above was carried out using an Orion model 97-08 oxygen probe. The oxygen uptake was recorded on a Sargent-Welch recorder. Care was taken to insure no ullage appeared above the reacting solution.

Initial Rates

The initial rates for the catalytic air oxidation of several *o*-diphenols to the corresponding *o*-quinones using the four dicopper complexes as catalysts were determined in the usual manner. Samples of the dicopper solutions buffered at pH 5, 6, 7, 7.5 were placed in a 1 cm cell which was thermostated to 25 °C. A sample of the *o*-diphenol was added to give starting concentrations of 10^{-3} *M* *o*-diphenol and 10^{-4} *M* dicopper. A change in the absorbance (and concentration) corresponding to the growing *o*-quinone peak was observed with time using wavelengths and molar absorptivities taken from literature [2, 15] [catechol (390 nm, 1417 M^{-1} cm^{-1}), 4-methylcatechol (495 nm, 2140 M^{-1} cm^{-1}), dopamine (465 nm, 2455 M^{-1} cm^{-1}), 3,4-dihydroxybenzonitrile (430 nm, 2880 M^{-1} cm^{-1}), 3, 4-hydroxybenzoic acid (390 nm, 1300 M^{-1} cm^{-1})]. The initial rates were calculated from the tangent of the absorbance *vs.* time curve at time t = 0.

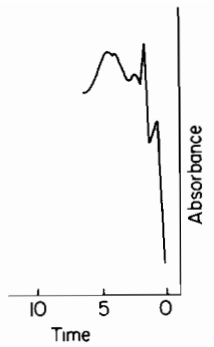


Fig. 3. The absorbance *vs.* time spectrum of the Fsal Gly (10^{-4} *M*) catalyzed oxidation of 4-methylcatechol (10^{-2} *M*).

Magnetic Moments

The magnetic moments of the four dicopper complexes were determined in ethanol solution using the nmr method of Evans [16, 17]. Other magnetic data reported were taken from the literature.

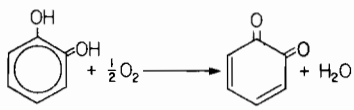
Electronic Spectra

The near infrared, visible and ultraviolet spectra were taken on a Cary 17 spectrophotometer.

Results and Discussion

Catechol Oxidation Studies

The copper metalloenzyme polyphenoloxidase (tyrosinase) was shown to catalyze the dioxygen oxidation of phenols and *o*-diphenols. Most often the catecholase reaction is given by the simple reaction 1.



(1)

Others have shown this reaction to be oversimplified [1, 2, 18].

Complexes prepared in this work also catalyze *o*-diphenols and like tyrosinase give much more com-

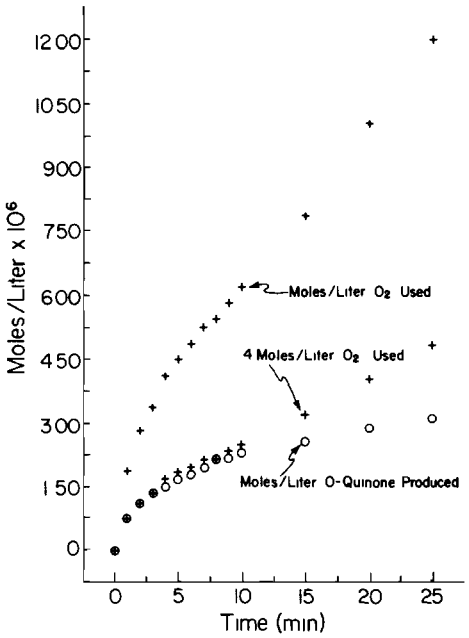
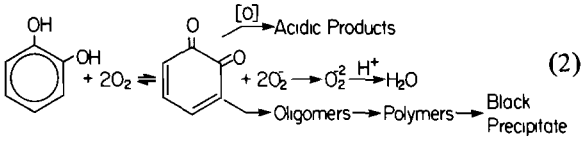


Fig. 4. The O_2 uptake and the *o*-quinone production is the Fsal Gly catalyzed oxidation of 4-methylcatechol. Initial concentrations: 4-methylcatechol- 10^{-3} *M*, Fsal Gly -10^{-4} *M*. *The* 0.4 moles/liter O_2 used is scaled down to illustrate that for the 1st 10 minutes, the O_2 and *o*-quinone reactions track at a ratio of $[O_2]/[O\text{-qui}] = 2.5$.

plex products which may tentatively be given by reaction 2.



(2)

Several experimental.results lead to the proposal of the more complex scheme in reaction 2. A pH profile of the oxidation of a 10^{-2} *M* solution of catechol with 10^{-4} *M* Fsal gly shows a decrease in the pH from 6.457 to 6.347 in 10 min. The pH after 2 hours reduced to pH = 5.950. Several peaks were observed to grow in the UV region which did not belong to the *o*-diphenol or the *o*-quinone spectrum. These acid products indicated by pH profile and UV studies are probably *cis, cis*-muconic acid and other ring open acidic products like α-hydroxy-muconic-ε-semialdehyde. Products of this type have previously been shown to result from copper and iron complex catalyzed air oxidation of catechols [9, 19]. Figure 3 is the absorption *vs.* time spectrum of a concentrated solution (10^{-2} *M*) of 4-methylcatechol being oxidized in the presence of Fsal Gly at the wavelength of 495 nm. The anomaly of the spectrum is the result of the formation of dimers and oligomers

TABLE I. Rate Ratio, R, of O_2 Uptake and *o*-Quinone Production.[a]

Complex	R	Coincidence Time (min.)
FSAL PN	3	7
FSAL HIS-RED	3	4
FSAL GLY	2.5	10

[a]Results for Fsal His are too irreproducable to report. Coincidence time–time over which the R ratio is constant R = Rate of $[O_2]$ used/Rate of [*O*-Qui] produced.

followed by the precipitation of a black polymer from solution.

Binuclear copper metalloenzymes such as laccase (which polymerizes lacquor) and tyrosinase (polyphenoloxidase) which polymerizes many polyphenols have long been known to polymerize phenol [1, 6, 7]. More recently simple copper complexes have been used for this purpose [11, 20]. Figure 4 is a plot of the moles of 4-methyl-*o*-quinone (0) and the moles of O_2 uptake (+) *vs.* time for the oxidation of 4-methyl-catechol catalyzed by Fsal Gly. The *o*-quinone measurements and the O_2 uptake measurements were performed under identical conditions. Both O_2 uptake and the moles of *o*-quinone produced during the first 10 minutes where shown to obey 1st order kinetics. During this reaction period the moles of O_2 used is constantly found to be 2.5 times greater than the production of *o*-quinone (the uncertainty in the ε of *o*-quinone [15] may cause the O_2/*o*-quinone ration to be ~2). The O_2 uptake begins to increase at an even greater rate than the production of *o*-quinone after 8–10 minutes. When plots were made for the 4-methylcatechol oxidation using Fsal Pn and Fsal His-red as catalysts, similar results were obtained for the *o*-quinone production and O_2 uptake measurements. Table I summarizes the results of these dates. In each case, much more oxygen is used than can be accounted for by the simple production of *o*-quinone and water. Thus, the first 8–10 minutes of the reaction during which O_2 uptake and *o*-quinone production follow in a rate ratio of approximately two can be explained by assuming a one electron transfer reaction which produces the superoxide ion, a product not unusual in oxidase reactions involving dioxygen [17, 21]. Gillette reports the use of two moles of O_2 per mole of catechol used in the oxidation catalyzed by Mn(II) and Co(II) [22]. Although it is widely held that dicopper in metalloenzymes participates in a 2e redox step [2, 6], Gagne's [23] electrochemical studies of dicopper complexes and Himmelwright's [24] preparation of half-methemocyanin demonstrate the existence of complexes possessing mix

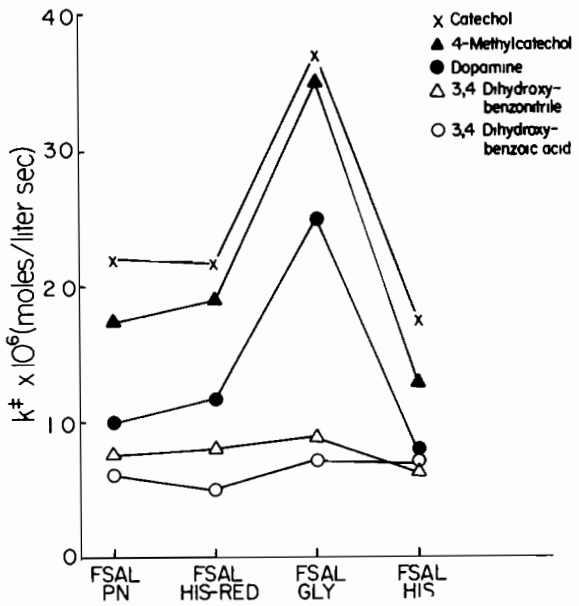


Fig. 5. Initial rates for the catalytic oxidation of *o*-diphenols by binuclear copper complexes. The reaction conditions were: [*o*-diphenol] = 10^{-3} *M*, [dicopper] = 10^{-4} *M*, pH = 7.0 (buffered w/phosphate buffer) and temperature of 25 °C.

valence dicopper. Thus, it is possible for one electron transfer to take place thru dicopper to produce the superoxide ion, a species which is short lived in acidic solution but which may exist coordinated to a metal ion or in aqueous solution if protected from the protonic environment [25]. After 8–10 minutes, the reaction becomes too complex for kinetic studies. Further kinetic studies are not possible until the reaction products have been identified and characterized. During this latter part of the reaction, the O_2 uptake to *o*-quinone ratio becomes even larger than 2.5. One factor for this increased oxygen uptake to *o*-quinone ratio may be the additional use of oxygen in the ring opening oxidation of the substrate which was indicated by optical and pH profiles of the reaction.

Initial Rate Studies

Although the rates for the various steps of the oxidation in reaction 2 are not measurable at this time because the products are not well defined, the relative catecholase activity (oxidation of *o*-diphenol to *o*-quinone) of the dicopper complexes can be measured as initial rates. Figure 5 summarizes the initial rates for the oxidation of substituted *o*-diphenols (with R = H, CH_3, C=N, $-CH_2CH_2NH_2$, COOH) which have been catalyzed by the four dicopper complexes. In a buffered solution of pH = 7, *o*-diphenol concentration = 10^{-3} *M* and dicopper concentration = 10^{-4}, the rates range from 5.0 × 10^{-7} to 4.0 × 10^{-6} mol/sec. The activity order (in

TABLE II. Initial Rates.[a]

o-Diphenol (10^{-3} *M*)	Initial Rates (mol/l min)	
	Tyrosinase	Fsal Gly
Catechol	7.1×10^{-3}	3.8×10^{-6}
4-Methylcatechol	6.5×10^{-3}	3.5×10^{-6}
Dopamine	7.7×10^{-3}	2.4×10^{-6}
3,4-Dihydroxybenzoic acid	1.25×10^{-3}	1.3×10^{-6}
3,4-Dihydroxybenzonitrile	2.62×10^{-3}	0.88×10^{-6}

[a] $[Cu]_{Tyr} = [Cu]_{Fsal}$.

general) for the substituted *o*-diphenols is H > CH_3 > $-CH_2-CH_2NH_2$ > C=N > COOH. The activity order for the dicopper catalysts is generally gly > his-red > pn > his. In the interest of comparing these synthetic catalyst with the natural enzyme, mushroom tyrosinase was purchased and analyzed for copper. The initial rates for catalyzing the oxidation of the above substituted *o*-diphenols at the same copper concentration as Fsal Gly under identical conditions are given in Table II. It can be seen that the tyrosinase activity is 1000 to 2000 times more active than the synthetic dicopper catalyst. The Table (and Fig. 5) also show that, for the synthetic dicopper complexes, the *o*-diphenol whose substituent is the best electron donating group gives the highest activity. Similar results are found for the oxidation activities of the substituted *o*-diphenol catalyzed by tyrosinase in this as well as other studies [2]. These results are consistent with catecholase activity which is dependent upon the formation of a Lewis acid/base bond between Copper(II) and *o*-diphenol oxygen atoms.

The effect of pH on the initial rates catalyzed by the dicopper complexes was measured between pH = 5.0 and 7.5. No catalytic activity was observed at pH = 5. The initial rates increased significantly with increase in pH. These results may be indicative of the removal of a catechol hydroxy proton before oxidation is initiated. However, a pH study of the complex stabilities revealed a decrease in the d–d transition intensity with decrease in the solution pH. This change in the copper(II) spectra indicate a structural/stability change in the dicopper complex. A likely cause may be the instability at low pH of the Schiff base C=N bond formed during the synthesis of the ligand.

Magnetic Properties

Copper ions in naturally occurring copper oxidases are often found coupled together in pairs [1, 6]. The paired structure is thought to be important in the electron transfer mechanism of the oxidases [7]. If these simple complexes are to behave catalytically

TABLE III. Optical Spectral Data.

Complex	Solid in Nujol λ_{max}[a]	CH_3OH[b,c]			H_2O (pH ≈ 7.0)[b,c]		
		Vis		Uv	Vis		Uv
		I	II		I	II	
Fsal Pn	660	680	605 (595)	340	680	595 (590)	350 (358)
Fsal His	650	680	595 (–)	355	680	605 (–)	365 (–)
Fsal His-Red	620	660	598 (594)	330	660	600 (–)	325 (340)
Fsal Gly	680	740	590 (582)	385	720	665 (660)	388 (400)

[a]λ_{max} in solid is the envelope of I and II in CH_3OH and H_2O. when oxygen was removed from the CH_3OH and H_2O solutions. to a deareated solution. (–) indicates no change in λ.

[b]Essentially no change in the solution spectra were observed [c]( ) give λ for transitions when 4-methylcatechol was added

TABLE IV. Magnetic Moments.

μ (BM) 25 °C Complexes	Solid	CH_3OH
Fsal Pn	0.59[a]	0.79
Fsal His	0.94[b]	0.92
Fsal His-Red	0.99[b]	1.15
Fsal Gly	1.71[c]	(1.69 in H_2O)[d]

[a]N. H. Pilkington *et al.*, *Aust. J. Chem.*, *23*, 2225 (1970). [b]J. J. Grzybowski *et al.*, *Inorg. Chem.*, *17*, 3078 (1978). [c]H. Okawa *et al.*, *Bull Chem. Soc Jpn.*, *45*, 1759 (1972). [d]Not sufficiently soluble in CH_3OH.

like naturally occurring metalloenzymes, the establishment of the binuclearity of copper ions is important. The single crystal X-ray study of Fsal Pn was previously reported [27]. The molecule contains two five coordinated copper ions bridged by two hydroxyl oxygen. Its magnetic moment in the solid state at 25 °C was also reported to be 0.59 B.M., [13] a value below the expected 1.85 B.M. normally found for mononuclear copper (II) complexes. The diminished μ_{eff} indicates that the two copper ions are near enough to antiferromagnetically couple their unpaired spins. In this laboratory, the magnetic moment of Fsal Pn was determined to be 0.79 B.M. in methanol solution. Differences between solid and solution magnetic moments may indicate dissociation of the dimer species in solution or the larger solution magnetic moment could result from solvent effects. Support for the stability of the binuclear complex in solution comes from a comparison of the d–d transitions of Cu(II) in the complex. Table III shows little difference between the d–d transition in solid

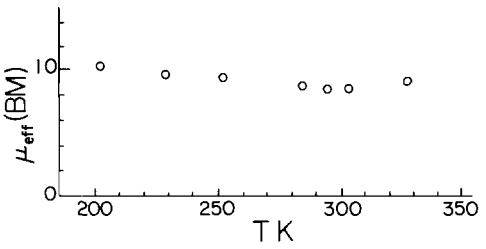


Fig. 6. The magnetic moment of Fsal His in methanol from 200 K to 330 K.

and solutions. Further support for the stability of the binuclear complex in solution is given in Fig. 6. The Evans method was used to measure the μ_{eff} of Fsal His in methanol over 130 °C range. Only a small change in μ_{eff} can be seen. Table IV compares the magnetic moments of the complexes in both the solid and solution states. From these data it can be concluded that the binuclearity of the solid complexes are maintained in solution.

Visible-Ultraviolet Studies

Table III gives the visible-ultraviolet spectra of the dicopper complexes in solid (nujol mull), methanol and water. The d–d bands of each complex in the visible region contains two transitions which range from 590 nm to 740 nm. The most intense transition for each complex is about 600 nm. There is no change between aqueous spectra which was deoxygenated and spectra containing dissolved oxygen. Presumably no oxygen–copper(II) bonds are formed, which is expected for oxygen and copper(II) ions. The addition of 4-methylcatechol to deareated solutions of the complexes generally gave slight changes in both the λ max (~600 nm) and its absorbance. The slight

changes for *o*-diphenols of 10 fold concentrations greater than concentrations of dicopper are indicative of only small equilibrium concentrations of the *o*-diphenol-dicopper complex, which may account for their low catalytic activities relative to tyrosinase if a good *o*-diphenol-dicopper bond is necessary for catalytic activity. Attempts to observe the spectral effect on the d–d transitions of oxygen bonding to dicopper in the presence of 4-methylcatechol were fruitless because the visible spectra were rapidly changed in the region of the d–d transitions by the oxidation of the 4-methycatechol to *o*-quinone.

Only a slight change occurred in the visible spectra between pH 7–8, but reduction of the pH down to pH = 5 showed significant changes. The initial rates catalyzed by the dicopper complexes were also decreased by decreasing the pH of the reaction media. The rate change with pH may result form a structural change in the dicopper complex, however, the rate change may also result from the removal of a hydroxyl proton on the *o*-diphenol.

Similarities exist between the visible spectra of the binuclear copper complexes and metalloenzymes containing binuclear copper active sites. Jolley [3] found tyrosinase to contain λ max at 600 nm. Malkin [5] and Dooley [26] found laccase to contain λ max at about 610 and 600 nm respectively. Presumably, when the metalloenzymes dicoppers are in +2 oxidation state, their coordination environment is similar to the dicopper complexes of this work. It would seem that the greater enzyme activities of oxidation by the metalloenzymes (tyrosinase) over that of the simple dicopper complexes must result from factors ascribed mostly to the accompanying protein matrix about the dicopper site. The protein matrix may induce a stereochemistry on copper which requires only a small reversable redox potential between Cu(II) and Cu(I). It may also enhance the bonding between *o*-diphenol and the dicopper site.

A prominate peak in the ultra-violet spectra of the dicopper complex is also given in Table III. The λ max for the spectra are found to exist between 325 nm and 400 nm. Similar λ max are found for tyrosinase [3] and lactase [26]. Various interpretations for the origin of the peaks have been given. Jolley [3] (on the study of tyrosinase) and Dooley [24] (on the study of laccase) assigned these peaks to a Cu → O_2^- charge transfer. This however, is not a possible explanation for simple bicopper complex transitions because these peaks are found in deoxygenated solutions. A more likely origin is a ligand-to-copper charge transfer band. Recently, dicopper complexes and other dimetal complexes were found to exhibit simultaneous paired electron transition in these spectral regions. These transitions were found to be twice the energy of the d–d-transition of the respective dimetal complexes [28–30]. It is noted that if the energy of transition I, Table II is doubled it is found to be equal in most cases to the λ max found in the UV region. Thus, it is possible that these transitions result from a simultaneous electron pair absorption.

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