

**CATALYTIC OXIDATION OF 3,5-DI-TERTBUTYL CATECHOL (3,5-DTBC)
AND 2,6-DI-TERTBUTYL PHENOL (2,6-DTBP) BY COPPER(II) AND
COBALT(II) COMPLEXES OF A BINUCLEATING
TETRAPYRROLE MACROCYCLE**

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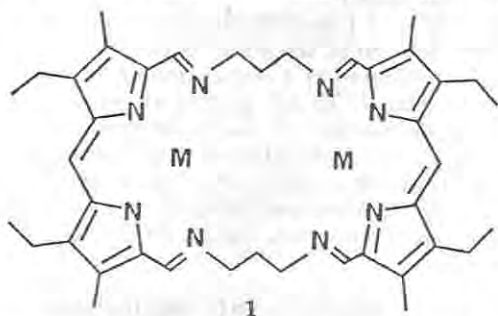
ABSTRACT. Binucleating copper(II) and cobalt(II) complexes of the ligand, 4,16,20,32-tetraethyl-5,15,21,31-tetramethyl-8,12,24,28,33,34,35,36-octaaza Pentacyclo[28.2.1.1³.6.1¹⁴.17.1¹⁹.22] hexatriaconta -1,3,5,7,12,14 (35), 15,17,19,21,23,28,30(33), 31-tetradecaene (bi-dptmd. 6H) catalyses the oxidation of 3,5-ditertbutyl-catechol and 2,6-ditertbutylphenol in the presence of oxygen respectively. The catalytic activity of copper(II) complexes with N_3^- , NCS^- , Cl^- , ClO_4^- and BF_4^- as anion were investigated. The copper(II) complex with N_3^- as anion was found to be the most active. A mechanism involving the formation of phenoxy radicals in the oxidative coupling of 2,6-DTBP by Co_2 (bi-dptmd) (Cl_2) is proposed.

INTRODUCTION

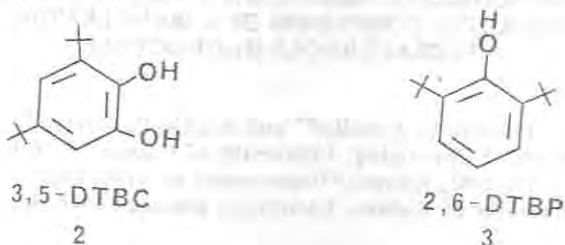
Porphyryns and porphyrin-related ligands exhibit diverse chemistry, which includes oxygenase and oxidase activity as well as the complex reactions mediated by chlorophyll and vitamin B₁₂ (1). Similarly, bimetallic systems such as certain cuproproteins play a major role in oxygen transport and oxidase activity (2).

The interest in the iron and cobalt porphyrins has focused primarily on the ability of the complexes to mimic the natural oxygen carrying hemeproteins (3-7). Binucleating systems are also extensively studied because of their ability to serve as simple model for multi-metal centered catalysts. For example, cofacial diporphyrins (8-10) and pillared porphyrins (11-13) show effective catalysis in the four electron reduction of dioxygen to water (11,12).

In our laboratories we have synthesized a hybrid porphyrin-like ligand **1** that allows the incorporation of two metals within one macrocyclic system.



We wish to report here the catalytic oxidation of 3,5-di-terbutyl catechol (3,5-DTBC, **2**) and 2,6-di-terbutylphenol (2,6-DTBP, **3**) by copper(II) and cobalt (II) complexes of ligand **1** respectively.



EXPERIMENTAL

Unless otherwise stated, all chemicals were reagent grade. Electronic spectra were recorded from 800 to 200 nm on a Hewlett-Packard Model 8450A Diode Array Spectrophotometer. Liquid chromatographic separations were performed on a column packed with 5 x 0143L-1 100-200 mesh silica gel MCB reagent grade. Mass spectra were recorded on a Ribermag R10-10 spectrometer at the University of Kansas by Dr. Charles Judson.

Synthesis. The abbreviations used for the ligand derive from its component parts, i.e. bi for two, dp for dipyrromethene and tmd for 1,3-propanediamine (trimethylenediamine).

The free base-ligand 4,16,20,32-tetraethyl-5,15,21,31-tetramethyl-8,12,24,28,33,34,35,36-octaazapentacyclo[28.2.13.6.1⁴.17.1¹⁹.22] hexatriaconta-1,3,5,7,12,14(35),15,17,19,21,23,28,30 (33), 31-tetradecaene (bidptmd.6H); $\text{Cu}_2(\text{bi-dptmd})(\text{X})_2$ $\text{X}=\text{N}_3^-$, SCN^- , Cl^- , ClO_4^- and BF_4^- , and $\text{Co}_2(\text{bi-dptmd})(\text{Cl})_2$ were synthesized and characterized according to our reported methods (14-16).

Oxidation of 3,5-DTBC. A 100 ml flask was equipped with a condenser and an inlet attached to oxygen gas tank. The flask was then immersed in a constant temperature water bath. A typical reaction consisted of 25 ml of $\text{Cu}_2(\text{bi-dptmd})(\text{X})_2$ ($1.00 \times 10^{-4}\text{M}$) and 25 ml of 3,5-DTBC ($1.00 \times 10^{-3}\text{M}$) which were mixed in the flask and put under a constant positive pressure of oxygen. The amount of quinone (3,5-DTBQ) formed was determined by the measurement of the absorbance at 408 nm ($\epsilon = 1800 \text{ M}^{-1} \text{ cm}^{-1}$) of aliquot samples periodically for up to 18 hr. Separation of the reaction mixture on a silica gel column using dichloromethane as the eluant, gave a yellow eluate which was concentrated and confirmed to be the quinone by UV-VIS λ_{max} 408 and 303 nm, mass spectrum gave $m/z = 220$ (M^+ , 3,5-DTBQ).

Oxidation of (2,6-DTBP). A procedure similar to that of the oxidation of catechol was followed without the use of the water bath.

A typical reaction consisted of a suspension of 4.0 mg or less of $\text{Co}_2(\text{bi-dptmd})(\text{Cl})_2$ in 25 ml of methanol. To the stirred suspension, 28 mg of 2,6-DTBP was added and the mixture stirred at room temperature under constant positive oxygen pressure for 24 hr. The mixture was concentrated to half the original volume and left to stand for a few hours. The crystalline product was separated by filtration and analyzed. Mass spectra gave $m/z = 408$ (M^+ for 3,3',5,5'-tetratert-butylidphenoquinone); m.p. 240°C; lit 246°C (17).

RESULTS AND DISCUSSION

Oxidation of 3,5-DTBC. Fig. 1 shows the change in absorbance at 408 nm as a function of time when 3,5-DTBC is oxidized by $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$ in the

ratio of 10:1 (substrate: complex) in acetonitrile at 20°C. The isosbestic point at 275 nm, the decrease in the catechol band at 285 nm and the increase in the quinone band at 408 nm clearly show a clean conversion of the catechol to the quinone. It was observed that at 20°C the band at 592 nm which is associated with the complex did not change appreciably which is indicative of low decomposition rate. However at 50°C the band at 592 was found to decrease appreciably indicating a higher rate of decomposition.

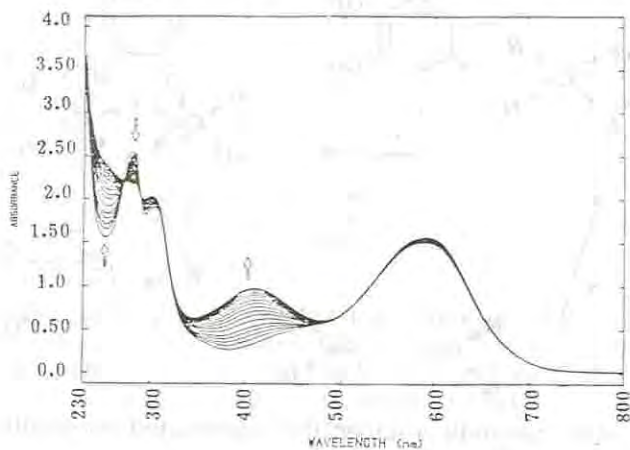


Fig. 1. Change in absorption spectra with time in the TBC-Cu₂ (bi-dptmd) (N₃)₂ system (1 × 10⁻³ M TBC and 1 × 10⁻⁴ M Cu₂ (bi-dptmd) (N₃)₂) in CH₃CN, under positive oxygen pressure at 20°C.

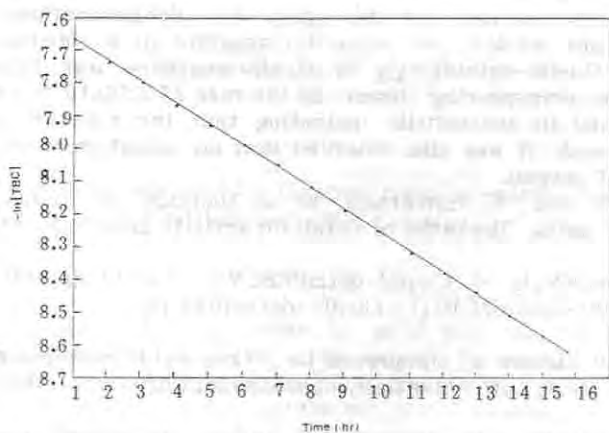
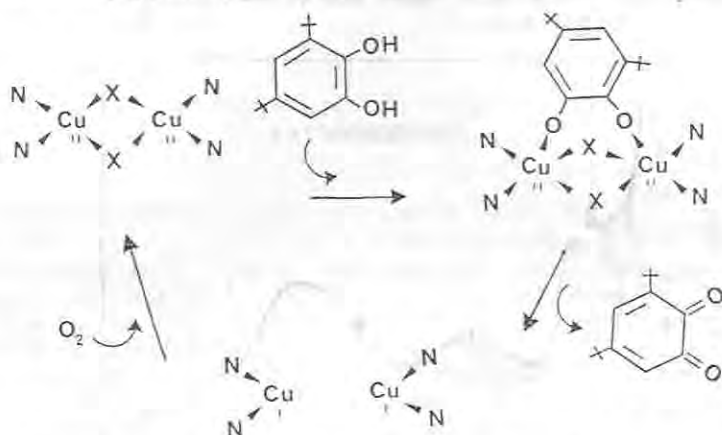


Fig. 2. The ln TBC vs time plot in the TBC-Cu₂ (bi-dptmd) (N₃)₂ system (10:1) in CH₃CN, under positive oxygen pressure at 20°C.

A first order plot in the substrate (Fig.2) gave a first order rate constant of 3.56 × 10⁻⁴ min⁻¹ at 20°C in acetonitrile. At 50°C in the same solvent

a value of $5.2 \times 10^{-4} \text{ min}^{-1}$ was obtained. Control experiments were carried out under similar reaction conditions. In the absence of oxygen and/or the complex $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$ gave no appreciable amount of the 3,5-di-terbutylquinone (3,5-DTBQ) even after 24 hr. This could only be explained by the fact that in the electron transfer process, two electrons are transferred from catechol of the two copper(II) centers which are subsequently reduced to two copper(I) centers. The copper(I) centers are then oxidised by molecular oxygen to regenerate the two copper(II) centers, followed by elimination of the product as shown below.

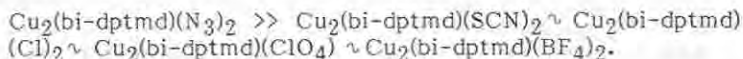


It is not known with certainty whether the regenerated copper(II) complex is μ -peroxo or simply copper(II) superoxo species.

Comparison of 3,5-DTBC oxidation by $\text{Cu}_2(\text{bi-dptmd})(\text{X})_2$, $\text{X}=\text{N}_3^-$, SCN^- , Cl^- , ClO_4^- and BF_4^- . In our previous studies (15) we showed that $\text{Cu}_2(\text{bi-dptmd})(\text{X})_2$ adopts different structures depending on the anion. We further showed that different anions had drastic effects on the electronic behaviour of the metal centers. For this reason, oxidation studies of 3,5-DTBC by $\text{Cu}_2(\text{bi-dptmd})^{2+}$ salt with different anion was undertaken.

The most suitable solvent for this study was dichloromethane in which all the complexes are soluble. At room temperature in a substrate-to-complex ratio of 10:1, $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$ in dichloromethane was found to oxidize 3,5-DTBC to the corresponding quinone at the rate of $3.56 \times 10^{-4} \text{ min}^{-1}$. A similar rate was obtained in acetonitrile indicating that the reaction is independent of the solvent used. It was also observed that no oxidation reaction took place in the absence of oxygen.

Fig. 3 shows the % conversion as a function of time for different $\text{Cu}_2(\text{bi-dptmd})^{2+}$ salts. The order of catalytic activity is as follows:



There are two classes of complexes i.e. those with coordinating anions (N_3^- , Cl^- , SCN^-) and those with potentially non coordinating (ClO_4^- , BF_4^-).

For the complexes with coordinating anions, we cannot account for the difference in their catalytic activity towards 3,5-DTBC on the basis of structure and electrochemical properties (15) since these properties are very similar for all the complexes.

However, there may be a steric match which may favour the electron transfer reaction between the catechol and $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$. A "steric match" mechanism between a donor and a binuclear complex has been proposed by Nishida (18) (Fig. 4) in electron transfer reactions between planar binuclear(II) complexes

and 3,5-DTBC. Therefore if the catechol can sterically fit in the elliptical cavity of the $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$ complex (15) then it is possible that this mechanism may favour its catalytic activity.

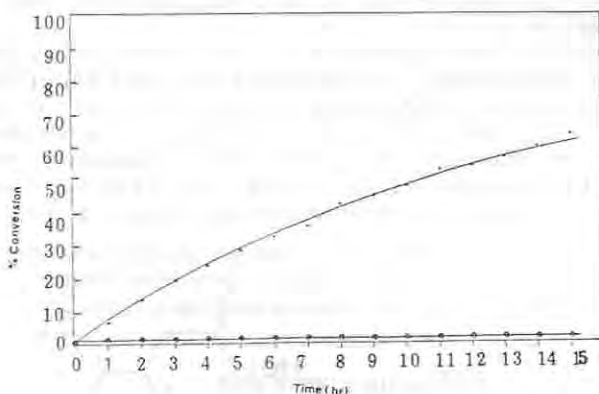


Fig. 3. Conversion for the oxidation of TBC Catalyzed by binuclear copper(II) complexes ($T = 20^\circ\text{C}$, initial TBC = 1×10^{-3} M in CH_2Cl_2 ; Complex / TBC = 0.1. Catalysts: X = $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$; O = $\text{Cu}_2(\text{bi-dptmd})(\text{SCN})_2$, $\text{Cu}_2(\text{bi-dptmd})(\text{Cl})_2$ (bi-dptmd) $(\text{ClO}_4)_2$. Conversion % = % of TBC oxidized.

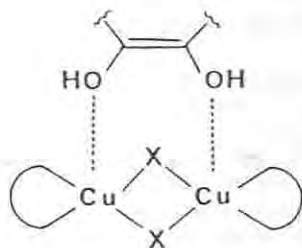


Fig. 4. "Steric match" proposed for electron transfer reaction between 3,5-DTBC and a binuclear copper(II) complex.

The lack of catalytic activity shown by salts with non coordinating anions may be attributed to the fact that they exhibit two sequential one-electron transfer processes at different potentials (15), which may not favour the electron transfer reaction between catechol and the binuclear copper(II) complexes.

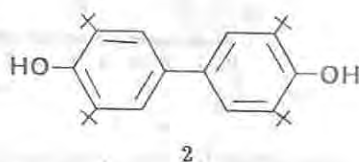
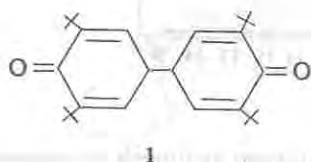
The fate of the $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$ is not known with certainty but it probably decomposes as evidenced by the decay in the band at 592 nm over a period of several days at room temperature. In this study, there is no direct evidence to support the formation of $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ intermediate discussed by Rogic (19).

Reaction of $\text{Co}_2(\text{bi-dptmd})(\text{Cl})_2$ with oxygen. In the solid state $\text{Co}_2(\text{bi-dptmd})(\text{Cl})_2$ is very stable and unreactive towards oxygen. However in coordinating

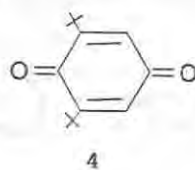
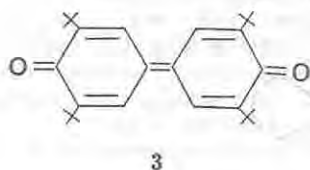
solvents e.g. DMF, CH_3CN or CH_3OH , it reacts with molecular oxygen to form purple solution within a few seconds.

The purple DMF solution has two strong bands at 300 and 544 nm, and shoulders at 654 and 742 nm. The band at 544 nm is attributed to the formation of an oxygen adduct of the complex (20).

Oxidation of 2,6-DTBP $\text{Co}_2(\text{bi-dptmd})(\text{Cl})_2$. Two procedures were followed, a direct addition of both complex and substrate or the addition of the substrate to the purple oxygen adduct. Both procedures resulted in the formation of the oxidation products. This probably suggests formation of a substrate oxygen adduct-complex in the transition state. The brown solution which contained the products showed the presence of species with m/z 410 in the mass spectrum. We attribute this to the presence of the intermediates (1) and (2) shown below.



This is based on the fact that the two compounds are well known intermediates in the oxidative coupling reactions of phenols (21). The major product 3 in the reaction was isolated as yellow needle shaped crystals after the solution was concentrated to about half its original volume.

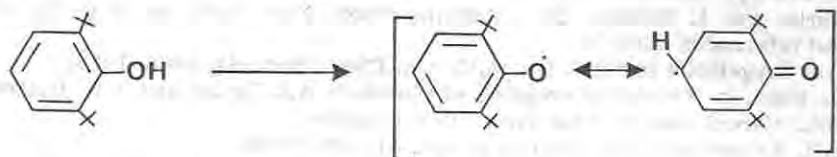


It showed λ_{max} 416 nm in methanol and a peak with $m/z = 408$ in the mass spectrum. The other minor product 4 was 2,6-ditartbutylbenzo-quinone.

The formation of diphenylquinone as the major product indirectly suggests that the oxygen adduct is μ -peroxo species as opposed to the superoxo Co-O_2 species in solution. This is because formation of superoxo species would favour higher yields of benzoquinone while on the other hand the μ -peroxo dimer favours higher yields of diphenylquinone (22, 23). It is therefore most probable that the purple solution which is formed when $\text{Co}_2(\text{bi-dptmd})(\text{Cl})_2$ is oxygenated is the μ -peroxo compound $[\text{Co}_2(\text{bi-dptmd})(\mu\text{-O}_2)(\text{Cl})_2]$.

We propose a mechanism which involves the transfer of one electron from phenol to the oxidant resulting in the formation of phenoxy radicals as shown below.

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It is the resultant phenoxy radicals which undergo a series of complex reactions leading to different products. Further work is in progress to ascertain the mechanism of the above reactions and the nature of the oxygen adduct.

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