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Stoichiometric and catalytic oxidations by dinuclear copper(I) and copper(II) complexes of a Schiff base ligand derived from the 2:2 condensation of pyridine 2,6-dicarboxaldehyde and 1,5,9-triazanonane

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Abstract

Dicopper(I) and dicopper(II) complexes of the macrocyclic ligand 3,7,11,19,23,27,33,34-octaazatricyclo[27.3.1.$1^{13,17}$]tetratriacontadeca-1(32),2,11,13,15,17(34)18,27,29(33),30-ene, $(PD)_2(DIPN)_2$, were prepared and examined for their reactivities. The dioxygen complex of $[Cu_2(PD)_2(DIPN)_2]^{2+}$ was generated in solution and was found to catalytically convert hydroquinone, *t*-butylhydroquinone, 2,6-di-*t*-butylphenol, and 2,6-dimethoxyphenols to their respective oxidation products, benzoquinone, *t*-butylbenzoquinone, 3,3',5,5'-tetra-*t*-butyldiphenoquinone, 3,3',5,5'-tetramethoxydiphenoquinone. The substrates 3,5-di-*t*-butylcatechol and 4-*t*-butylcatechol were converted to 3,5-di-*t*-butyl-1,2-benzoquinone and the γ-lactone of 3-hydroxy-4-*t*-butylmuconic acid ester respectively whereas for 4-methylcatechol the complex was inactive. The dicopper(II) complex of $(PD)_2(DIPN)_2$, $[Cu_2(PD)_2(DIPN)_2]^{4+}$ gave products with these substrates that were identical to the products obtained with the Cu(I) dioxygen complex. In addition, 4-methylcatechol was converted to the γ-lactone of 3-hydroxy-4-methylmuconic acid ester. The oxidation of 3,5-di-*t*-butylcatechol by $[Cu_2(PD)_2(DIPN)_2]^{2+}$ and dioxygen was found to be first order in the complex. The oxygenated form of the complex $[Cu_2(PD)_2(DIPN)_2]^{2+}$ was determined to be more effective (gave more turnovers) than oxygenated forms of analogous dicopper(I) complexes of ligands prepared from furan-2,5-dicarboxaldehyde and 1,4,7-triazaheptane and from pyridine-2,6-dicarboxaldehyde and 1,4,7-triazaheptane.

Keywords: Stoichiometric oxidation; Oxidation (catalytic); Copper complexes; Dioxygen complex; Schiff base; Macrocyclic ligands; Phenols; Catechols

1. Introduction

There is considerable interest in the investigation of dinuclear copper(I) complexes as catalysts from the point of view of their reactivities with dioxygen [1] and oxidation reactions [2] of their dioxygen complexes pertinent to the study of the functioning of enzymes such as tyrosinase and dioxygen transport proteins such as hemocyanin. Although copper(I)–dioxygen adducts [3–6] are indicated in the catalytic performance of dicopper complexes, the factors affecting the effectiveness of such catalysts are not well understood [7]. The reactivities of dicopper(I)–dioxygen complexes and dicopper(II) complexes with macrocyclic Schiff base ligands were described in previous papers [8–11]. For the systems investigated (the ligands of which are shown as **1** and **2** below) it was discovered that, whereas the improvement of catalysis was

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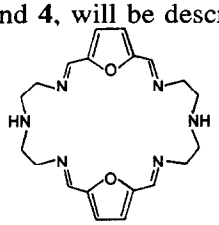
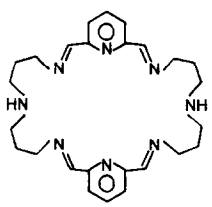
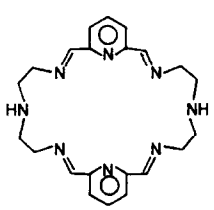
not dramatic for dicopper complexes of **2** compared with **1** for hydroquinones and phenols, the effectiveness of **2** over **1** for substituted catechols is clear cut. The improved efficiency for catechols is considered to be associated with the internuclear separation of copper ions in the complex [12]. Therefore, the next logical step seemed to be the preparation of a dicopper complex that allows a greater interionic separation. This was attempted in the synthesis of **3**, which was expected to coordinate copper in the cavities created by the pyridine and imine functions, thereby producing a greater internuclear separation between the copper ions than previously obtained in dicopper complexes of **1** and **2**. Physical studies [13] on the ligand and on the related dicopper complex of the macrocycle $(PD)_2(DIPN)_2$ formed from the 2:2 condensation of pyridine-2,6-dicarboxaldehyde and 1,5,9-triazanonane have shown that a ring-contracted isomer of the ligand, **4**, is obtained as the main product. The dicopper(I) complex of this form of the ligand was prepared and examined for its reactivity towards dioxygen. An oxygenated form of the dicopper(I) complex was studied spectroscopically and this complex ultimately was converted to a mononuclear copper(II) complex. In this report the oxidation of various substrates by the dicopper(I)–dioxygen and dicopper(II) complexes of $(PD)_2(DIPN)_2$, **3** and **4**, will be described.



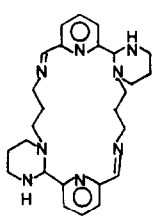
1 $(FD)_2(DIEN)_2$



3 $(PD)_2(DIPN)_2$



2 $(PD)_2(DIEN)_2$



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2. Experimental

2.1. Instrumentation

The products of the oxidation reactions were identified by melting point determinations, ^1H and ^{13}C NMR spectroscopy and IR spectrophotometry. Melting point determinations were performed on a Fisher–Johns melting point apparatus. Proton and carbon-13 NMR spectra were measured in chloroform-*d* on a Varian XL 200 FT spectrometer. Chemical shifts are reported relative to tetramethylsilane as an internal standard. Infrared spectra were obtained on a Mattson Galaxy Series FTIR 300 spectrophotometer. Ultraviolet–visible spectra were recorded on a Perkin Elmer Model 553 Fast Scan spectrophotometer. Mass spectral data were obtained by direct probe fast atom bombardment (FAB) on the Departmental VG analytical VG-705 high resolution double-focusing magnetic sector spectrometer with an attached VG Analytical 11/250J data system.

2.2. Materials

Preparation of the copper(I) complexes and stoichiometric reactions were accomplished under argon. Deoxygenated solvents were obtained by sonication prior to purging with argon for approximately 30 min, and used in experiments on the stoichiometric and catalytic oxidation of substrates. Solid reagents and solvents employed were reagent grade commercially available chemicals supplied by the Aldrich Chemical Co. Anhydrous methanol and anhydrous acetonitrile were dispensed from Sure Seal™ bottles and stored under argon.

2.3. *3,7,11,19,23,27,33,34-Octaazatricyclo[27.3.1.1^{13,17}]tetratriacontadeca-1(32),2,11,13,15,17(34),18,27,29(33),30-ene, $(PD)_2(DIPN)_2$*, **4**

This ligand was prepared from pyridine-2,6-dicarboxaldehyde and 1,5,9-triazanonane as previously described [13]. The crude product was recrystallized from a chloroform/acetonitrile mixture ($m/e = 461$).

2.4. Catalytic oxidation reactions

Reactions performed in an atmosphere of oxygen were catalytic in nature. The reaction flask which was thermostated at 25.0 ± 0.1°C was equipped with inlet and outlet adapters for argon and oxygen purging and evacuation. When oxygen uptake was measured, the pressure in the reaction vessel was maintained at 1.0 atm by use of a manometer. Catalytic reaction solutions with $[Cu_2(PD)_2(DIPN)_2]^{2+}$, **5**, and dioxygen were prepared by oxygenation of 40 ml of a 4:1 solution of methanol/acetonitrile containing 0.10 mmol of ligand, 0.20 mmol of $Cu(CH_3CN)_4PF_6$ and 4.0 mmol of substrate. The reaction was continued for 48 h, after which the oxidation product was isolated by evaporation of the solvent followed by extraction with chloroform and separation on silica gel (grade 62 special). The procedure for oxidations with the copper(II) complex was identical to that for the oxygenated complex.

2.5. Reactions with the oxygenated $[Cu_2(PD)_2(DIPN)_2]^{2+}$ complex

2.5.1. Oxidation of hydroquinones

Hydroquinone (HQ). To a solution of complex **5** (prepared from 56.8 mg of $(PD)_2(DIPN)_2$ and 91.6 mg of $Cu(CH_3CN)_4PF_6$) was added 386 mg of hydroquinone in a 4:1 methanol/acetonitrile mixture. The reaction system was purged with oxygen and, on termination of the reaction, the solvent was removed on a rotary evaporator. The product was then extracted with CH_2Cl_2 and chromatographed on silica gel. Benzoquinone was eluted from the column with $CHCl_3$. ^{1}H NMR ($CDCl_3$) (benzoquinone) δ 5.30(s). ^{13}C NMR ($CDCl_3$) δ 136.50 (CC), 187.20 (CO); mp 111–114°C, lit. 115°C.

t-Butylhydroquinone (TBHQ). To a solution of the complex **5** (prepared from 35.2 mg of ligand and 54.1 mg of $Cu(CH_3CN)_4PF_6$) in a 4:1 methanol/acetonitrile solvent was added 440 mg of TBHQ. The reaction system was purged with oxygen and, on termination of the reaction, the product was extracted with dichloromethane and chromatographed on silica gel. Elution with *n*-hexane gave *t*-butylbenzoquinone. ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 9H) 6.68 (d, 1H) 6.60 (t, 2H). ^{13}C NMR ($CDCl_3$) δ 29.05 (CH_3), 35.25 ($C(CH_3)_3$). 131.48 ($CCC(CH_3)_3$), 134.88 (*C*CO), 138.63 (*C*CCO), 156.02 ($CCC(CH_3)_3$), 187.50 (CO), 188.30 (CO); mp 58–60°C, lit. 56–57°C.

2,6-Di-t-butylphenol (2,6-DTBP). The substrate (737 mg) was added to a 4:1 methanol/acetonitrile solution of the complex **5** (36.2 mg of $(PD)_2(DIPN)_2$ and 45.4 mg of $Cu(CH_3CN)_4PF_6$) and the reaction was purged with oxygen. A dark purple precipitate formed during the reaction. The solid was filtered, dried and identified as 3,3′,5,5′-tetra-*t*-butyldiphenoquinone. ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 36H) 7.71 (s, 4H), ^{13}C NMR ($CDCl_3$) δ 29.58 (CH_3), 36.02 ($C(CH_3)_3$), 126.00 ($CCC(CH_3)_3$), 136.12 ($CCC(CH_3)_3$), 150.43 (CC), 186.46 (CO); mp 245°C, lit. 243°C.

2,6-Dimethoxyphenol (2,6-DMP). The substrate (830 mg) was added to a 4:1 methanol/acetonitrile solution of the complex **5** (35.8 mg of $(PD)_2(DIPN)_2$ and 54.8 mg of $Cu(CH_3CN)_4PF_6$) in the presence of excess dioxygen. The precipitate which formed was filtered, dried and identified as 3,3′,5,5′-tetramethoxydiphenoquinone. ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 12H) 7.35 (s, 4H); mp 287 (dec.) lit. 290 (dec.).

2.5.2. Oxidation of catechols

3,5-Di-t-butylcatechol (3,5-DTBC). The substrate (324 mg) was allowed to react with a 4:1 methanol/acetonitrile solution of complex **5** (38.8 mg of $(PD)_2(DIPN)_2$ and 61.1 mg of $Cu(CH_3CN)_4PF_6$) in an oxygen atmosphere. On termination of the reaction the solvent was removed on a rotary evaporator, extracted with dichloromethane and chromatographed on silica gel. Elution with chloroform gave 3,5-di-*t*-butyl-1,2-benzoquinone. ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 9H), 1.26 (s, 9H), 6.20 (d, 1H), 6.92 (d, 1H). ^{13}C NMR δ 27.87 (CH_3), 29.20 (CH_3),

35.47 ($C(CH_3)_3$), 36.02 ($C(CH_3)_3$), 122.08 (CH), 133.46 (CH), 149.93 ($CC(CH_3)_3$), 163.32 ($CC(CH_3)_3$), 180.03 (CO), 181.12 (CO).

4-t-Butylcatechol (4-TBC): The oxidation of 4-TBC was accomplished with 522 mg of the substrate in a 4:1 methanol/acetonitrile solution of complex **5** (60.6 mg of $(PD)_2(DIPN)_2$ and 91.6 mg of $Cu(CH_3CN)_4PF_6$) in the presence of excess dioxygen. When the reaction was completed the reaction mixture was reduced to approximately 3 ml and then chromatographed on silica gel. On elution with chloroform the second fraction obtained was found to be the γ-lactone of 3-hydroxy-4-*t*-butylmuconic acid ester. Only a small amount of the lactone was obtained. ^1H NMR ($CDCl_3$) δ 1.32 (s, 9H) 3.90 (s, 3H), 5.79 (s, 1H), 6.30 (s, 1H).

4-Methylcatechol (4-MC). Oxidation of 4-MC (243 mg) was accomplished with the catalyst prepared with 53.0 mg of $(PD)_2(DIPN)_2$ and 80.1 mg of $Cu(CH_3CN)_4PF_6$ in a 4:1 methanol/acetonitrile solvent. On termination of the reaction the solution was reduced to approximately 3 ml on a rotary evaporator, then filtered. The filtrate was chromatographed with chloroform on silica gel. Three components were eluted with increasing fractions of methanol. No product was detected.

2.6. Reactions with the $[Cu_2(PD)_2(DIPN)_2]^{4+}$ complex

Hydroquinones, phenols and catechols were oxidized in excess dioxygen in the presence of the $[Cu_2(PD)_2(DIPN)_2]^{4+}$ complex which was prepared with typically 0.10 mmol of ligand and 0.20 mmol of $CuCl_2$ in 40 ml of methanol. The substrate was added in thirty-fold excess and the reaction was carried out in excess dioxygen. The procedures and products were identical to those for the copper(I) dinuclear complexes except for the oxidation of 4-methylcatechol where the γ-lactone of 3-hydroxy-4-methylmuconic acid ester was obtained. ^1H NMR ($CDCl_3$) δ 2.20 (s, 3H), 3.82 (s, 3H), 5.72 (s, 1H), 6.24 (s, 1H).

2.7. Stoichiometric oxidations reactions

These reactions, performed under argon, were conducted in order to establish first order initial rates for the reaction between the catalyst and a substrate. For reactions with the dicopper(I)–dioxygen complex, approximately 0.010 mmol of the substrate was dissolved in 10 ml of methanol and added to 0.020 mmol of the dicopper(I) complex in 60 ml of a 4:1 methanol/acetonitrile mixture. The reaction system was purged with oxygen for approximately 1 h and then the oxygen was removed by purging with argon. The ensuing oxidation reaction was allowed to take place under argon. Product formation was followed by monitoring the absorbance of the solution at a wavelength which is characteristic of the product. The reaction solution was maintained at 25.0 ± 0.1°C and circulated through a 1.00 cm quartz flow cell by means of a peristaltic pump. When reactions were performed with the dicopper(II) complex as the active species, the system was purged with argon from the beginning, since no oxygen was needed here to activate the complex and the procedure described above for oxidation with the dicopper(I)–dioxygen complex was also used for the dicopper(II) complex.

2.8. Kinetic studies

The reaction kinetics between 3,5-DTBC and the dioxygen complex of Cu(I)–$(PD)_2(DIPN)_2$ was investigated in 4:1 methanol/acetonitrile. The reaction vessel was connected to a 1.00 cm quartz flow cell which was thermostated together with the reaction vessel at 25.0 ± 0.1°C and the formation of product was observed by the absorbance of the 410 nm band characteristic of the product. The kinetics of oxidation was determined by observing the time dependence of the absorption of this band. The identical procedure was used to investigate the reaction kinetics between 3,5-DTBC and both dicopper(I)–dioxygen and dicopper(II) complexes of $(PD)_2(DIPN)_2$.

3. Results and discussion

3.1. Preparation and reaction of catalysts

The ligand was prepared by a straightforward non-template procedure. The main product isolated was the ring-contracted form of the Schiff base which was obtained as a crystalline solid containing both water and acetonitrile of solvation as shown by X-ray diffraction analysis [13]. The dicopper(I) complex was usually prepared in situ by addition of a stoichiometric quantity of copper(I) (usually in the form of $Cu(CH_3CN)_4PF_6$) to a solution of the ligand. The solution species has been characterized as a dicopper(I) complex of the ligand **4** by ^1H NMR spectroscopy [13]. Oxygenation of this compound produces a dicopper(I)–dioxygen complex which has an estimated half life of 240 min. This oxygenated complex (which was detected spectroscopically) was also prepared in situ by exposing the reaction solution, containing both substrate and complex, to dioxygen. The reaction between the oxygenated complex and the substrate is assumed to be more rapid than the spontaneous conversion of the Cu(I)–dioxygen complex to the catalytically active dicopper(II) species. This is a reasonable assumption since related systems were found to have first order rates for the reactions of dicopper(I)–dioxygen complexes with substrates at least an order of magnitude greater than the oxidation reaction for the dicopper(II) complex of the same ligand [9,11]. In addition, the concentration of the oxygenated complex is assumed to be a constant fraction of the dicopper(I) complex at constant pressure of dioxygen implying that kinetic measurements of the order of the oxidation rate dependence on the dicopper(I) complex also applies to the oxygenated complex. Oxygenation of the dicopper(I) complex is a slow reaction with Kobs determined as 5.6×10^{-5} s^{-1} for the process (cf 1.6×10^{-3} s^{-1} for the oxygenated form of $[Cu_2(PD)_2(DIEN)_2]^{2+}$). When considering the kinetics of the reaction between the oxygenated form of

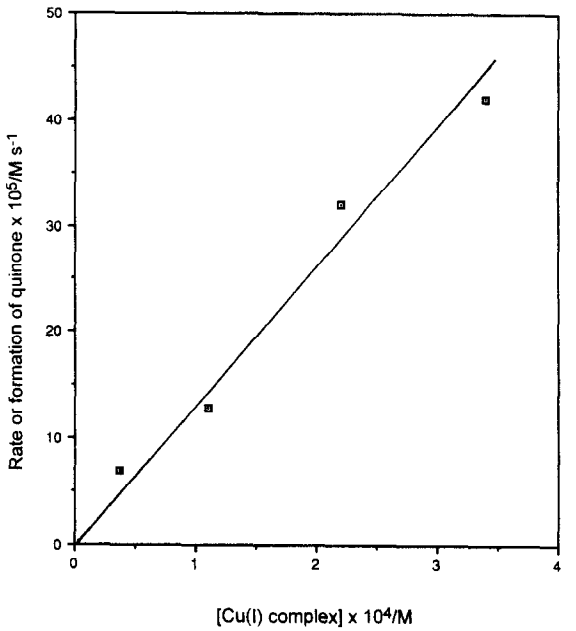


Fig. 1. Dependence of the rate of formation of 3,5-di-*t*-butyl-1,2-benzoquinone on the concentration of $[Cu_2(PD)_2(DIPN)_2]^{2+}$. The reaction was performed in methanol.

$[Cu_2(PD)_2(DIPN)_2]^{2+}$ and 3,5-di-*t*-butylcatechol, it is found that the initial rate is dependent on the concentration of complex (Fig. 1).

A time course for the formation of 3,5-di-*t*-butyl-1,2-quinone (Fig. 2) shows two slopes corresponding to oxidation processes. Since the initial species is the $[Cu_2(PD)_2(DIPN)_2]^{2+}$

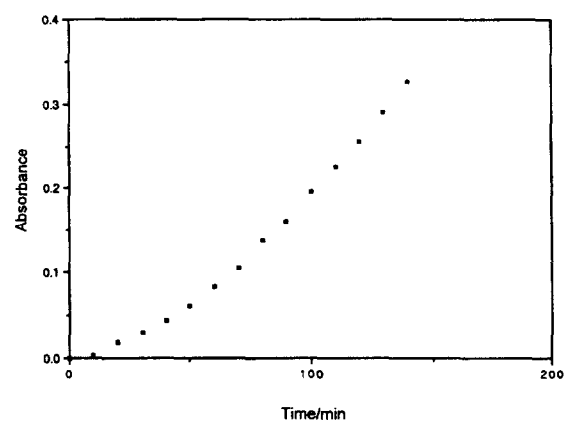
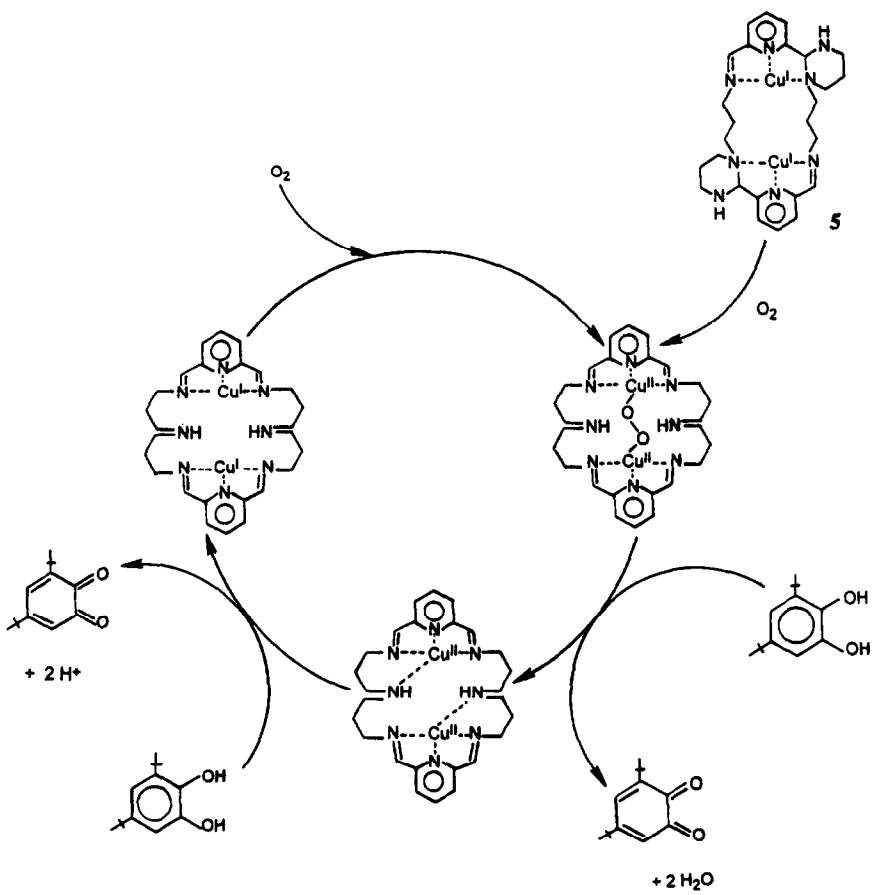


Fig. 2. Time course for the formation of 3,5-di-*t*-butyl-1,2-benzoquinone in the presence of $[Cu_2(PD)_2(DIPN)_2]^{2+}$ and dioxygen. The absorbance was measured at 410 nm in 4:1 methanol/acetonitrile.

Table 1
Dependence of initial rate of oxidation on the concentration of 3,5-di-*t*-butylcatechol

[3,5-DTBC]/M	Initial rate/M s^{-1}
0.4×10^{-3}	9.3×10^{-5}
0.9×10^{-3}	7.8×10^{-5}
1.5×10^{-3}	8.6×10^{-5}
2.3×10^{-3}	11.1×10^{-5}

complex then the first slope describes oxidation by the oxygenated form of the complex. When initial rates are measured as a function of the concentration of 3,5-di-*t*-butylcatechol within the first 120 min of the reaction no concentration dependence is observed (Table 1), if $[Cu_2(PD)_2(DIPN)_2]^{2+}$ and not its oxygenated form, is the initial species. This fact suggests that the reaction proceeds through an intermediate which is the oxygenated form of $[Cu_2(PD)_2(DIPN)_2]^{2+}$ in this case. The comparatively slow initial reaction kinetics implies that the ligand undergoes a rearrangement process in order to produce a form which is amenable to oxygenation (Scheme 1). Ring expansion is a reasonable process since a higher coordination number is achieved by the copper ions which are now oxidized to copper(II). Copper(I) ions usually have low coordination numbers such as two or three whereas copper(II) ions are able to expand their coordination numbers to four or five. The second slope of Fig. 2 which corresponds to a higher rate of oxidation is considered to involve the catalytic process since oxidation, at this point, is occurring through the use



Scheme 1.

of both oxygenated $[Cu_2(PD)_2(DIPN)_2]^{2+}$ and $[Cu_2(PD)_2(DIPN)_2]^{4+}$ as catalysts, where the ligand $(PD)_2(DIPN)_2$ is in the ring-expanded form, **3**.

The dicopper(II) complex was prepared by addition of a stoichiometric quantity of copper(II) chloride to a solution of the ligand. The copper(II) complex of the ring-contracted form of the ligand is considered to be produced initially and this is also an active form of the dicopper(II) catalyst. The kinetics of the reaction between the dicopper(II) complex and 3,5-DTBC shows that there is a period of induction before the appearance of oxidation product but such kinetics is not interpreted as ring expansion prior to reaction since the ring expansion is slow compared with the oxidation reaction.

When the dicopper(II) complex $[Cu_2(PD)_2(DIPN)_2]^{4+}$ is reacted with 3,5-di-*t*-butylcatechol and the process is followed spectrophotometrically, the green color characteristic of the copper(II) complex changes to a dark green–orange on addition of the substrate. Spectrophotometrically, there is an increase in the background absorbance (with respect to the absorption of the product) prior to the appearance of the characteristic peak of 3,5-di-*t*-butyl-1,2-benzoquinone product at 410 nm. It is evident that there are two sequential processes occurring here. The increase in background absorbance is associated with binding of the substrate to form a complex which is the precursor to electron transfer. The subsequent process must be the oxidation of the substrate. Analysis of the processes through a plot of ln absorbance vs. time (Fig. 3) shows that the curve may be represented by the sum of two exponential terms of the form ae^{-mt} (where a is a pre-exponential constant, m is a constant which is derived from the root of the integrated first order rate expression and t represents time) [14]. The curvature observed at low values of t means that the data describes two consecutive processes which overlap significantly. The first reaction is very rapid when compared with the second process (estimated difference in rate $> 10^2$ M s^{-1});

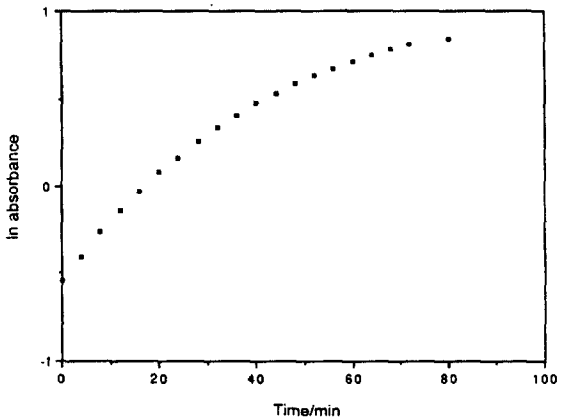


Fig. 3. Plot of ln absorbance vs. time for the formation of 3,5-di-*t*-butyl-1,2-benzoquinone in the presence of $[Cu_2(PD)_2(DIPN)_2]^{4+}$. Absorbance was measured at 410 nm.

therefore, the reactions may be regarded as separate processes in kinetic analysis [14] and were treated as such.

For catalytic reactions with the Cu(II) complex as the initiator, the dinuclear Cu(II) complex of the contracted macrocycle probably is first formed, since the initial binding of the metal ion is fast and the ring opening reaction is relatively slow. This complex is reduced to the dinuclear Cu(I) complex, **5**, by the substrate, and the complex then combines with dioxygen to form the dinuclear copper dioxygen complex with the macrocycle in the ring expanded form. This occurs since the Cu(I) complex must undergo ring expansion in order to form the dioxygen complex. From that point on the Cu(I) and Cu(II) complexes in the catalytic cycle probably involve only the ring-expanded form of the macrocyclic ligand, as indicated by the Scheme 1.

The catalytic cycle is basically the same as proposed for macrocycles **1** [9] and **2** [11]. However the difference here is the initial ring opening process to produce the oxygenated form of the dicopper(I) compound. As observed before, catalytic activity is present only in those cases where both the dicopper(I) and dicopper(II) complexes are active oxidants. In contrast to dicopper complexes of **1** and **2**, the dicopper(II) complex of **4** gives a faster initial

rate than the corresponding dicopper(I) complex. The explanation may be found in terms of the low concentration of oxygenated complex in solution due to slow ring expansion followed by oxygen uptake of $[Cu_2(PD)_2(DIPN)_2]^{2+}$.

If the cycle is initiated with $[Cu_2(PD)_2(DIPN)_2]^{2+}$ then the activity does not commence until there is ring expansion and formation of the dioxygen complex. After the substrate is oxidized, an active dicopper(II) complex is produced which oxidizes another molecule of the substrate to give the Cu(I) complex; hence perpetuation of the cycle. If the initiator is the dicopper(II) complex then oxidation of the substrate would produce a dicopper(I) complex which is oxygenated as described above to continue the cycle.

3.2. Reactions of the Cu(I)–$(PD)_2(DIPN)_2$ and the Cu(II)–$(PD)_2(DIPN)_2$ complexes

The scope of the catalytic process was examined with hydroquinones, phenols and catechols and the oxidation reaction data obtained for $[Cu_2(PD)_2(DIPN)_2]^{2+}$ and $[Cu_2(PD)_2(DIPN)_2]^{4+}$ are summarized in Ta-

Table 2
Oxidations with $[Cu_2(PD)_2(DIPN)_2]^{2+}$ and dioxygen

Substrate	% Conversion	Turnover	Product
2,6-dimethoxyphenol	34	25	3,3′,5,5′-tetramethoxydiphenoquinone
2,6-di-*t*-butylphenol	39	19	3,3′,5,5′-tetra-*t*-butyldiphenoquinone
hydroquinone	16	5	benzoquinone
t-butylhydroquinone	21	12	*t*-butylbenzoquinone
3,5-di-*t*-butylcatechol	67	12	3,5-di-*t*-butyl-1,2-benzoquinone
4-*t*-butylcatechol	19	4	γ-lactone of 3-hydroxy-4-*t*-butylmuconic acid ester
4-methylcatechol	–	–	

Table 3
Oxidations with the $Cu^{II}_2(PD)_2(DIPN)^{4+}_2$ complex

Substrate	% Conversion	Turnover	Product
2,6-dimethoxyphenol	27	8	3,3′,5,5′-tetramethoxydiphenoquinone
2,6-di-*t*-butylphenol	54	21	3,3′,5,5′-tetra-*t*-butyldiphenoquinone
hydroquinone	51	14	benzoquinone
t-butylhydroquinone	80	24	*t*-butylbenzoquinone
3,5-di-*t*-butylcatechol	45	4	3,5-di-*t*-butyl-1,2-benzoquinone
4-*t*-butylcatechol	23	5	γ-lactone of 3-hydroxy-4-*t*-butylmuconic acid ester
4-methylcatechol	< 1	< 1	γ-lactone of 3-hydroxy-4-methylmuconic acid ester

Table 4
Turnover numbers for the oxidation of various substrates with dioxygen copper(I) complexes

	$[Cu_2(FD)_2(DIEN)_2]^{2+}$ [a]	$[Cu_2(PD)_2(DIEN)_2]^{2+}$ [b]	$[Cu_2(PD)_2(DIPN)_2]^{2+}$ [c]
2,6-dimethoxyphenol	5	3	25
2,6-di-*t*-butylphenol	4	3	19
t-butylhydroquinone	1	4	12
hydroquinone	7	5	5
3,5-di-*t*-butylcatechol	< 1	4	12
4-*t*-butylcatechol	< 1	< 1	4

[a] Ref. [9].
[b] Ref. [11].
[c] This work.

bles 2 and 3, respectively. The oxidation products are also presented in Tables 2 and 3 and are shown to be identical for each catalyst. For reactions with copper(II) the catalyst was prepared directly by the addition of copper(II) to a solution of the ligand in 2:1 stoichiometry, whereas oxidations with copper(I) took place in a reaction system containing the reactants in the presence of excess dioxygen.

Table 4 gives a comparison of the catalytic effectiveness for the dicopper complex of **4** with those of **1** and **2**. Although the former catalyst is somewhat slower, it produces a dramatic increase in the number of turnovers. It is evident that there is an overall improvement with the $[Cu_2(PD)_2(DIPN)_2]^{2+}$ complex when compared with dicopper complexes of **1** and **2**. The low values for turnovers with hydroquinone are noteworthy and may be accounted for in terms of the unstable nature of the product quinone. Longer oxygenation times were needed for $[Cu_2(PD)_2(DIPN)_2]^{2+}$ because of the slow oxygenation process resulting in longer reaction times which would eventually lead to substantial decomposition of the product by the time the reaction was terminated.

An enhanced stability of the oxygenated complex of $[Cu_2(PD)_2(DIPN)_2]^{2+}$ is considered to be responsible for the improved effectiveness of this catalyst. Such stability is evident in the half life of the oxygenated complex which is more than twice that for oxygen complexes of $[Cu_2(PD)_2(DIEN)_2]^{2+}$ and $[Cu_2(FD)_2(DIEN)_2]^{2+}$ (3,6,9,16,19,22-hexaaza-27,28-dioxatricyclo-[22.2.1.1^{11,14}]-octacosa-1(26),11,13,24-tetraene). A greater half life means that there is a longer solution lifetime of the complex leading to greater activity. The actual structural and electronic factors which are responsible for the stability of the dioxygen complex of $[Cu_2(PD)_2(DIPN)_2]^{2+}$ are not well understood at this point in time. However it is thought that the increased length of the methylene chain in the ligand gives greater flexibility to the copper internuclear distance since the ligand is now a 28-membered macrocycle compared with $[Cu_2(FD)_2(DIPN)_2]^{2+}$ and $[Cu_2(PD)_2(DIEN)_2]^{2+}$ which are 24-membered macrocycles. The structural flexibility imparted by the longer methylene chains results in an improved accommodation of dioxygen between the copper ions since they are able to approach each other at a more convenient separation.

3.3. Oxidation of hydroquinones and phenols

A solution of hydroquinone or *t*-butylhydroquinone was not oxidized to any significant extent when purged with dioxygen in the absence of the dicopper complexes. However, in the presence of $[Cu_2(PD)_2(DIEN)_2]^{2+}$ the solution gradually changed color from red to yellow-green. Whether the reaction was allowed to occur under argon or in excess dioxygen the product in each case was the corresponding benzoquinone. The identical products were obtained for both copper(I) and copper(II) catalysts and in both instances the complex existing at the end of the reaction displayed copper(II) characteristics (i.e. a broad absorption around 620 nm).

The substrates 2,6-DMP and 2,6-DTBP were oxidized in the presence of dicopper(I) and dicopper(II) complexes and the products were identified as 3,3′,5,5′-tetramethoxydiphenoquinone and 3,3′,5,5′-tetra-*t*-butyldiphenoquinone, respectively. Reactions occurring both in an argon atmosphere and in excess dioxygen gave the same product. For 2,6-DMP the product was obtained as a purple–brown precipitate whereas with 2,6-DTBP a purple precipitate was obtained.

Oxidation reactions with both the dicopper(I)–dioxygen and dicopper(II) complexes probably proceed in a manner previously described [11] where the initial step is the development of a redox unstable precursor consisting of the substrate bound to the metal in the complex. In the case of oxidations with the dioxygen complex of $[Cu_2(PD)_2(DIEN)_2]^{2+}$ substrate binding is presumed to occur at the dicopper site of the peroxo intermediate. Two phenolate

units are expected to bind to adjacent dicopper centers, dissociating after electron transfer to produce the quinone products [5].

3.4. Oxidation of catechols

Mechanistic aspects of the reaction between 3,5-DTBC and $[Cu_2(PD)_2(DIPN)_2]^{2+}$ were investigated and discussed previously [13] and found to be similar to those for 3,5-DTBC and $[Cu_2(PD)_2(DIEN)_2]^{2+}$ [11]. When the initial rates were examined as a function of concentration of complex (Fig. 1), first order rate dependence was observed. First order kinetics is expected for mechanisms involving the catechol–dicopper complex as a reaction intermediate.

Catechol oxidations assisted by copper usually result in either the production of 1,2-quinones or ring-cleaved oxidation products [15]. The ring-cleaved product is usually the muconic acid, which may be further oxidized to the γ-lactone of the muconic acid ester [9,16,17]. In general it is found that the highly substituted catechols produce quinones whereas the ring-cleaved γ-lactone of the muconic acid ester is the product when the less substituted catechols are used.

Perhaps the most dramatic demonstration of the improved effectiveness of $[Cu_2(PD)_2(DIPN)_2]^{2+}$ is in the catalytic oxidation of catechols. Within the group of catechols investigated it is noticed that oxidation was most effective for the more highly substituted catechols, which is in keeping with the findings of Capdevielle and Maumy [18,19] and also Speier and Tyeklar [20]. The ease of oxidation of the substituted catechols is explained by the electronic effects imparted by the substituents. Kinetic studies have indicated that the catalytic oxidation of substituted catechols by copper(II) complexes occurs through the formation of a dicopper–catechol complex [17,21] which is a precursor to the electron transfer. The stability of this complex and that of the ensuing copper–semiquinone or copper–quinone complex subsequent to electron transfer depends to a significant extent on the nature of the substituents on catechol. Electron withdrawing groups give rise to high redox potentials and high stability of the catechol–dicopper complex [22]. On the other hand redox unstable systems are produced when the substituents on the catechol are electron releasing in nature. When complexes are formed from 3,5-DTBC, an unstable quinone complex is formed subsequent to oxidation, and this complex dissociates to give the products. It is noted that reaction of the quinone with the dicopper complex did not produce a muconate or γ-lactone, presumably because of the high redox potential of the product quinone. The electronic effects of substituents are demonstrated as well in the success of conversion of 4-*t*-butylcatechol as opposed to extremely small extents of conversion for 4-methylcatechol since there are more electron releasing groups on 4-TBC.

Other factors such as structure of the dicopper catalyst [23–28] and internuclear separation [12] of the copper ions, which contribute to the oxidation properties of catalysts, have been addressed previously in the literature. The overall improvement in turnover numbers in oxidation of catechols for $[Cu_2(PD)_2(DIPN)_2]^{2+}$ compared with $[Cu_2(PD)_2(DIEN)_2]^{2+}$ and $[Cu_2(FD)_2(DIEN)_2]^{2+}$ may be attributed to an improved 'steric match' between the substrate and the dicopper complex as proposed by Oishi et al. [12]. Such improvement is understandable especially in terms of the adjustable interionic distance in complex $[Cu_2(PD)_2(DIPN)_2]^{2+}$ compared with the more rigid nature of $[Cu_2(FD)_2(DIEN)_2]^{2+}$ and $[Cu_2(PD)_2(DIEN)_2]^{2+}$.

4. Conclusions

Oxidation catalysts based on dicopper(I) and dicopper(II) complexes of the ligand $(PD)_2(DIPN)_2$ have been prepared and used effectively in the oxidation of hydroquinones, phenols and catechols giving 1,4-benzo-

quinones, diphenoquinones and 1,2-benzoquinones respectively as the oxidation products. The kinetics of oxidation of 3,5-DTBC with $[Cu_2(PD)_2(DIPN)_2]^{2+}$ and $[Cu_2(PD)_2(DIPN)_2]^{4+}$ have shown that the reaction is first order with respect to the concentration of catalyst. The reaction mechanism probably involves a catechol bound intermediate which serves as a precursor to electron transfer.

Acknowledgements

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