

Copper(I) and copper(II) dinuclear complexes of a macrocyclic ligand derived from the 2:2 condensation of pyridine-2,6-dicarboxaldehyde and 1,4,7-triazaheptane

David A. Rockcliffe, Arthur E. Martell *

Department of Chemistry, Texas A & M University, College Station, TX 77843-3255, USA

Received 30 November 1994; accepted 6 February 1995

Abstract

The macrocyclic Schiff base ligand 3,6,9,17,20,23,28,29-octaazatricyclo[23.3.1.1^{11,15}]tridecanedecal(28),2,9,11,13,15(30),16,23,25(29),26-ene (PD)₂(DIEN)₂, **1**, was prepared from the 2:2 condensation of diethylenetriamine and pyridine-2,6-dicarboxaldehyde. A copper(I) dinuclear complex **2** was formed by the reaction of **1** with two equivalents of Cu(CH₃CN)₄PF₆ in 3:1 methanol/acetonitrile solvent. The complex **2** was oxygenated at 25°C to the extent of a 1:1 molar ratio of dioxygen to complex and a copper(I)–dioxygen complex **3** was spectroscopically indicated as an initial species which degraded to a copper(II) complex, **4**, of **1**. A dinuclear copper(II) complex **5** was formed by the reaction of **1** with two equivalents of Cu(ClO₄)₂·7H₂O. The X-band EPR spectra of both **4** and **5** are characterized by axial signals with *g*_⊥ values of 2.076 and 2.085 respectively. Conductivity measurements have shown that **4** is a 3:1 electrolyte when dissolved in acetonitrile. EPR and ultraviolet–visible spectral parameters suggest that **4** and **5** have distorted pyramidal structures in solution.

Keywords: Copper; Dinuclear complexes; Dioxygen copper(I) complex; Macrocyclic copper(II) complex; Octaaza macrocycle; Schiff base macrocycle

1. Introduction

Interest in the investigation of dinuclear copper complexes, which interact with dioxygen, has been extensive because of their relevance to biological systems [1–4]. Oxygen-active multicopper sites are found in hemocyanin, tyrosinase and polynuclear copper oxidases. There has been considerable attention given to oxygenated model complexes, with a coupled dinuclear site [5–10], which display spectroscopic characteristics similar to the active sites of oxyhemocyanin or oxytyrosinase [11–33]. A review on copper–

dioxygen complexes [34] has recently appeared in the literature. Macrocyclic complexes [21,35,36] have been assessed as potential models for type III copper systems and these complexes demonstrated catalytic capabilities in performing oxidation reactions on phenolic and catecholic substrates [37]. In pursuing this aspect of the chemistry of copper(I) macrocycles, a cyclic ligand based on the 2:2 condensation of *m*-phthalaldehyde and diethylenetriamine was prepared [35,36] and an endogenous hydroxylation reaction was accomplished on the xylyl function by an implicit short-lived dioxygen adduct of the copper(I) dinuclear complex. In order to inves-

* Corresponding author.

tigate the oxidation process a related macrocyclic dinuclear copper(I) complex, the ligand of which was formed by 2:2 condensation of furan-1,4-dicarboxaldehyde and 1,4,7-triazaheptane(diethylenetriamine), was prepared [21]. The dioxygen adduct was detected spectroscopically and successfully used to perform catalytic oxidation reactions on hydroquinones, phenols and ascorbic acid [37]. The performance of such models is thought to be influenced by the ability of the dinuclear copper(I) complex to form a dioxygen adduct, the activity of which in turn is dependent on how well dioxygen is accommodated between the two copper ions.

In this research, a dinuclear $[\text{Cu}(\text{I})_2(\text{PD})_2(\text{DIEN})_2]^{2+}$ complex with a ligand prepared by a 2:2 condensation of pyridine-2,6-dicarboxaldehyde and diethylenetriamine, was synthesized in order to investigate the effects of donor atom and internuclear distance on the ability of the macrocyclic complex to function as a catalyst in oxidizing substrates which are pertinent to the function of tyrosinase. CPK models demonstrate that four-coordination of copper is likely. With this ligand, the internuclear distance between the coordinated copper ions is probably greater than 2.94 Å, which is the separation observed for the previously prepared $[\text{Cu}(\text{II})_2(\text{FD})_2(\text{DIEN})_2]^{4+}$ complex [21], and consequently will bear a closer resemblance to the conditions present in the active site of tyrosinase.

2. Experimental

2.1. Instrumentation

Proton and carbon-13 NMR spectra were recorded in CDCl_3 or CD_3CN , as was convenient, on a Varian XL200 FT spectrometer. Chemical shifts are reported relative to tetramethylsilane (TMS) as an internal standard. X-band electron paramagnetic resonance (EPR) measurements were made on a Bruker ESP 300 spectrometer. Field calibration was accomplished with an NMR O3SM gaussmeter. Samples for infrared spectra

were prepared as KBr discs and recorded on a Mattson Galaxy Series FTIR 300 spectrophotometer. Ultraviolet–visible spectrophotometric measurements were made on a Perkin Elmer Model 553 Fast Scan spectrophotometer. Melting points were determined on a Fisher–Johns melting point apparatus. Mass spectral data were obtained at the Michigan State University Spectrometry Facility on a JEOL HX 110 spectrometer and at Texas A & M University on a VG Analytical VG-705 spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Conductivity measurements were made in acetonitrile on an Orion Model 160 conductivity meter with a Barnstead E3411 electrode. Oxygen uptake measurements were made as previously described [38]. Thermogravimetric analyses were performed on a Du Pont 950 thermogravimetric analyzer interfaced with a Thermal Analyst 2000 computer.

2.2. Materials

Preparation of the copper(I) complex was carried out under argon by use of Schlenk line techniques. Argon (99.98% AIRCO) was prescrubbed with a 3% solution of pyrogallol in 0.8 M NaOH and dried by passage through H_2SO_4 and Drierite (CaSO_4). Solvents were deoxygenated by sonicating them prior to purging with argon for approximately 30 min. Deoxygenated solvents were used in experiments on oxygen uptake. Anhydrous methanol and anhydrous acetonitrile were dispensed under argon from Sure Seal bottles for the storage of air-sensitive reagents. All other reagents were of the highest grade commercially available, supplied by the Aldrich Chemical Company Inc. and were used without further purification.

2.3. Pyridine-2,6-dicarboxaldehyde

This compound was prepared by the method of Alcock et al. [39]. The crude product was recrystallized from a chloroform/petroleum ether mixture.

2.4. 3,6,9,17,20,23,28,29-
Octaazatricyclo[23.3.1.111,15]tridecanedeca-
1(28),2,9,11,13,15(30),16,23,25(29),26-ene,
(PD)₂(DIEN)₂, **1**

The macrocyclic ligand was prepared as previously described [40]. The crude product was recrystallized from a methanol/acetonitrile mixture. Mp: 279–281°C. $m/e = 405$ (M + H)⁺.

2.5. Oxygenation of the
[Cu(I)₂(PD)₂(DIEN)₂]²⁺ complex, **2**

The Schiff base ligand **1** (0.1779 g) was dissolved in 30 ml of methanol and Cu(CH₃CN)₄PF₆ (0.2286 g) dissolved in 10 ml of acetonitrile was added to the methanolic solution under argon, to give the Cu(I) complex, **2**. Argon was removed by evacuating the system; then the reaction vessel and gas burette were filled with oxygen. Oxygen uptake of the solution was recorded by reading the mercury level on the gas burette while maintaining a pressure of 1 atm. In a separate experiment oxygen uptake was monitored spectroscopically during the formation of the dioxygen adduct **3** and its subsequent degradation. Ultimately a green precipitate **4** formed on evaporating the solvent to approximately 5 ml. The solid was filtered off and recrystallized from a methanol/chloroform mixture. The elemental composition (%) of **4** calculated for C, H and N, based on the formula Cu₂C₂₂H₂₈N₈(OCH₃)(PF₆)₃·CH₃OH is: C, 28.00; H, 3.43; N, 10.88. Observed: C, 28.40; H, 3.49; N, 11.03.

2.6. Analysis of the macrocyclic ligand

The Schiff base ligand **1** was analyzed by the procedure established for (FD)₂(DIEN)₂ [21]. The green copper(II) complex (0.327 g) (**4**) was decomposed with 20 cm³ dilute HCl. The pH of the solution was adjusted to 7 prior to extraction with two 60 ml portions of CHCl₃. On evaporation of the organic solvent ¹H NMR analysis of the solid product showed it to be pyridine-2,6-dicar-

boxaldehyde. ¹H NMR (CDCl₃) δ 8.00–8.25 (m), 10.18 (s).

The acidic aqueous layer was reduced to approximately 1 ml and the residue was dissolved in 75 ml of water. Copper was removed from the aqueous phase with the addition of excess Na₂S (0.2 g) until precipitation was complete. The solution was then filtered through Celite, made alkaline (pH = 12) and extracted with two 50 ml portions of CHCl₃. The organic phase was dried over magnesium sulfate and, on evaporation of the solvent, the residue was identified by ¹H NMR as diethylenetriamine. ¹H NMR CDCl₃ δ 1.2(s), 2.50–2.90(m).

2.7. Preparation of [Cu(II)₂(PD)₂(DIEN)₂]_X₄
complexes

Copper(II) complexes of **1** were prepared by adding either CuCl₂ or Cu(ClO₄)₂·7H₂O to a methanolic solution of the ligand in a 2:1 stoichiometric fashion. When X = ClO₄⁻ a green solid, **5**, is obtained initially. This solid acquires a blue color on prolonged exposure to moisture. The blue color is obtained almost immediately when the synthesis is performed in methanol which has not been dried. The green color persists when dry methanol is used as solvent. The solid was filtered and recrystallized from an acetonitrile/chloroform mixture. The elemental composition (%) of **5** for C, H, and N, based on the formula Cu₂C₂₂H₂₈(ClO₄)₄·2CH₃CN·4H₂O is C, 28.82; H, 3.91; N, 12.93. Observed: C, 28.66; H, 4.06; N, 12.71. When X = Cl⁻ a pale green complex, **6**, was obtained by evaporating the methanol solvent and recrystallizing the crude solid from a methanol/chloroform mixture.

2.8. Spectral and magnetic measurements

For spectral changes of solutions of **2**, monitored by UV-visible spectroscopy, the ligand (0.00457 g) was placed in an argon-flushed reaction cell containing 40 ml of a deoxygenated 3:1 methanol/acetonitrile solution. The compound Cu(CH₃CN)₄PF₆ (0.00909 g) was added to the

cell and the solution was stirred for approximately 10 min in order to facilitate formation of the dinuclear copper(I) complex. The solution was then circulated through a flow cell with a peristaltic pump, the flow cell being placed in the cell compartment of a UV–visible spectrophotometer and thermostated at 25°C. An initial measurement was taken and then the argon in the reaction cell was replaced with oxygen and the gas uptake reaction was followed by changes in the UV–visible spectrum of the solution.

Samples for EPR measurements of copper(II) complexes were prepared as glasses in acetonitrile, dichloromethane or aqueous (pH 9) solution. The solutions were frozen in liquid nitrogen prior to placement in the cavity of the spectrometer. Spectra were recorded at a cavity temperature of 177 K.

¹H NMR measurements in oxygen uptake experiments with the $[\text{Cu}(\text{I})_2(\text{PD})_2(\text{DIEN})_2]^{2+}$ complex were made in 3:1 chloroform-*d*/acetonitrile-*d*₃ on samples which were prepared with the aid of Schlenk line techniques. The sample was then transferred to an argon-flushed 5 mm NMR tube and the initial spectrum was recorded. Argon in the sample tube was removed by an oxygen purge and the time-dependent ¹H NMR spectrum was recorded at a probe temperature of 22°C.

Magnetic susceptibility measurements on **4** and **5** were accomplished by the Evans method in acetonitrile at 295 K [41].

2.9. Molecular modeling

Molecular modeling of the dioxygen adduct **3** was accomplished with the commercially available program SYBYL [42]. For a given set of bond parameters the functioning of this program is such that the geometry around the central metal ion is generated by considering van der Waals repulsive forces between donor atoms instead of force constants and bond angles. The parameters for metal–ligand bond angles were those suggested by Hancock [43]. All other parameters used were those contained in the TRIPOS 5.2 force field in

SYBYL. Initially, the force constants corresponding to torsional strain about the metal–ligand bonds were set at zero [44]. The structure of the macrocyclic complex was first generated by use of the DRAW model building module of SYBYL, then the energy of the system was minimized. Once the initial parameters were set up, the DYNAMICS subroutine was applied to the molecular system in order to force the molecule out of false energy minima. The structure having minimum strain energy was considered to represent the macrocyclic complex.

3. Results and discussion

3.1. Synthesis and characterization of the ligand $(\text{PD})_2(\text{DIEN})_2$

A direct condensation method was used to prepare the ligand. Such a method is well established for amines and aldehydes [21]. Ligand analyses by ¹H and ¹³C NMR spectroscopy indicate that a chloroform solution of the ligand contains a mixture of isomeric species; however, two N–H proton resonances at 4.29 and 4.45 ppm and two azomethine resonances at 7.87 and 8.21 ppm are clearly observed. The ligand was therefore characterized by mass spectrometry and infrared spectroscopy. The FAB-MS (positive ion) spectrum shows a major peak at $m/e = 405$ which corresponds to the $(\text{M} + \text{H})^+$ parent ion of the 2:2 condensation product. No peak ascribable to the 1:1 condensation product was observed around $m/e = 202$. The infrared spectrum does not show any peaks around 1721 cm^{-1} which is characteristic of the carbonyl group of pyridine dicarboxaldehyde; therefore the condensation was considered to be complete. A $\nu(\text{C}=\text{N})$ absorption for the imine group of the Schiff base was observed at 1642 cm^{-1} . In addition, the split pyridine ring $\nu(\text{C}=\text{N})$ absorption was observed at 1588 and 1572 cm^{-1} and the $\nu(\text{C}=\text{C})$ ring vibration was identified at 1444 cm^{-1} . The sharp nature of the N–H stretch at 3257 cm^{-1} indicates a cyclic secondary amine in which there is no hydrogen

bonding. The mass and infrared spectra correspond to what would be expected for a 2:2 macrocycle, **1**.

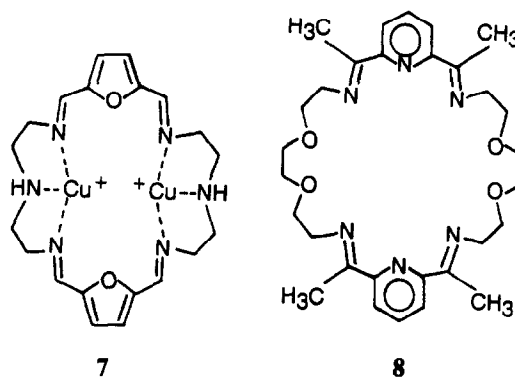
The complex nature of the ^1H NMR spectrum for **1** is attributed to the existence of more than one species in solution. The presence of two clearly observed N–H proton resonances is an indication that there are at least two isomeric forms in chloroform. The ligand contains two secondary amine protons which may undergo an addition reaction with the proximal imino group resulting in formation of an isomer such as that shown in Scheme 1 (b). Similar cyclization isomerizations have been observed in analogous ligand systems [21,45–48]. In fact, an X-ray crystal structure [49] has shown that only the **b** form (Scheme 1) is present in the solid phase in a related ligand where dipropylenetriamine replaces diethylenetriamine. An equilibrium between the **a** and **b** forms is considered to be present in solution.

3.2. The $\text{Cu(I)}_2(\text{PD})_2(\text{DIEN})_2$ complex

The dinuclear copper(I) complex (**2**) was prepared by addition of a colorless acetonitrile solution of $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ or $\text{Cu}(\text{CH}_3\text{CH})_4\text{ClO}_4$ to a methanolic solution of **1** in a stoichiometric manner, resulting in a purple solution. The ^1H NMR and UV–visible spectra of the resulting compound are independent of the source of copper(I). The only differences observed for the infrared spectra are the absorptions associated with counter ions. Although there are expected to be predominantly two isomeric forms of the ligand **1** in solution, the species which reacts with copper(I) is considered to be **a** (Scheme 1). Inspection of CPK molecular models has shown that the **b** form contains a cavity which is too small for the accommodation of two copper(I) ions. Furthermore, should the complex be mononuclear in nature the molecular models have also shown that not all the imine and pyridine nitrogens will be involved in bonding to copper(I). The infrared spectrum of the isolated copper(I) complex did not reveal any C=N or C=N vibrations pertaining to uncoordinated imine or pyridine nitrogen atoms. Therefore it is concluded

that the dicopper(I) complex is of the **a** form of the ligand.

Complex **2**, when measured in a 3:1 methanol/acetonitrile mixture, displays an electronic spectrum having characteristic absorption bands with maxima at 575, 430 and 275 nm, which have molar extinction coefficients around 2370, 3410 and $4220\text{ cm}^{-1}\text{ M}^{-1}$, respectively. The absorption features are unlike those exhibited by similar copper(I) complexes [21,50] which usually show no features in the visible region. In addition to the large values of the molar extinction coefficients, the band widths at 575 and 430 nm are relatively narrow ($\Delta\nu_{1/2} = 70\text{ nm}$ and 50 nm respectively). Such intense charge transfer bands are not apparent in a related complex [37] $[\text{Cu(I)}_2(\text{FD})_2(\text{DIEN})_2]^{2+}$, **7**, in which a furan group replaces the pyridine unit and in the pyridine-containing hexamine polycyclic dicopper(I) complex prepared by Marrs et al. [51], in which case a crystal structure shows that the pyridine nitrogen is not coordinated to copper. In view of the ease of oxidation of copper(I), the relatively narrow band half widths, and the absence of d–d transitions, the origin of the spectrum is believed to arise from charge transfer between copper(I) and the pyridine moiety. Whereas copper(I) complexes are usually featureless in the visible region, a dicopper(I) complex of **8** was found to exhibit two intense absorptions in the visible–near UV region [52].



It is therefore concluded that the observed visible spectrum for **2** is a consequence of coordination of the pyridine moiety. The dinuclear copper(I)

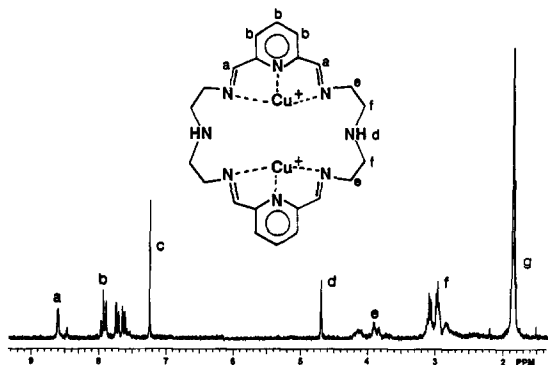


Fig. 1. 200 MHz ^1H NMR spectrum of the $[\text{Cu}(\text{I})_2(\text{PD})_2(\text{DIEN})_2]^{2+}$ complex under argon in CDCl_3 at 22°C .

complex **2** probably has the central metal ions each coordinated to two imine and one pyridyl nitrogen atoms as shown in Fig. 1.

The ^1H NMR spectrum of the complex formed under argon in 3:1 chloroform- d /acetonitrile- d_3 solution is illustrated in Fig. 1. Signals labeled c and g are attributed to the solvent. The signal at 8.60 ppm arises from the Schiff base proton, while d is assigned to the N–H proton of the diethylenetriamine group. Multiplets e are considered to be resonances from methylene protons adjacent to the imine nitrogen and those labeled f are ascribed to methylene protons adjacent to the amine nitrogen. Results of the ^1H NMR spectrum are consistent with retention of the macrocyclic structure in a $\text{CD}_3\text{CN}/\text{CDCl}_3$ mixture and formation of a dinuclear copper(I) complex, **2**. The resolution of resonances e and f provides evidence that an ordered structure, relative to the free ligand, exists in solution. Protons which are adjacent to coordinated nitrogen atoms usually show a downfield shift in resonance relative to the free ligand upon complex formation [53,54]. This coordination-induced effect is most pronounced for the azomethine protons (a, Fig. 1) for which a downfield shift of 0.35 ppm is recorded. Signals arising from aromatic protons are also significantly shifted as well. This may be a consequence of the electronic effects of conjugation of the aromatic ring with the $\text{C}=\text{N}$ linkage. The equivalence of the azomethine protons is also evidence that a dinuclear complex is formed although the weak resonance at 8.45 ppm is probably an indication that a small

amount of the mononuclear complex may be present. Evidence of copper coordination is also provided by the shifts in resonances for the methylene protons of **2**. The small downfield shift of the N–H proton requires special attention. The observed displacement for this resonance is within the range 0.20–0.35 ppm depending on which isomeric form is considered for the free ligand. The small change in resonance is attributed to a rearrangement in conformation of the ligand system brought about by coordination to two copper(I) centers. The hard amine nitrogen atoms are not considered to be involved in direct coordination of the soft copper(I) ion.

3.3. The dioxygen complex, **3**

On oxygenating the system the purple color attributed to the complex **2** changes to a purple brown color, indicating formation of a dioxygen adduct, **3**. This color change occurs over a period of 20 min. Spectral changes accompanying the oxygenation process are such that the maxima at 575 and 430 nm disappear and isosbestic points appear at 260 and 715 nm. An intermediate spectrum consisting of a shoulder at 410 nm and a broad absorption at 590 nm evolves (a, Fig. 2). In an additional experiment, H_2O_2 was added to a methanolic solution of a $[\text{Cu}(\text{II})_2(\text{PD})_2$

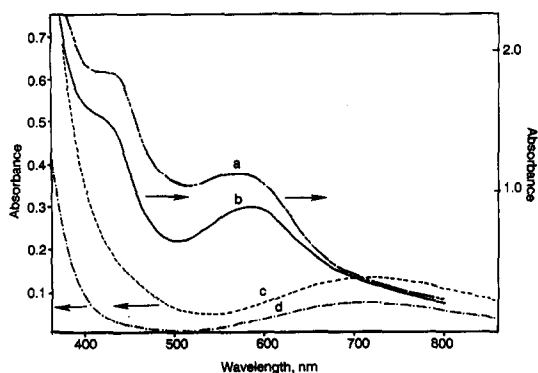


Fig. 2. Electronic spectra of a, ----, dioxygen complex **3** (1.46×10^{-3} M $[\text{Cu}(\text{I})_2(\text{PD})_2(\text{DIEN})_2]^{2+}$ in 3:1 methanol/acetonitrile); b, —, **5** (1.22×10^{-3} M in methanol) + H_2O_2 + triethylamine; c, ···, degradation product of **3** (5.57×10^{-4} M in methanol); d, - · - ·, $[\text{Cu}(\text{II})_2(\text{PD})_2(\text{DIEN})_2]^{4+}$ chloride complex, **6** (1.26×10^{-4} M in methanol).

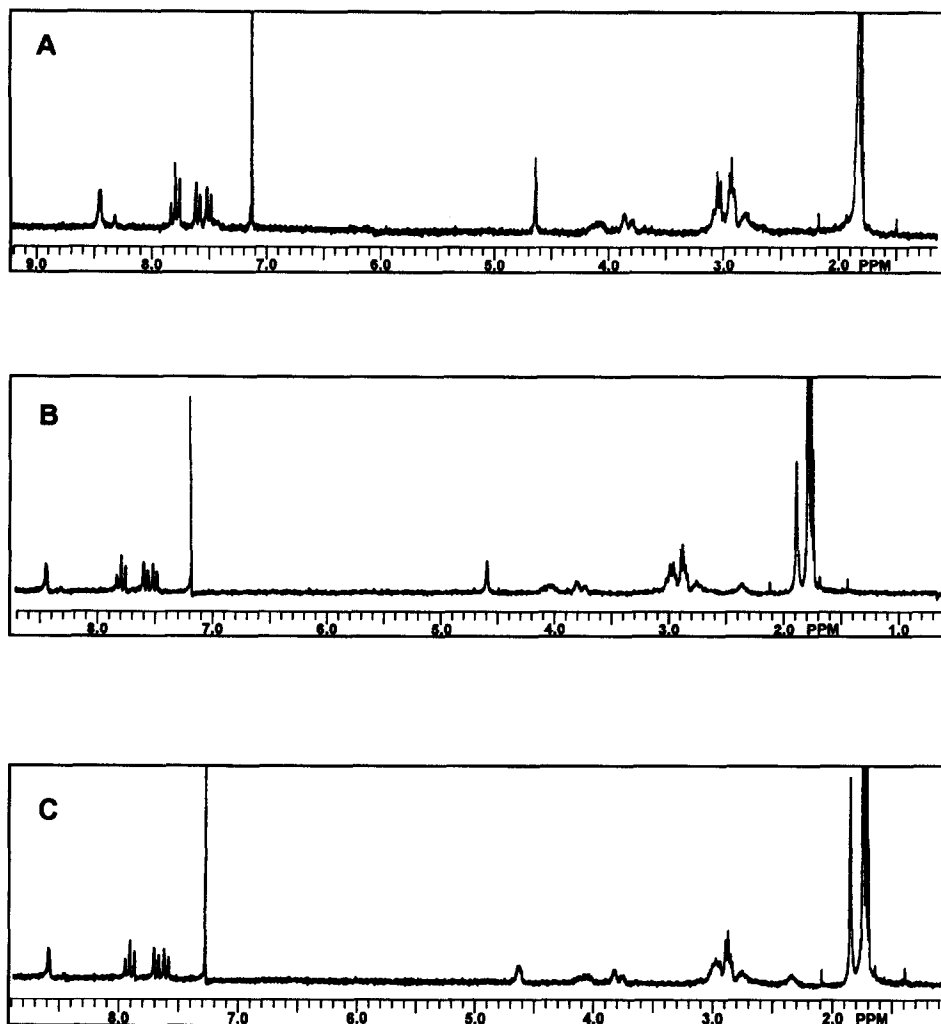


Fig. 3. ^1H NMR spectrum (200 MHz) of Cu(II)-dioxygen complex in 3:1 $\text{CDCl}_3/\text{CD}_3\text{CN}$ (A) 5 min, (B) 30 min, (C) 90 min after treating the solution with oxygen.

$(\text{DIEN})_2]^{4+}$ chloride complex in the presence of triethylamine. The electronic spectrum of the resulting solution (b, Fig. 2) was found to be similar to the spectrum obtained during the oxygenation of **2**.

Changes in the ^1H NMR spectrum which are associated with oxygenation of **2** are shown in Fig. 3. It is noted that even under an atmosphere of dioxygen the recorded signals are reasonably sharp and unshifted. The resonance which is located at 1.90 ppm in the oxygenated solution requires special attention. This signal increased in intensity with time at the expense of the resonances of the methylene and N–H protons. It is

also evident that the imine proton resonance (a, Fig. 1) loses its integrity more rapidly than the aromatic resonances. In other words the paramagnetic center introduced upon oxygen binding interacts with the resonances which are in close proximity. The signal which is located at 1.90 ppm is assigned to the H_2O produced by four-electron reduction of dioxygen. The position of the proton signal for H_2O was confirmed by addition of external water to the solvent system. After approximately 45 min, evidence of paramagnetism appears as is demonstrated by the broadening of signals, especially the N–H peak at 4.62 ppm and the spectrum becomes shifted completely out of

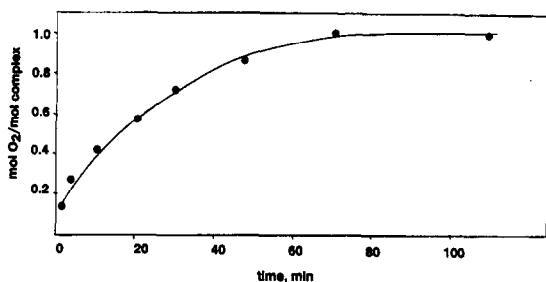


Fig. 4. Oxygen uptake by $[\text{Cu}(\text{I})_2(\text{PD})_2(\text{DIEN})_2]^{2+}$ complex ($1.19 \times 10^{-2} \text{ M}$) at 25°C and $P_{\text{O}_2} = 1.00 \text{ atm}$ in 3:1 methanol/acetonitrile.

the spectral window after approximately 2 h. It is particularly noted that no signal corresponding to H_2O_2 , which should be around 8.4 ppm, was observed during the oxygenation process.

The diamagnetic nature of an oxygenated solution of **2** suggests that a copper(I)–dioxygen adduct is formed in which case antiferromagnetic coupling of the unpaired electrons on copper(II), through the peroxide bridge, brings about a partial quenching of paramagnetism, enabling proton relaxations which permit the recording of a normal ^1H NMR spectrum.

Changes in the electronic absorption and ^1H NMR spectra, described above, show that complex **2** absorbs oxygen at 25.0°C in a 3:1 methanol/acetonitrile solvent mixture. The oxygen absorption curve (Fig. 4) shows a leveling off after approximately 60 min of exposure to dioxygen. The reaction between **2** and dioxygen was also monitored at $25.0 \pm 0.2^\circ\text{C}$ and $P_{\text{O}_2} = 1.0 \text{ atm}$ by following the time dependence of the intensity of the characteristic absorption band with maximum at 575 nm ($\epsilon = 2370 \text{ M}^{-1} \text{ cm}^{-1}$). Assuming that only a very small extent of decomposition occurs initially, the half life of oxygen absorption is estimated as 7 min and the observed rate constant is $1.6 \times 10^{-3} \text{ s}^{-1}$. Subsequent removal of the oxygen atmosphere and/or bubbling argon through the solution for a period of 30 min does not result in regeneration of the copper(I) complex.

The primary steps for formation and degradation of the dioxygen adduct are illustrated in Scheme 2. The oxygen uptake curve (Fig. 4), absorbance spectra (Fig. 1) and the time evolution

of the ^1H NMR spectrum of an oxygenated solution of **2** (Fig. 3) support the presence of a peroxo-bridged dioxygen adduct **3**. Oxygen uptake data, when corrected for solution saturation, show that one mole of dioxygen adduct is formed per mole of complex. The color change from purple to purple–brown and the accompanying appearance of isosbestic points which develop at 715 and 270 nm, indicate that the only two species in solution during the initial part of the oxygen uptake process are the copper(I) complex **2** and its oxygenated form. The spectral characteristics of the intermediate spectrum (a, Fig. 2) bear a close resemblance to a solution of **6** in the presence of H_2O_2 and triethylamine, in which circumstances a peroxo adduct is expected. From the similarities in spectral features between **3** and $\text{6} + \text{H}_2\text{O}_2$ it is reasonable to conclude that the intermediate spectrum pertains to a dioxygen adduct of **2**. The positions of the absorption maxima for the proposed copper(I)–dioxygen adduct are similar to those of a dinuclear macrocyclic dioxygen adduct reported by Ngwenya et al. [21], and also the dinuclear functional models investigated by Karlin [14,28,30] and Kitajima [15]; however the intensity relation is somewhat unexpected for a copper(II)–peroxo species. The absorption in the vicinity of 340–360 nm is usually ten to twenty times more intense than the low energy band, a feature which is not observed in the electronic absorption spectrum of **3**. The differences in position and intensity of absorption maxima may reflect differences in dioxygen binding and ligand coordination.

Molecular modelling of the dioxygen complex. Although endeavours for crystallizing the dioxygen adduct of **2** for X-ray diffraction studies were fruitless, it was expected that a reasonable idea of its structure could be obtained from molecular modeling. For the SYBYL-generated structure (Fig. 5) reasonable torsion strain values were obtained for typical Cu–N and Cu–O bond lengths even though all nitrogen atoms are considered to be involved in bonding. A five coordinate species is suggested here since the metal ions are no longer copper(I) centers; therefore an expansion in coor-

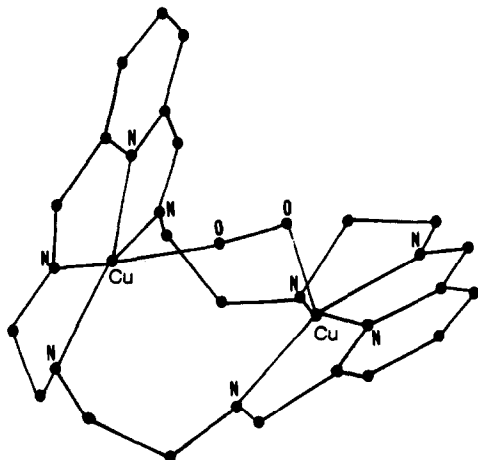


Fig. 5. Structure of the peroxo-bridged copper dioxygen complex deduced with the aid of the molecular modeling program SYBYL.

dination number is possible. Fig. 5 shows that conformational adjustments for **2** are required prior to accommodation of dioxygen. The energy demands on conformational rearrangement are considered to be reasonable in view of the flexible nature of the ligand system. Other structures were also investigated by molecular modeling and were found to have higher strain energy than the structure presented in and were therefore discarded.

3.4. The $(\text{Cu(II)})_2(\text{PD})_2(\text{DIEN})_2\text{PF}_6$ degradation product

Copper dioxygen complexes are found to be unstable at room temperature and usually undergo thermal degradation to copper(II) systems [11–13,21,28,33]. The spectrum of the dioxygen adduct **3** decays with a half life of approximately 100 min at 25.0°C. The ultimate degradation product **4** was obtained as a green solution which displays an electronic absorption spectrum with a broad weak band centered on 710 nm (Fig. 2) and a shoulder at 260 nm. On evaporating the solvent, a green solid, **4**, was obtained.

A separate experiment was performed in which, during the oxygenating process samples were removed for detection of H_2O_2 with starch iodide paper. No H_2O_2 was detected at any time during the $\text{Cu(I)} \rightarrow \text{Cu(II)}$ air oxidation reaction. As time progresses and the dioxygen adduct decom-

poses, paramagnetism becomes evident by the broadening of signals (Fig. 3c). Signals ascribable to a copper(II) complex are expected to be broadened appreciably because of the paramagnetic nature of the metal ion.

Thermogravimetric analysis of the green complex **4** shows weight loss at 75.9°C prior to decomposition at 249.0°C. The weight loss at 75.9°C is related to removal of lattice water from the sample. One transition is observed for **5** at 96.0°C. The green product **4** was obtained as a methanol solvate, as is evident from infrared spectroscopic analysis, and analyzed according to the formula $[\text{Cu}_2(\text{PD})_2(\text{DIEN})_2\text{OCH}_3](\text{PF}_6)_3 \cdot \text{CH}_3\text{OH}$.

Mass spectral analysis of **4** (when prepared with $\text{Cu}(\text{CH}_3\text{CN})_4\text{ClO}_4$, Table 1) shows a major peak at $m/e = 468$ mass units, which corresponds to the mononuclear copper(I) complex of $(\text{PD})_2(\text{DIEN})_2$. This assignment is supported by the isotope ratio data (theoretically 1:2.3 $^{65}\text{Cu}:^{63}\text{Cu}$) which is presented in Table 1. Another major peak which appears at 531 mass units is assigned to the $[\text{M}_2\text{LH}]$ dinuclear complex. The fact that the isotopic distribution of the peaks around 531 is not in agreement with the natural distribution is probably due to the presence of species, without copper, which possess masses very close to 531 mass units. A weak isotopic cluster is also observed around $m/e = 630$ corresponding to the $[\text{M}_2\text{LClO}_4]$ unit.

An acetonitrile solution of **4** exhibits a weak absorption around 700 nm which is similar to those of copper(II) complexes of $(\text{PD})_2(\text{DIEN})_2$ (**5** and **6**) which have low-intensity absorptions in the same wavelength region. The broad absorptions in this region are indications of a square

Table 1
Comparison of calculated and observed intensities for parts of the FAB mass spectrum of $[\text{Cu}_2(\text{PD})_2(\text{DIEN})_2(\text{OCH}_3)](\text{ClO}_4)_3$

	CuL		Cu ₂ L		
observed m/e	467	469	531	533	535
ratio	1	2.5	1	6.4	23
calculated m/e	467	469	531	533	535
ratio	1	2.3	1	4.4	4.9

Table 2
EPR, magnetic conductance, electronic absorption and infrared absorption data for dicopper(II) complexes

Complex	g_{\parallel}	g_{\perp}	μ_{eff} (BM) ^a	Λ ($\text{S cm}^2 \text{ mol}^{-1}$)	λ_{max} (nm)	$\nu(\text{N-H})$ (cm^{-1})	$\nu(\text{C=N})$ (cm^{-1})	$\nu(\text{C=N})(\text{py})$ (cm^{-1})
$[\text{Cu}(\text{II})_2(\text{PD})_2(\text{DIEN})]^{4+}$ (degradation product)	≈ 2.18	2.076	1.79	331	260(sh), 710	3250	1630	1598
$[\text{Cu}(\text{II})_2(\text{PD})_2(\text{DIEN})_2]^{4+}$ (direct preparation)	≈ 2.14	2.085	1.84	700	285, 640	3219	1637	1586

^a Magnetic moment per copper ion.

planar or tetragonal site for copper(I) in the particular complex. Conductivity data for **4** are consistent with that of a 3:1 electrolyte (Table 2). Therefore, in conjunction with results of elemental analysis, **4** is formulated as a dicopper(II) complex of $(\text{PD})_2(\text{DIEN})_2$ containing a coordinated methoxy unit. A methoxo species produced by irreversible degradation of a copper(I)–dioxygen complex of **7** has been previously encountered [21] and, in view of the absence of H_2O_2 , a four-electron reduction to water is proposed as the reaction pathway.

The fact that complex **4**, when initially precipitated, is hydrated explains why the infrared spectrum in the 3500 cm^{-1} region is complicated by a broad, intense $\nu(\text{O-H})$ absorption. A shoulder on the high energy side of the $\nu(\text{O-H})$ band is observed around 3630 cm^{-1} and is assigned to the O–H stretch of lattice water. The assignment of the absorption at 3630 cm^{-1} is supported by the presence of a shoulder to the band at 1630 cm^{-1} , which is the absorption from a $\nu(\text{O-H})$ bending mode of lattice water. The infrared spectrum for **4** also displays a broad band at 3250 cm^{-1} which arises from a symmetric $\nu(\text{N-H})$ stretch. The magnitude of the half width suggests that this nitrogen atom is bonded to copper. Within the region $1720\text{--}1590 \text{ cm}^{-1}$ the spectrum displays strong absorptions at 1630 and 1598 cm^{-1} , which are assigned to the $\nu(\text{C=N})$ imine and $\nu(\text{C=N})$ pyridine ring functions respectively. Absorptions arising from PF_6^- are located at 850 and 575 cm^{-1} . When complex **4** is dried at 80°C prior to recording the infrared absorption spectrum, the resulting disappearance of shoulders at 3630 and 1630 cm^{-1}

is interpreted as loss of lattice water from the solid complex. An O–H stretch now observed at 3443 cm^{-1} is due to the presence of lattice methanol. When the $[\text{Cu}(\text{II})_2(\text{PD})_2(\text{DIEN})_2]^{4+}$ complex was prepared with $\text{Cu}(\text{CH}_3\text{CN})_4\text{ClO}_4$ and dioxygen, it was found to have an infrared spectrum with two split perchlorate absorptions at 626 and 1028 cm^{-1} , indicating that an anion is at least weakly coordinated.

Two copper(II) complexes were prepared directly from a copper(II) source and **1** in order to assist in characterizing the degradation product **4**. A perchlorate complex of $[\text{Cu}(\text{II})_2(\text{PD})_2(\text{DIEN})_2]^{4+}$, **5**, gives a blue solution, in methanol, which displays an absorption spectrum consisting of a broad weak absorption at 640 nm and a narrow band at 285 nm . In contrast, the electronic absorption spectrum of a green solution of the $[\text{Cu}(\text{II})_2(\text{PD})_2(\text{DIEN})_2]^{4+}$ chloride complex, **6**, contains a weak maximum at 720 nm when recorded in methanol. Addition of water to a methanolic solution of **6** results in a blue solution which displays the electronic absorption characteristics of **5**. An acetonitrile solution of **4** exhibits a weak absorption around 700 nm which is similar to those of copper(II) complexes of $(\text{PD})_2(\text{DIEN})_2$ (**5** and **6**) which have low-intensity absorptions in the same wavelength region. These electronic spectra all indicate a square planar or tetragonal site for copper(II) in the particular complex.

The $[\text{Cu}(\text{II})_2(\text{PD})(\text{DIEN})_2]^{4+}$ complex, **5**, exhibits a very similar IR spectrum to that of **4** with only a slight variation (Table 2). The complexes **5** and **6** display almost identical IR spectra, the only difference being attributed to the different

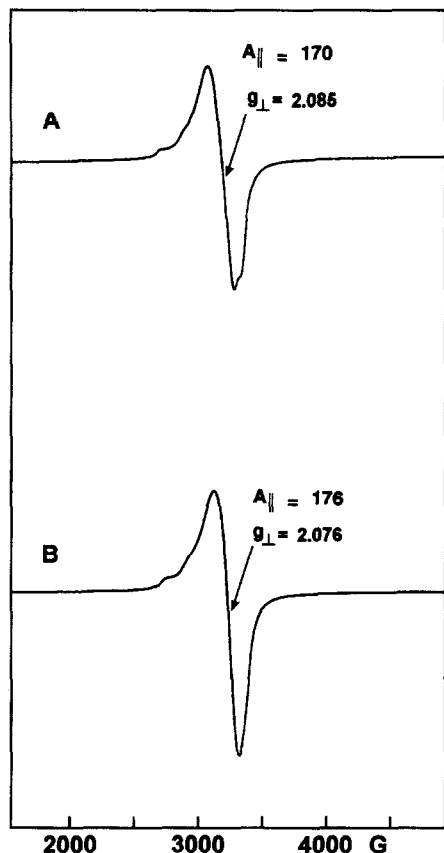


Fig. 6. EPR spectrum of (a) $\text{Cu(II)}_2(\text{PD})_2(\text{DIEN})_2\text{ClO}_4$ complex and (b) $\text{Cu(II)}_2(\text{PD})_2(\text{DIEN})_2$ degradation product in CH_3CN at 177 K.

counter ions. The O–H absorption is observed as a broad band at 3450 cm^{-1} and also a broad N–H absorption occurs at 3219 cm^{-1} . The $\nu(\text{C}=\text{N})$ stretch is located at 1637 cm^{-1} and is of medium intensity while the pyridine ring $\nu(\text{C}=\text{N})$ band occurs at 1586 cm^{-1} . Perchlorate absorptions are observed as bands at 1110 and 640 cm^{-1} both of which are split.

The similarities in the infrared and electronic absorption spectra for **4** and **5** demonstrate that the degradation product of the dioxygen complex **3** may be described as a dicopper(II) complex of the ligand **2**. Structural similarities between **4** and **5** are also supported by the similarities in their g_{\perp} values and magnetic moments which are also in close range (Table 2 and Fig. 6). In addition the EPR data strongly suggests that there are no bridging entities in each of the two complexes. Since a

chemical analysis of **4** does not show any modification to the amine and aldehydic functions of the ligand the important conclusion made here from the spectroscopic, magnetic and chemical analysis information is that the ligand unit of **2** was preserved over the $\text{Cu}_2^{\text{I}}\text{L}^{2+} \rightarrow \text{Cu}_2^{\text{II}}\text{L}^{4+}$ reaction.

3.5. EPR spectra of copper(II) complexes

The EPR spectra of complexes **4** and **5** are shown in Fig. 6. The X-band absorption shows an axial type signal with the g_{\parallel} values occurring higher than those for g_{\perp} . Both g_{\parallel} and g_{\perp} values are within the range expected for square pyramidal or tetragonal copper(II) complexes. The hyperfine splitting is apparent on the g_{\parallel} signal; however it is largely overshadowed by the more intense g_{\perp} signal. Neither spectrum shows the singlet–triplet forbidden $m = -1$ to $m = +1$ ($\Delta M_s = 2$) transition which is usually observed in the $g = 4$ region for copper(II) dimers.

Whereas electronic absorption data suggest tetragonal sites for the copper(II) ions, elemental analysis indicates that there is methoxy coordination in the complex. The nature of methoxy coordination is suggested by the EPR spectrum of **4** in the $g = 2$ region. The spectrum is characterized by an axial type structure containing hyperfine splitting, resulting from coupling of electronic and nuclear spins, which is typical of copper(II) complexes. The fact that $g_{\parallel} > g_{\perp}$ is consistent with a $d_{x^2-y^2}$ ground state for what is probably a distorted square pyramidal disposition of atoms about the central copper ion [55]. Since there are no lines appearing in the high field region of the g_{\perp} signal, the g_{\parallel} signal is interpreted as the first two lines of a four-line pattern. The absence of a singlet–triplet transition means that spin–spin coupling is not present to an appreciable extent; therefore there is a strong likelihood that there are no bridging ligands in the copper(II) complex **4**. Furthermore, the rather large A_{\parallel} value is a definite sign of the absence of a spin exchange interaction which is facilitated by bridging moieties. The values obtained for A_{\parallel} lie well outside of the range

typically observed for strongly coupled dimeric copper complexes [56] and the large value of the magnetic moment of the complex (Table 2) precludes magnetic superexchange, providing further evidence of the absence of bridging ligands. The small separation between the g_{\parallel} and the g_{\perp} lines indicates that the unpaired electron on copper may be significantly delocalized into the ligand system. A pathway for electron delocalization is provided by the pyridine entity directly linked to the copper ion by the nitrogen atom through overlap of d orbitals of copper with the π system of pyridine. The above interpretation of the structure of **4** is substantiated by the EPR spectrum of the $[\text{Cu}(\text{II})-(\text{PD})_2(\text{DIEN})_2]^{4+}$ complex **5** which contains similar parameters (Fig. 6 and Table 2).

EPR and electronic spectral parameters of **4** may be conveniently compared with those for the dimeric halide-bridged complexes of Brown et al. [57] and Hoffmann et al. [58]. In those cases the complexes contain weakly bridging halide ions which are dismantled in the solution phase. Their EPR spectra are characterized by relatively well separated g_{\parallel} and g_{\perp} signals and A_{\parallel} values of 168 and 194 G which are unlike those of complexes for which there is a significant bridging interaction. The g_{\parallel} signal also shows a four line pattern, which is a feature of the non-interacting and complexed copper ion. Similarities in the EPR spectra between **4** and those of Brown et al. [57] strengthen the argument that the copper(II) ions are largely isolated leading to the conclusion that there are no bridges in the complex.

Spectroscopic and magnetic susceptibility data indicate that **4** may be described as a dinuclear copper(II) complex in which each cation is bonded to two imine, one pyridine, and one secondary amino nitrogen in a distorted square pyramidal arrangement. There is axial coordination of a methoxy unit which does not function as a bridging moiety in the solution phase. When perchlorate is the anion, one unit is coordinated probably in an axial or bridging manner. A structurally characterized copper(II) complex of a macrocyclic ligand formed by 2:2 condensation of 2,6-diacetylpyridine and dipropylenetriamine

has been reported by Drew et al. [59]. This system differs from **4** in that there is axial coordination of thiocyanate and an extra $-\text{CH}_2-$ in the alkane chain of the ligand. It is proposed that the structure of **4** is similar to the complex prepared by Drew et al. [59] although in the present case, the shorter bridging groups may bring about a higher degree of rigidity in the overall structure.

4. Conclusion

A dinuclear copper(I) complex of the ligand $(\text{PD})_2(\text{DIPN})_2$ has been prepared and the complex was found to react with dioxygen forming an oxygen adduct. Evidence of formation of the dioxygen complex is provided by (a) the characteristic absorptions at 410 and 590 nm in the electron absorption spectrum, (b) the similarity between this spectrum and that resulting from a solution of the $[\text{Cu}_2^{\text{II}}(\text{PD})_2(\text{DIEN})_2]^{4+}$ complex in the presence of H_2O_2 and triethylamine and (c) the diamagnetic nature of an oxygenated solution of $[\text{Cu}_2^{\text{I}}(\text{PD})_2(\text{DIEN})_2]^{2+}$ within the time period for the formation of the proposed dioxygen adduct. The dioxygen complex of $[\text{Cu}_2^{\text{I}}(\text{PD})_2(\text{DIEN})_2]^{2+}$ was found to be thermally unstable, degrading with a half-life of about 100 min to a dinuclear copper(II) complex of the ligand $(\text{PD})_2(\text{DIEN})_2$, with a metal-coordinated methoxy group. The mechanism of degradation seems to involve the four-electron reduction of dioxygen to water. Electronic absorption and EPR data demonstrate that copper(II), in the degradation product, is in either a tetragonal or square planar environment and the methoxy moiety does not act as a bridging entity.

In additional experiments the oxygenated form of the $[\text{Cu}_2^{\text{I}}(\text{PD})_2(\text{DIEN})_2]^{2+}$ complex was found to oxidize phenols and catechols catalytically. This is reported in a subsequent paper.

Acknowledgements

This research was supported by the Office of Naval Research. The authors would like to

acknowledge assistance given by Paul Lindahl in recording and interpreting EPR data.

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