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Catalytic oxidation with dinuclear Cu(I) macrocyclic dioxygen complexes as intermediates

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Abstract

The investigation of dinuclear copper complexes which interact with dioxygen has been extensive because of their relevance to biological systems and oxygen active multicopper sites are found in hemocyanin, tyrosinase and polynuclear copper oxidases. Oxygenated model copper dinuclear complexes have characteristics similar to those of the dinuclear copper sites of oxytyrosinase and oxyhemocyanin. In this paper the dinuclear Cu(I) complexes of macrocyclic ligands are described and the reactivities of their dioxygen complexes for the oxidation of various substrates will be examined. Macrocyclic ligands were prepared by the 2 + 2 condensation of an aromatic dialdehyde with diethylenetriamine and with ditrimethylenetriamine. The dinuclear Cu(I) complex of the macrocyclic ligand formed by the 2 + 2 condensation of isophthaldehyde and diethylenetriamine, forms a dioxygen adduct which rapidly hydroxylates one of the benzene rings of the macrocyclic ligand. Oxygen insertion was not possible for the Cu(I) dioxygen complex of the macrocyclic ligand with furane bridging groups, and the oxygen complex was found to be stable at room temperature. In this complex the coordinated dioxygen is activated so that it readily oxidizes various substrates, such as phenols and catechols. When the Cu(II) complex thus formed oxidizes the same substrate, a catalytic system results. The substrate was oxidized by the Cu(I) dioxygen complex, which was converted to a Cu(II) complex. The latter was in turn reduced to the Cu(I) complex by oxidation of the substrate, which then combined with oxygen to continue the catalytic cycle. Similar results were obtained with the Cu(I)/Cu(II) complexes of the ligand prepared by the 2 + 2 condensation of pyridine-2,6-dialdehyde and diethylenetriamine. Results obtained with analogous dinuclear-Cu(I)/Cu(II) complexes with larger macrocyclic rings are described. Examples of substrates that undergo catalytic oxidation, with turnovers from 2 to 30, are 2,6-dimethoxyphenol, 2,6-ditertiarybutylphenol, hydroquinone, tertiarybutylhydroquinone and 3,5-ditertiarybutylcatechol. Schemes illustrating catalytic cycles for the oxidation of 2,6-ditertiarybutylphenol and 3,5-ditertiarybutylcatechol by molecular oxygen with the dinuclear Cu(I)/Cu(II) complexes of macrocyclic ligands are presented. An interesting aspect of the present work is that the catalytically active Cu(I) dioxygen complexes with macrocyclic ligands are stable enough at room temperature, and have long enough lifetimes, to carry out two-electron oxidation of various phenolic and catecholic substrates. These models of tyrosinase are unique in that they

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function at room temperature. Copper dioxygen complexes reported previously decompose above −70°C with very few exceptions. Also, the Cu(I) dioxygen complexes described in this paper are the first tyrosinase models to oxidize substrates catalytically, a process that requires that the Cu(II) complexes also oxidize the same substrates.

Keywords: Copper(I) dioxygen complexes; Copper(II) complexes; Macrocyclic ligands; Catalytic oxidation; Catechols; Phenols

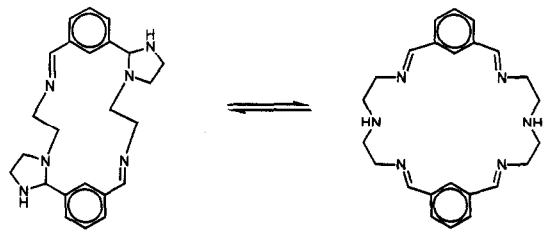
1. Introduction

The purpose of this paper is to describe relatively stable macrocyclic dinuclear Cu(I) dioxygen complexes and to explore their reactivities as oxidants for various substrates such as phenols and catechols. Dinuclear Cu(I) complexes are of interest because of their relationship to Cu(I)-containing proteins such as hemocyanin and tyrosinase [1]. Also the possible use of these complexes in synthesis has been pointed out [2]. A number of dinuclear copper(I) complexes of acyclic ligands have been investigated for oxygen complex formation [3]. A significant advance was the description of a side-on dimer prepared by Kitajima et al. [4], which led to a reinterpretation of the active sites of oxyhemocyanin and its model complexes [4]. There are mainly three possibilities for oxygen binding at the active site of the dinuclear copper(I) enzyme and its model compounds: *cis*-μ-1,2, *trans*-μ-1,2, and side-on μ-η^2:η^2. In some cases the oxygen complexes were found to be reversible, and some are stable enough to have been isolated.

In searching for macrocyclic ligands that would form dinuclear Cu(I) complexes, the synthesis of OBISDIEN [5] and its analogs was discarded as a general method because of the many reaction steps required, and the cumbersome use of tosyl groups to protect the secondary amino functions, followed by their removal. On the other hand the one-step synthesis of dinucleating macrocyclic tetra Schiff bases by the 2 + 2 condensation of a dialdehyde with a *bis*-primary amine seemed very attractive. A few examples of this method of synthesis have appeared in the literature [6]. The formation of Schiff base macrocycles seemed especially attractive for complexing relatively soft metal ions such as Cu(I) since the unsaturated Schiff base nitrogen donors are also relatively soft.

2. Results and discussion

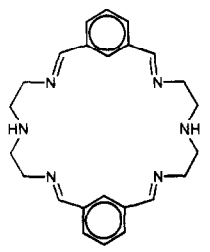
The Schiff base 2 + 2 condensation method was used successfully to synthesize the macrocyclic ligands in Scheme 1. The yield of **1** was reported to be 72% and the reaction was carried out without a metal ion as template [7,8]. The equilibrium between **1** and **1a** was postulated, corresponding to a [24] → [18] ring contraction, since **1a** crystallized out of the reaction mixture and its structure was determined by X-ray crystallography. It was proposed that the condensation product is a mixture of the 18-membered and 24-membered macrocycles, and that, under crystallization conditions, the 18-membered macrocycle crystallizes more readily. Internal nucleophilic addition of two secondary amine functions across adjacent imine bonds led to the formation of two imidazolidine rings. Two closely related examples of such inner-ring contractions were reported by Drew et al. [9] and Adams et al. [10], respectively. The procedure used for the synthesis of all the macrocyclic ligands **1–5** in Scheme 1 was a modification of the method of Alcock et al. [11].



1a **1**

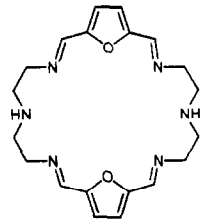
In all Schiff base condensations employed for the formation of macrocyclic ligands **1–5**, the

Macrocyclic tetra-Schiff base ligands formed by the 2+2 condensation of a dialdehyde and diethylenetriamine or ditrimethylenetriamine



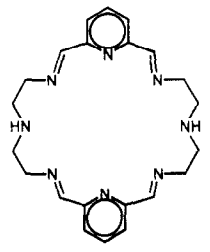
1 From isophthaldehyde and diethylenetriamine

$(MX)_2(DIEN)_2$



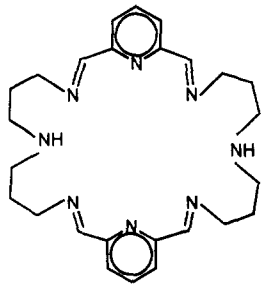
2 From furan-1,5-dicarboxaldehyde and diethylenetriamine

$(FD)_2(DIEN)_2$



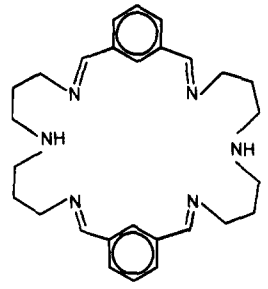
3 From pyridine-2,6-dicarboxaldehyde and diethylenetriamine

$(PD)_2(DIEN)_2$



4 From pyridine-2,6-dicarboxaldehyde and ditrimethylenetriamine

$(PD)_2(DIPN)_2$



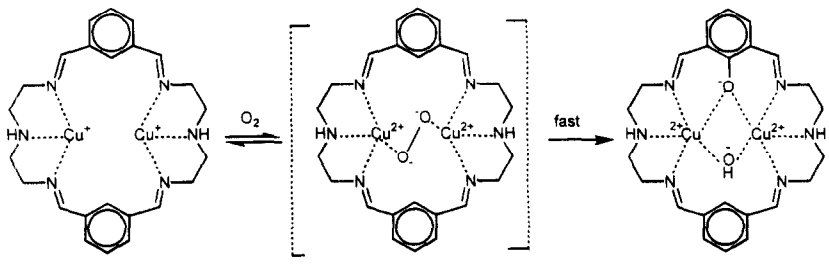
5 From isophthaldehyde and ditrimethylenetriamine

$(MX)_2(DIPN)_2$

Scheme 1.

solution obtained contained some of the ring-contracted form. Because the equilibrium seemed to be sufficiently mobile to interconvert the macrocycles obtained, reaction with two equivalents of Cu(I) yielded the dinuclear Cu(I) complex for **1**, **2**, **3** and **5**. In the case of **4**, however, the product was mainly the ring-contracted form, and the Cu(I) and Cu(II) complexes that formed showed widely different catalytic reaction rates, as will be described below.

When the dinuclear Cu(I) complex of **1** was treated with dioxygen, one of the oxygen atoms

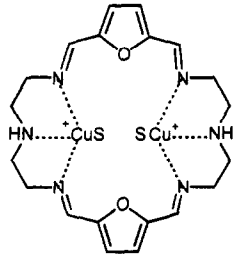


6 **7** **8**

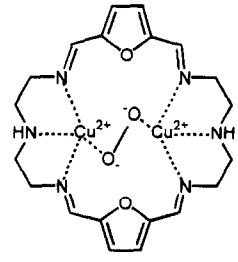
Scheme 2. Oxygen insertion in the dinuclear Cu(I) complex of $(MX)_2(DIEN)_2$.

inserted immediately into a benzene ring, forming a bridging phenolate group, while the other oxygen was reduced to water, in accordance with the sequence of reactions shown in Scheme 2 [8,12]. The intermediate oxygen complex was not isolated, since the insertion reaction was very rapid.

In order to design a macrocyclic dinuclear copper(I) dioxygen complex that would not undergo oxygen insertion and therefore may be expected to have an appreciable lifetime, the benzene rings employed as bridging groups in **1** were replaced by furane rings, giving the macrocycle **2**, in Chart 1 [13,14]. The dinuclear Cu(I) complex of **2**, formula **9**, forms a dioxygen adduct which has a half life of over one hour at room temperature. During the time of existence of this dioxygen complex, **10**, its reactivity toward externally introduced reducing substrates was determined [15,16]. The rates for the oxidation of six substrates by **10** are given in Table 1, along with the rates for oxidation by the corresponding Cu(II) complex. It is seen that the rates for oxidation by the dioxygen complex are much larger (about an order of magnitude) than rates involving the dinuclear Cu(II) complexes.



9 Dinuclear Cu(I) complex of **2** (S = solvent)



10 Copper(I) dioxygen complex of **2**

It is seen in Table 1 that four of the substrates are oxidized by the macrocyclic complexes of both Cu(I) and dioxygen and of Cu(II). Also, it was found that the dinuclear Cu(I) dioxygen complex is converted to the dinuclear Cu(II) complex, and the dinuclear Cu(II) complex is converted to the dinuclear Cu(I) complex. Thus the conditions exist for a cyclic catalytic system in the presence of excess oxygen. Scheme 3 shows such a catalytic cycle with 2,6-ditertiarybutylphenol as substrate. The four substrates in Table 1 are oxidized catalytically by this system with the turnover rates given in Table 2.

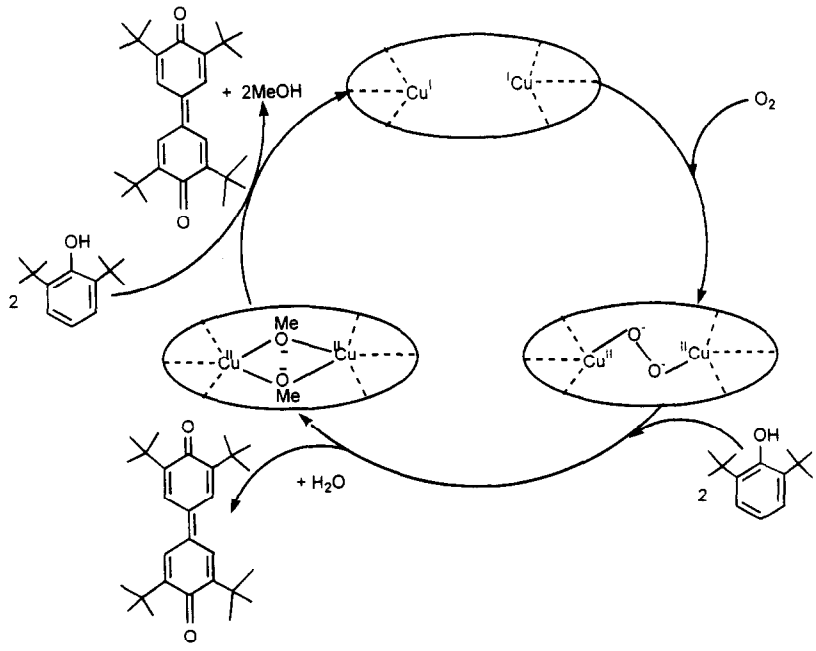
It is seen (Table 1) that 3,5-ditertiarybutylcatechol is not catalytically oxidized by this chelate system even though it is oxidized by the oxygen complex of the dinuclear copper(I) macrocyclic chelate of **2**, showing the necessity for catalysis that the substrate be oxidized by both the Cu(I) dioxygen complex and the corresponding dinuclear Cu(II) complex.

With **3** as the macrocyclic ligand, the dinuclear Cu(I) dioxygen complex and the dinuclear Cu(II) complex both oxidize 3,5-ditertiarybutylcatechol to the corresponding quinone, giving rise to the catalytic cycle indicated by Scheme 4 [17,18]. A total of five turnovers was obtained with 75% of the excess substrate oxidized. The initial pseudo first order rates measured for oxidation of five substrates (in the presence of excess substrate) are given in Table 3.

Although attempts to obtain crystals of the oxygen adduct of the dinuclear Cu(I) complex of **3** were not successful, the structure of the complex was simulated by molecular mechanics [17], and the structure obtained is illustrated by Fig. 1, which shows the minimum strain configuration to have an end-on coordination of the dioxygen.

The absorption curves [18] corresponding to the formation of 3,5-ditertiarybutyl-1,2-benzo-

Catalytic cycle for the oxidation of 2,6-ditertiarybutylphenol by dinuclear Cu(I)/Cu(II) complexes of $(FD)_2(DIEN)_2$, **2**, in the presence of excess dioxygen



Scheme 3.

Table 2
Catalytic activity of $[Cu_2L]^{2+}$ in the oxidation of various substrates (ligand is $(FD)_2(DIEN)_2$, **2**)

Substrate	Turnover (h)	Time of reaction (min)
hydroquinone	7	60
t-butylhydroquinone	5	43
2,6-di-*t*-butylphenol	15	5
2,6-dimethoxyphenol	30	10

quinone, Fig. 2, give a striking representation of the oxidation of the catechol by the Cu(I) dioxygen complex illustrated by Fig. 1. Also, an interesting measure of the rate of formation of the oxidation product under catalytic conditions (excess dioxygen and substrate) is given in Fig. 3 [18]. The initial slow reaction is due to the fact that the oxidant is initially the dinuclear

Table 1
Initial rates in the oxidation of substrates by Cu(I)-dioxygen and Cu(II) complexes of **2**

Substrate	Product	Initial, pseudo-first-order rate ($M\ s^{-1}$)	
		Cu(I) + O_2	Cu(II)
hydroquinone	benzoquinone	1.1×10^{-4}	2.2×10^{-5}
t-butylhydroquinone	*t*-butylbenzoquinone	1.2×10^{-4}	1.6×10^{-5}
2,6-di-*t*-butylphenol	3,3′,5,5′-tetra-*t*-butyldiphenoquinone	2.4×10^{-4}	5.8×10^{-5}
2,6-dimethoxyphenol	3,3′,5,5′-tetramethoxydiphenoquinone	7.4×10^{-3}	5.6×10^{-5}
3,5-di-*t*-butylcatechol	3,5-di-*t*-butyl-1,2-benzoquinone	1.4×10^{-8}	~ 0
3,4-dimethylaniline	3,4-dimethylnitrosobenzene	6.5×10^{-5}	~ 0

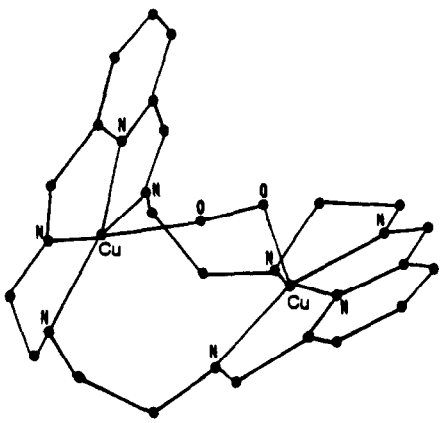
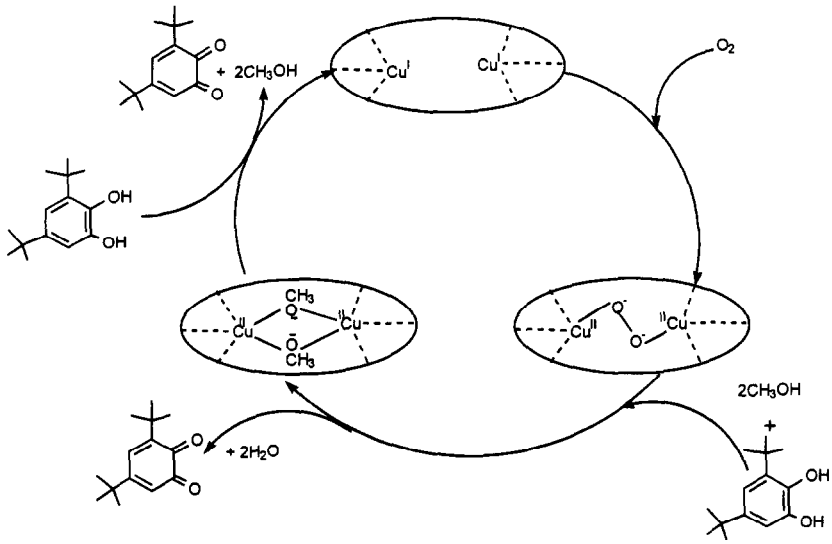


Fig. 1. Structure of the dinuclear peroxo-bridged copper(I) dioxyen complex deduced with the aid of the molecular modeling program SYBYL.

Cu(II) complex of **3**. As some of the catalyst is reduced to Cu(I), it combines with dioxygen and the reaction speeds up. (The rate for the oxidation by Cu(I) and dioxygen listed in Table 3 is ten times the rate listed for the corresponding Cu(II) complex). The rates for the stoichiometric reactions in Table 3 are determined to be greater for the Cu(I) complex and dioxygen than for the Cu(II) complex by factors which range from 5 to 100.

For the dinuclear redox systems set up with the Cu(I) and Cu(II) chelates of **4**, the rates obtained are reversed, with the initial rates for the dinuclear Cu(I) complex with dioxygen being much lower than those of the Cu(II) com-

Catalytic cycle for the oxidaton of 3,5-ditertiarybutylcatechol by dinuclear Cu(I)/Cu(II) complexes of $(PD)_2(DIEN)_2$, **3**, in the presence of excess dioxygen



Scheme 4.

Table 3
Initial rates for Cu(I)-dioxygen and Cu(II) oxidations of various substrates (ligand is **3**, $(PD)_2(DIEN)_2$)

Substrate	Product	Initial pseudo first order rates ($M\ s^{-1}$)	
		Cu(I) + O_2	Cu(II)
2,6-dimethoxyphenol	3,3′,5,5′-tetramethoxydiphenoquinone	7.7×10^{-5}	1.5×10^{-5}
2,6-di-*t*-butylphenol	3,3′,5,5′-tetra-*t*-butyldiphenoquinone	6.7×10^{-5}	1.2×10^{-5}
hydroquinone	benzoquinone	8.3×10^{-4}	8.9×10^{-5}
t-butylhydroquinone	*t*-butylbenzoquinone	9.3×10^{-4}	1.9×10^{-4}
3,5-di-*t*-butylcatechol	3,5-di-*t*-butyl-1,2-quinone	3.8×10^{-4}	3.8×10^{-5}

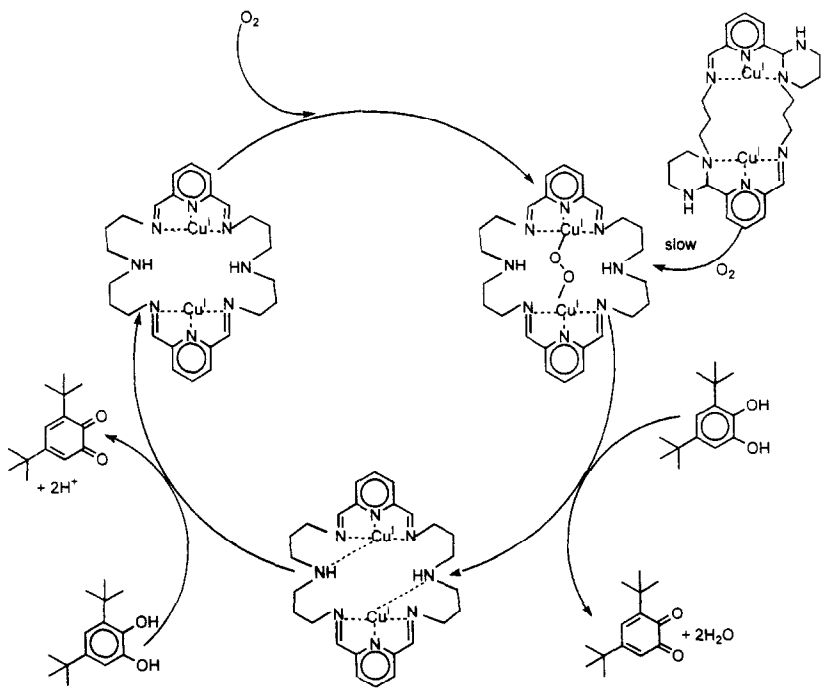
Table 4
Turnover numbers for the catalytic oxidation of various substrates with dioxygen copper(I) complexes

	$[Cu_2(FD)_2(DIEN)_2]^{2+}$	$[Cu_2(PD)_2(DIEN)_2]^{2+}$	$[Cu_2(PD)_2(DIPN)_2]^{2+}$
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

plexes [19,20]. This unusual behavior was ascribed to the fact that **4** was obtained initially in the ring-contracted form, and that formation of the dinuclear Cu(I) dioxygen complex requires a conformational change of the macrocyclic ligand to the ring-expanded form to accommodate the dioxygen. This conformation change is a relatively slow reaction, so that the overall initial rate is slow even though the dioxygen complex, once formed, may react rapidly with the substrate. Oxidation by the dinuclear Cu(II) complex does not require a conformational change, and can be relatively rapid.

Six reducing substrates were found to be oxidized catalytically. These are listed in Table 4, along with the number of turnovers observed for this macrocyclic ligand $(PD)_2(DIPN)_2$, **4**, and for ligands **2** and **3**. The large increase in

Catalytic cycle for the oxidation of 3,5-ditertiarybutylcatechol by dinuclear Cu(I)/Cu(II) complexes of $(PD)_2(DIPN)_2$, **4**, in the presence of excess dioxygen



Scheme 5.

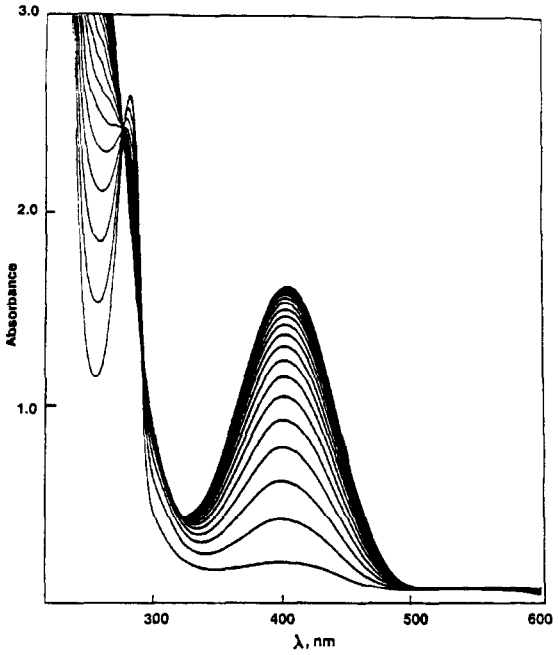


Fig. 2. Spectral changes accompanying the oxidation of 3,5-DTBC with $[Cu(I)_2(PD)_2(DIEN)_2]+O_2$ under argon (concentration of complex is 2.86×10^{-4} M).

the number of turnovers observed for this ligand may be ascribed to the higher lifetime of the oxygen complex. With over twice the lifetime of the dinuclear Cu(I) dioxygen complex ($t_{1/2}$ = 240 min), there would be more time to oxidize the substrate in the cyclic oxidation process. The catalytic cycle for the oxidation of 3,5-ditertiarybutylcatechol by the Cu(I) and dioxygen and by the Cu(II) complexes of $(PD)_2(DIPN)_2$, is illustrated in Scheme 5. Although the oxygenation of the Cu(I) complex of the contracted 20-membered macrocyclic ring is

Table 5
Initial rates in the oxidation of 3,5-DTBC to 3,5-DTBQ by $LCu(I)_2$-dioxygen and $LCu(II)_2$

Macrocyclic ligand L [a]	Initial, pseudo-first-order rate ($M\ s^{-1}$)	
	$LCu(I)_2+O_2$	$LCu(II)_2$
$(FD)_2(DIEN)_2$	1.4×10^{-8}	0.0
$(PD)_2(DIEN)_2$	3.8×10^{-4}	3.8×10^{-5}
$(PD)_2(DIPN)_2$	1.3×10^{-4}	4.6×10^{-3}
$(MX)_2(DIPN)_2$	7.8×10^{-3}	1.1×10^{-4}

[a] 2:2 dialdehyde (FD = 2,5-furan; PD = 2,6-pyridine; MX = 1,3-benzene) condensation products with triamines (DIEN = 1,4,7-triazaheptane; DIPN = 1,5,9-triazanonane).

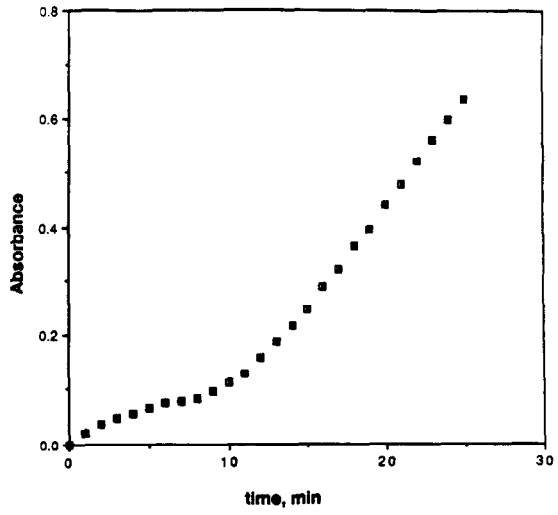


Fig. 3. Time dependence of the catalytic formation of 3,5-di-*t*-butyl-1,2-benzoquinone in the presence of **3** (1.76×10^{-4} M) and excess dioxygen (P_{O2} = 1 atm) monitored at 400 nm.

slowed by the conformational change to a 28-membered macrocyclic ring to accommodate the dioxygen, once the expanded macrocyclic ring is formed, the catalytic cycle can proceed as usual without any further conformational changes.

The ligand $(MX)_2(DIPN)_2$, **5**, forms a dinuclear Cu(I)dioxygen complex [21] which does not undergo oxygen insertion in the phenyl ring, in sharp contrast to its macrocyclic analog $(MX)_2(DIEN)_2(O_2)^{2+}$. This difference seems to be the result of the enlargement of the macrocyclic cavity. The dinuclear dicopper(I) macrocyclic complex of **5** is an efficient and selective catalyst for the oxidation of 3,5-ditertiartybutylcatechol by dioxygen and the oxidation rate is much faster than that of any of the related macrocyclic systems reported to date. Table 5 compares the initial rates of oxidation of 3,5-ditertiarybutylcatechol by the macrocyclic dinuclear copper(I) dioxygen and copper(II) complexes described in this paper.

No long-lived dioxygen complex could be detected by standard spectrophotometry, but by the use of a stopped-flow UV-vis spectrophotometer an intermediate (presumably the dinuclear Cu(I)-dioxygen adduct) was detected. The slow rate of the electron transfer process

for the formation of the dinuclear Cu(II) complex allowed the building up of the concentration of the intermediate dioxygen complex, according to the following reaction sequence:

$$Cu_2L^{2+} + O_2 \overset{fast}{\rightarrow} \text{oxygen adduct} \overset{slow}{\rightarrow} Cu_2L^{4+}$$

Thus the oxidation reaction was found to be zero order in O_2 and first order in the dinuclear copper(I) complex, Cu_2L^{2+}.

The fact that the initial rate of oxidation of 3,5-ditertiarybutylcatechol by the dinuclear copper(I)) complex of $(MX)_2(DIPN)_2$ and dioxygen is about seventy times faster than that of the Cu(II) complex may be taken as additional evidence for the dioxygen adduct.

Acknowledgements

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