Oxygenation of a Copper(I) Complex of a Binucleating Macrocyclic Schiff Base Ligand Derived from 1,4,7-Triazaheptane and Furan-2,5-dicarboxaldehyde

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The ligand 3,6,9,16,19,22-hexaazatricyclo[22.2.1.1^{12,14}]octacosa-1(26),2,9,11,13,15,22,24-octaene ((FD)$_2$(DIEN)$_2$) was prepared from 1,4,7-triazaheptane and furan-2,5-dicarboxaldehyde. A dinuclear copper(I) complex is formed by reacting (FD)$_2$(DIEN)$_2$ with 2 equiv of Cu(CH$_3$CN)$_4$(ClO$_4$) in medium formed by a 1:3 mixture of acetonitrile and methanol. The oxygenation reaction of the dinuclear Cu(I) complex was followed spectrophotometrically and by oxygen absorption at pH 9.0 and 5 °C. The crystal structure of the green degradation product formed from the dioxygen complex was determined by X-ray analysis. The results reveal that the copper centers are bridged by hydroxo and methoxo groups. Crystals are monoclinic, space group *C2/c*, with *a* = 22.248 (8) Å, *b* = 10.194 (4) Å, *c* = 13.986 (10) Å, *β* = 110.48 (4)°, and *Z* = 4. The Cu···Cu distance is 2.958 (3) Å. An unusual coordination mode, which is distorted square planar, is found around each copper atom. The formation of a binuclear Cu(I) dioxygen complex within the macrocycle and the lack of a oxygen insertion reaction are explained on the basis of the bridging oxygen-containing furan groups in place of an aromatic *o*-xylyl group.

Introduction

Copper(I) complexes are of relevance because of their occurrence in natural systems and, in particular, because of their biological function in proteins.[1] As a result, binuclear copper proteins such as hemocyanin, which serves as an oxygen carrier in molluscs and anthropods,[2] and tyrosinase[3] have attracted a great deal of interest on the part of chemists and biochemists alike, as each group tries to understand the coordination or binding behavior of copper and dioxygen in these systems. As a consequence, many synthetic models of these naturally occurring proteins have been reported.[4,5] Thus far, much of the most promising research undertaken has placed emphasis on the use of acyclic or open-chain ligands as potential models. For example, Karlin et al. has used open-chain ligands with alkylpyridyl and phenyl groups for modeling tyrosinase and hemocyanin.[6,7] In our endeavor to develop suitable synthetic models that elucidate the active site of oxyhemocyanin and tyrosinase, we have concentrated on the use of macrocyclic ligands, because of their relatively less flexible and more highly preorganized nature, which we anticipate to be well suited for holding copper(I) ions at appropriate positions for promoting reversible oxygen binding ability in solution.[8] A typical example is that of our recently published work[9] whereby a dinuclear Cu(I) complex of a macrocyclic ligand, MX$_2$(DIEN)$_2$ (L$_1$), was investigated as a model for tyrosinase. The complex was found to bind molecular oxygen to form the corresponding dinuclear Cu(II) complex and also resulted in the hydroxylation of the para position of one of the aromatic rings of the ligand. In this work, we report the synthesis of a macrocyclic binucleating Schiff-base ligand, (FD)$_2$(DIEN)$_2$ (L$_2$), which contains two furan bridge moieties and two terdentate bis(imine) nitrogen sites. The oxygenation of the Cu(I) complex of this ligand in the absence of an endogeneous bridge or oxidizable substrate is also reported. The structural differences between (FD)$_2$(DIEN)$_2$ (L$_2$) and MX$_2$(DIEN)$_2$ (L$_1$) lie in the fact that the phenyl rings found in the latter have been replaced by furan rings in the former, thus

removing the possibility of aromatic hydroxylation.

Experimental Section

Instrumentation. The ligand and metal complex were characterized by standard techniques for compounds, namely, melting-point determination, infrared spectroscopy, nuclear magnetic resonance spectroscopy, and microanalysis for carbon, hydrogen, and nitrogen. Melting point determinations were performed on a Fisher-Johns melting-point apparatus. Infrared spectra were recorded on an IBM IR/44 Version 1.0 spectrometer. The oxygen absorption measurements were carried out as previously described.[10] Solid samples were used as KBr pellets. The NMR spectra were recorded with a Varian XL 200 spectrometer. Elemental analysis for carbon, hydrogen, and nitrogen was carried out by Galbraith Laboratories, Inc., Knoxville, TN. UV-vis spectrophotometric measurements were performed with a Perkin-Elmer Model 553 fast scan UV-vis spectrophotometer.

Materials. All reagents and chemicals were of highest grade commercial quality and were used without further purification.

Furan-2,5-dicarboxaldehyde (1). Initially, one of the precursors, Furan-2,5-dicarboxaldehyde, was prepared by modifying an established method.[11,12] Furan-2,5-dimethanol (4.00 g) was dissolved in CHCl$_3$ (400 cm^3) in a 1000 cm^3 round bottomed flask. After complete dissolution, 50 g of molecular sieves (3 Å) was added. Thereafter 60 g of activated MnO$_2$ was introduced followed by the addition of more CHCl$_3$ (300 cm^3). The reaction mixture was left to stir at room temperature for 18 h and filtered, the residue washed with more CHCl$_3$, and the volume of solvent reduced to about one-third its original. The solvent was again filtered through a sintered glass funnel of very fine porosity to remove some traces of the activated charcoal. The yellow green solution that resulted was then evaporated to complete dryness. Recrystallization was carried out with a mixture of petroleum ether and chloroform, resulting in a creamy, fluffy solid (1.69 g, yield = 42.0%). Mp: 109-110 °C. ^{1}H NMR (CDCl$_3$): 7.28 ppm (2 H, singlet, C—C*H*=O); 9.79 ppm (2 H, singlet, C=C*H*).

3,6,9,16,19,22-Hexaazatricyclo[22.2.1.1^{12,13}]octacosa-1(26),2,9,11,13,15,22,24-octaene, (FD)$_2$(DIEN)$_2$ (2). Exactly 1.075 g (10.4 mmol) of DIEN (diethylenetriamine) was dissolved in 400 cm^3 of pure acetonitrile, in a 1000 cm^3 round-bottomed flask. An equivalent amount of furan-2,5-dicarboxaldehyde (1.196 g, 9.64 mmol) was dissolved separately in 250 cm^3 of acetonitrile. The latter was then added dropwise to the stirred amine solution over a period of 3 h, during which the color of the solution changed from clear to yellow. The drop rate was continuously monitored (one drop per 2–3 s). The reaction mixture was stirred for 12 h upon which a creamy precipitate was formed. Thereafter the creamy product was filtered, weighed (1.07 g, 53.7% yield) and then recrystallized from a CHCl$_3$/MeCN mixture. The ^{1}H NMR spectrum of the product was complex indicating the presence of an isomeric mixture in solution.

Characterization of the product was as follows. Mp: 183-185 °C. Anal. Calcd for C, H and N based on the formula C$_{20}$H$_{26}$N$_6$O$_2$: C, 62.81; H, 6.85; N, 21.97. Found: C, 62.60; H, 6.73; N, 21.88.

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Oxygenation of the Copper(I) Complex of (FD)₂(DIEN)₂. The Schiff base $(FD)_2(DIEN)_2$ (0.65 g) was dissolved in 50 cm³ CH_2Cl_2. The $Cu^I(MeCN)_4(ClO_4)$ complex (0.38 g), prepared as previously reported,[13] in 20 cm³ of MeCN was then added under an inert argon atmosphere, thus forming a solution having a dark orange color. The solution was thereafter exposed to molecular oxygen for an hour, at ambient temperature, resulting in the precipitation of a green solid. The solvent was removed, and the green residue was recrystallized from MeCN and CH_2Cl_2. The recrystallized product weighted 0.215 g (92%). Characterization of the green product was as follows. The IR absorption bands of the green complex were identified as follows: A sharp peak of medium intensity in the region of 3300 cm⁻¹ is found, which is characteristic of the N–H stretch. At 2916 cm⁻¹, a CH– stretch band is identified, and at 2795 cm⁻¹ a sharp peak of medium intensity is identified as the ⁻OMe stretch band. A medium to strong band at 1643 cm⁻¹ is ascribed to (C=N) vibration. A very strong and broad band about 1100 cm⁻¹ is indicative of the uncoordinated perchlorate ion, and further evidence of the presence of this ion is provided by appearance of a peak of weaker intensity around 600 cm⁻¹. UV–vis spectrophotometry: A very strong band in the UV region at 360 nm and a broad band of weaker intensity about 622 nm were found. Mp: >190 °C.

Analysis of the Macrocyclic Ligand. The green product was treated with concentrated HCl (20 cm³, ca. 10 M) and water (20 cm³) to give an intense yellow-green solution. The latter was transferred to a 100 cm³ separatory funnel and extracted with three 60 cm³ portions of CHCl₃. The combined extracts were evaporated to dryness, weighed (0.04 g, ~20%) and analyzed by proton NMR with TMS as an internal reference standard. The clean proton NMR spectrum recorded was identified as that of furan-2,5-dicarboxaldehyde, as characterized by the two singlet peaks positioned at 7.28 and 9.8 ppm, respectively.

The acidic aqueous layer was transferred to a 250 cm³ round-bottom flask, and the volume was reduced to near dryness. The residue was then dissolved in 150 cm³ water and excess Na_2S (6.00 grams) carefully added, which resulted in the precipitation of a black solid (CuS). The solution was stirred at room temperature for an hour and then allowed to stand in the fume hood for 15 h to complete the precipitation and to allow the precipitate to consolidate and settle out of solution. The solution was then filtered and further purified by the use of charcoal and filtration through Celite. The clean solution thereafter was made basic to about pH 10 and extracted with two 50 cm³ portions of CHCl₃. The chloroform extracts were combined and dried over anhydrous $MgSO_4$ for an hour. This was followed by filtration and removal of solvent (CHCl₃). The residue was identified as the starting material, diethylenetriamine with 92.0% recovery.

X-ray Crystal Structure Analysis of $[Cu_2(DF)_2(DIEN)_2)(OH)-(OMe)](ClO_4)_2$: Crystals suitable for X-ray diffraction were prepared as described above. A green plate crystal with dimensions of 0.10 × 0.26 × 0.28 mm was used for the X-ray analysis. The diffraction intensities were collected at room temperature on a Nicolet R3m/V X-ray diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The cell dimensions were calculated from the least-squares fitting of the setting angles ($2\theta_{av}$ = 19.7°) for 25 reflections. The intensity data were corrected for Lorentz, polarization, and absorption effects.

Crystal data: $C_{21}H_{30}N_6Cu_2Cl_2O_{12}$, mol wt = 756.49, monoclinic, space group $C2/c$, a = 22.248 (8) Å, b = 10.194 (4) Å, c = 13.986 (10) Å, β = 110.48 (4)°, V = 2972 (3) Å³, Z = 4, D_c = 1.691 g cm⁻³, μ = 1.683 mm⁻¹, F(000) = 1544, θ–2θ range 4.0–50.0°, scan type θ–2θ, scan speed variable (2.00–15.00° min⁻¹), scan range 1.60° plus Kα separation, $-26 \leq h \leq 24$, $0 \leq k \leq 12$, $0 \leq l \leq 16$. A total of 2915 reflections were collected, of which 2634 (R_{int} = 1.92%) were considered unique and 1636 were considered to be significant ($I > 2.0\sigma(I)$).

The structure was solved by direct methods and refined by full-matrix least-squares methods. All the non-hydrogen atoms of the cation were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined with common isotropic thermal parameters fixed at 0.08 Å². The bridging atoms in the cationic structure were found to fill their respective sites in the unique volume of the unit cell and were refined as follows. The O(2), O(3), and C(12) atoms were placed at special positions and all given a site occupancy factor of 0.50. The hydrogen atoms bonded to C(12) (H(12), H(13), and H(14)) were all assigned a common site occupancy factor of 0.50 at a fixed position and refined as with other hydrogen atoms. For the perchlorate anions which are disordered, the positions of each of the following distinct pairs of oxygen atoms, O(4) and O(4'), O(5) and O(5'), O(6) and O(6'), and O(7) and O(7'), were assigned site occupancy factors of 0.65 and 0.35, respectively, and refined isotropically. The refinement converged to final residuals R and R_w of
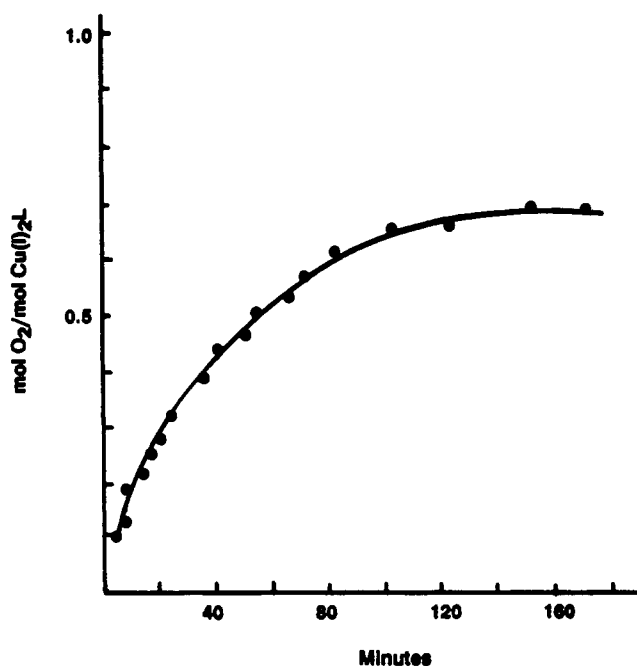

Figure 1. Oxygen absorption by Cu(I)–(FD)₂(DIEN)₂ complex (1.8 × 10⁻³ M) at 25 °C. P_{O_2} = 153 mm; mol of O₂/mol of Cu(I)₂L is plotted vs minutes; $t_{1/2}$ = 57 min.

0.086 and 0.074 respectively with weights based on counting statistics.

Results

Synthesis and Characterization of the Ligands. The preparation of the Schiff-base ligand was carried out by the use of a well-established direct condensation method of amines and aldehydes.[14,15] The reaction, which was quite facile and quantitative, resulted in a white product that was purified by recrystallization. Analysis of the ligand by proton NMR and carbon-13 NMR in CDCl₃ revealed complex spectra, indicating the presence of a mixture of components (see below).

Oxygenation and Spectral Measurements. The binuclear Cu-(I)–(FD)₂(DIEN)₂ complex absorbs oxygen from air at 5 °C at pH 9.0 in the presence of a borax buffer. The oxygen absorption curve given in Figure 1 shows a rapid rate of oxygen absorption at the beginning followed by slower and slower oxygen uptake as the degradation starts to occur, which results in a leveling off of the oxygen uptake at about 150 min. The half-life of oxygen uptake is estimated at about 50 min on the basis of the fact that not much degradation reaction occurs initially. The color changes that were observed are indicated below. The final solution obtained had a pale green color characteristic of the dibridged binuclear copper(II) macrocyclic complex.

The spectral measurements of complexes in solution to monitor oxygenation behavior were carried out at 5 °C in a 3:1 methanol–acetonitrile medium. At room temperature, the reaction rate was found to be quite rapid as witnessed from the shorter life spans of the spectral changes. At 5.0 °C the spectral changes were monitored over a period of 45–60 min. Due to the limitations resulting from the very strong background absorption, the most intense peak, which occurs near the UV region, around 360 nm, as a shoulder, could not be measured accurately. Nevertheless, the spectral data from the other recorded peaks are sufficient to allow reliable observations and comments. Prior to oxygenation, the yellow-orange Cu(I)–(FD)₂(DIEN)₂ complex displays no spectral bands in the visible region of the spectrum except for one intense peak around 330–340 nm, in the UV region. On oxygenation, a change in the color of the solution to red-brown occurs. The UV–vis spectrum of this solution shows that, besides the

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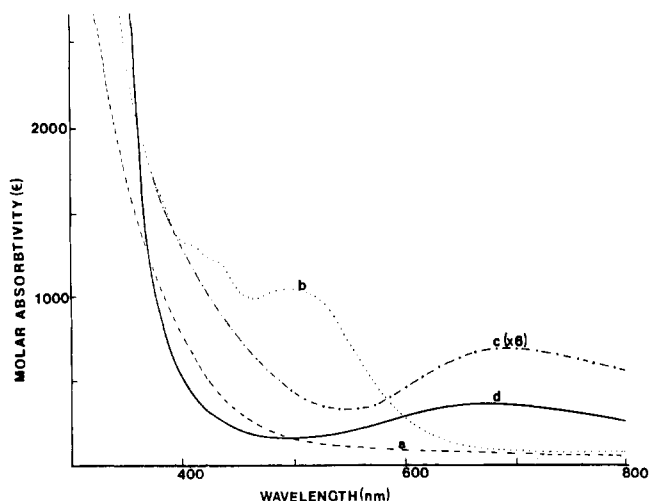
Figure 2. Absorption spectra of the copper–(FD)₂(DIEN)₂ complexes in 1:3 acetonitrile–methanol solution: (a, – –) 1.84 × 10⁻⁴ M Cu(I) complex of (FD)₂(DIEN)₂ prior to oxygenation; (b, ⋯) system a during oxygenation; (c, – · –) the irreversible degradation product of b, 1.05 × 10⁻³ M; and (d, —) the Cu(II) complex of FD₂(DIEN)₂, 1.84 × 10⁻⁴ M.
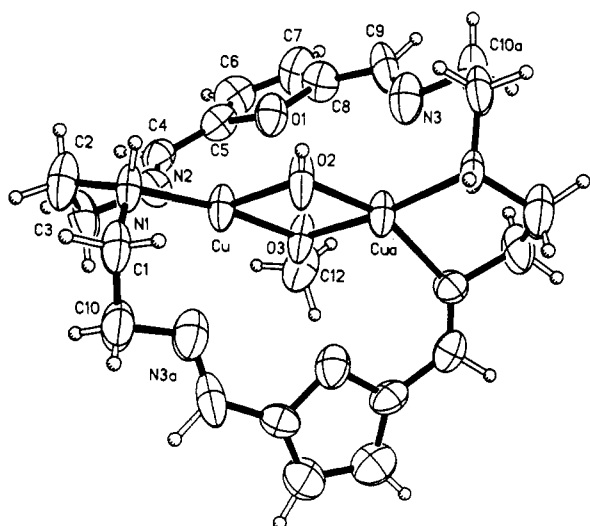

Figure 3. Cationic structure of [Cu₂((FD)₂DIEN₂)(OH)(OMe)]²⁺ with 50% probability ellipsoids, showing the labeling scheme used for the atoms.

Table I. Selected Interatomic Distances (Å) and Bond Angles (deg)

Cu⋯Cu(A)	2.958 (3)	Cu–N(3)	2.542 (13)
Cu–N(1)	2.049 (8)	Cu–O(2)	1.964 (8)
Cu–N(2)	2.004 (11)	Cu–O(3)	1.899 (6)
N(1)–Cu–N(2)	84.0 (4)	O(2)–Cu–N(3)	98.4 (3)
N(1)–Cu–N(3)	75.9 (4)	N(2)–Cu–O(3)	100.4 (3)
N(2)–Cu–N(3)	108.6 (4)	O(3)–Cu–N(3)	95.9 (2)
N(1)–Cu–O(2)	99.4 (4)	Cu–O(2)–Cu(A)	97.7 (5)
N(2)–Cu–O(2)	152.8 (3)	Cu–O(3)–Cu(A)	102.3 (4)
N(1)–Cu–O(3)	171.6 (4)		

Table II. Atomic Coordinates (× 10⁴) and Equivalent Isotropic Displacement Parameter (Å² × 10³) for [Cu₂(DF₂DIEN₂)](ClO₄)₂

	x	y	z	$U(eq)^a$
Cu	4292 (1)	6080 (1)	2035 (1)	49 (1)
C(1)	3557 (5)	4360 (12)	347 (11)	58 (6)
N(1)	3551 (4)	4820 (9)	1335 (8)	47 (5)
C(2)	2928 (5)	5489 (12)	1222 (12)	72 (7)
C(3)	3022 (5)	6999 (12)	1320 (11)	67 (7)
N(2)	3604 (4)	7192 (9)	2239 (8)	45 (5)
C (4)	3553 (5)	7845 (12)	2944 (11)	49 (6)
C(5)	4063 (6)	8009 (12)	3930 (11)	47 (6)
C(6)	4138 (7)	8775 (13)	4734 (12)	65 (7)
C(7)	4742 (7)	8442 (13)	5453 (12)	72 (7)
C(8)	4998 (7)	7503 (12)	5064 (11)	54 (6)
O(1)	4584 (3)	7183 (7)	4099 (7)	54 (4)
C(9)	5597 (6)	6754 (13)	5404 (12)	69 (7)
N(3)	5824 (5)	6173 (11)	4837 (9)	66 (5)
C(10)	3602 (5)	5394 (14)	–363 (11)	68 (7)
O(2)	5000	4812 (11)	2500	71 (6)
O(3)	5000	7248 (9)	2500	51 (5)
C(12)	5000	8618 (14)	2500	66 (9)
Cl	3239 (2)	1370 (3)	2070 (4)	74 (2)
O(4)	2815 (8)	2381 (17)	1631 (16)	103 (7)
O(5)	3837 (14)	1808 (14)	2071 (12)	82 (6)
O(6)	3318 (7)	988 (16)	3118 (13)	91 (6)
O(7)	3104 (8)	283 (20)	1370 (16)	120 (8)
O(4')	3074 (12)	2677 (26)	2423 (24)	70 (10)
O(5')	3229 (27)	1440 (60)	1052 (53)	234 (30)
O(6')	3736 (25)	903 (49)	2751 (42)	190 (21)
O(7')	2764 (11)	488 (23)	1996 (19)	59 (10)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.
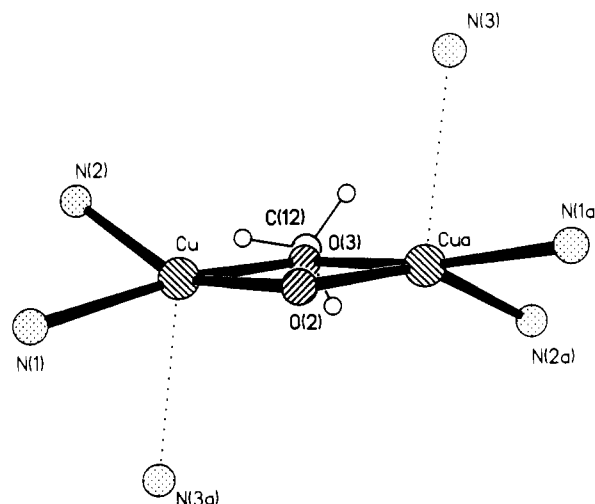

Figure 4. ORTEP plot showing the copper coordination spheres of the [Cu₂((FD)₂(DIEN)₂)(OH)(OMe)]²⁺ complex.

presence of the strong band with a λ_{max} about 360 nm, another broad band of moderate intensity is located at 504 nm (ϵ = 1060 cm⁻¹), as indicated in Figure 2, curve b. Also shown in Figure 2 is the absorbance curve d of the final product following oxygenation and degradation, together with the absorbance curves of the original dinuclear Cu(I) complex, curve a, formed anaerobically, and that of the dinuclear Cu(II) complex of (FD)₂(DIEN)₂, formed directly from copper(II) nitrate and the macrocyclic ligand, curve c.

Structure of [Cu₂((FD)₂(DIEN₂)₂)(OH)(OMe)](ClO₄)₂. A thermal ellipsoid plot (with 50% probability) of the cationic structure of [Cu₂((FD)₂(DIEN)₂)(OH)(OMe)]²⁺, together with the atomic labeling scheme is shown in Figure 3. Table I gives a list of selected interatomic distances and angles. The complex sits on a crystallographic 2-fold axis, which passes through the ⁻OH and ⁻OMe ligands.

The coordination environment around each copper(II) atom, which is four-coordinate, involves one imine nitrogen and one secondary nitrogen of the macrocycle as well as one hydroxy and one methoxy group. The latter two groups are common bridging groups between the two copper(II) centers. The geometric configuration of the coordination sphere may be best described as a distorted square-planar arrangement. The dihedral angle formed by the displacement of the Cu–N(1)–N(2) least-squares plane

from the Cu–O(2)–O(3) least-squares plane is 29.8°. This value infers that the coordination geometry is square planar with distortion toward a tetrahedral arrangement. Preference for the latter, of course, would have been indicated by a larger angle of displacement. Furthermore, for a Cu(II) ion, a square-planar arrangement is commonly the most preferred mode of coordination. The copper(II) atom lies 0.16 Å out of the N(1)–N(2)–O-(2)–O(3) plane. Figure 4, which gives a much clearer picture

Scheme I
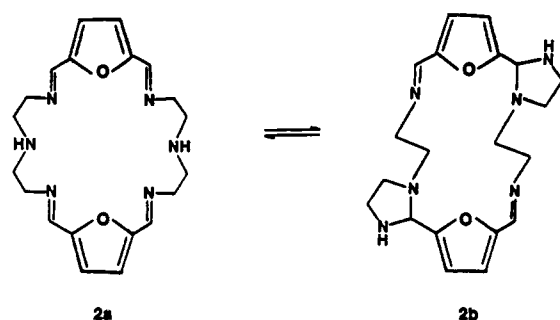
of the copper(II) coordination spheres, shows that the N(3) atom occupies an axial position relative to the positions of the other nitrogens in the complex.

The final atomic coordinates and equivalent isotropic temperature factors are listed in Table II. Additional material comprising full tables of bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and observed and calculated structure factors are supplied as supplementary material. Scattering factors were taken from ref 16.

Discussion

The Schiff-base ligand **2** has two secondary NH groups that may undergo addition reactions with adjacent imine groups, as indicated in Scheme I. The complex ^{1}H NMR spectra indicate the presence of more than one compound in solution, which is attributed to the ability of the ligand to adopt more than one structural conformation, thus resulting in a mixture of isomers as shown in Scheme I. Indeed, an analogous ligand, (MX)$_2$-(DIEN)$_2$,[9] has been found to behave in a similar manner, and one of its isomers that has been identified by X-ray crystallography corroborates this point. Other related examples have also been reported by Drew et al.[17] and Adams et al.,[18] respectively. It should be emphasized, though, that in solution an equilibrium between the isomeric forms is considered to exist, as indicated in Scheme I, as well as in a similar scheme suggested by Menif et al.[9]

Dioxygen Complex Formation. The oxygen uptake curve in Figure 1 and the absorbance bands illustrated in Figure 2 provide evidence for the formation of a peroxo-bridged dioxygen adduct. Curve a shows no measurable absorbance, a fact that seems reasonable since copper(I) has no spectrophotometric handles as the consequence of its d^{10} electron configuration. The change of color on oxygenation to red-brown (curve b) is presumed to be the intermediate dioxygen adduct with a formally peroxo bridge coordinating two formally Cu(II) centers. This concept is useful for electron bookkeeping although it is understood that coordination of dioxygen to Cu(I) occurs with partial electron transfer.[19] The UV–vis spectrum in Figure 2 shows that, besides the presence of the strong band with a maximum absorption peak about 360 nm, another broad band of moderate intensity located at 504 nm (ϵ = 1060 cm^{-1}) also occurs. These spectral changes are similar to those observed by Nishida et al.[20] in a methanol–acetonitrile system in which the intermediate copper–dioxygen adduct exhibits an additional broad band around 550–600 nm. Furthermore, Karlin's binuclear functional models[6,7] have also revealed UV–vis spectral data of the copper–dioxygen adducts with peaks around 360 nm (ϵ = 18 000 cm^{-1}) and 550 nm (ϵ = 1200 cm^{-1}). It should be pointed out, however, that the μ-η^2:η^2-dioxygen complex reported recently by Kitajima et al.[21] also shows two characteristic

bands at about 350 and 500 nm. In the cases mentioned above, the additional band around 500–560 nm is attributed to the copper(II)–peroxo species. Therefore, from the similarities of the above spectral data and those observed in this study, it seems reasonable at this point to suggest that the red-brown intermediate is indeed the Cu(II)–peroxo species. It is interesting to note that oxyhemocyanin[22] has absorbance spectral features that display a trend similar to those found in this study, with peak maxima about 550 nm (ϵ = 540 cm^{-1}) and 350 nm (ϵ = 20 000 cm^{-1}). It should also be noted that the features associated with the spectra of Kitajima et al.[23] are similar to the peak maxima found in oxyhemocyanin.[22] The shifts in the wavelength values may well be indicative of the structural differences in the coordinating ligands.

Further bubbling of oxygen through the solution produces complete degradation to an inert green product. Attempts at deoxygenation by vacuum cycling showed the oxygenation process to be irreversible after sufficient time had been allowed to complete the degradation process. The green product would seem to be the result of the decomposition of the dicopper(II)–peroxo adduct to form a hydroxo complex that has a weak absorption band around 690–700 nm. This band is very similar to that of an authentic copper(II) complex of (FD)$_2$(DIEN)$_2$, which has a low-energy band around the same region, as shown in Figure 2. The formation of hydroxo-bridged species through the irreversible oxidation of a Cu(I) complex is well-known,[6,7,24,25] and it is suggested that the final fate of dioxygen is possibly four-electron reduction to water.[24]

Structure of the Dinuclear Cu(II) Degradation Product. Structural characterization of the green complex by single-crystal X-ray determination does indeed confirm our conclusion about the formation of hydroxo species as a result of Cu(I) oxidation to Cu(II). However instead of the two hydroxo bridges being present between the copper centers as normally would be expected from a peroxo species, one of the bridges was identified as a methoxo bridge. There is, however, some evidence that the reaction of the dioxyen can be affected by the type of solvent medium that is used.[6,26] It has been found that in alcoholic medium, a hydroxo bridge may be replaced by an alkoxo bridge.[26] An additional related example is an oxygen-insertion reaction by Kitajima et al.[27] conducted in an organic solvent, dichloromethane, which resulted in an oxygenation product with two hydroxo bridging linkages between two copper(II) atoms.

The average Cu–N distance in the structure, excluding that involving the N(3) atom, which seems to be weakly coordinated, is 2.03 Å. This value appears to fall in the normal range of copper(II) to nitrogen distances found in complexes of binucleating ligands cited in the literature.[28,29] Figure 4, which gives a much clearer representation of the copper coordination spheres, shows that the N(3) atom occupies an axial position relative to the position of the other nitrogens in the complex. However the Cu–N(3) distance of 2.54 Å is found to be longer than the 2.3–2.4 Å usually found for the weak axial N donor. Taking the suggestion of Freeman,[30] the axial N donated by the macrocycle may have three-fourths of the normal bond strength already weakened by the Jahn–Teller effect. If the N(3) atom is coordinated, then the coordination geometry would be distorted square pyramidal with

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Scheme II

2

3

5

4
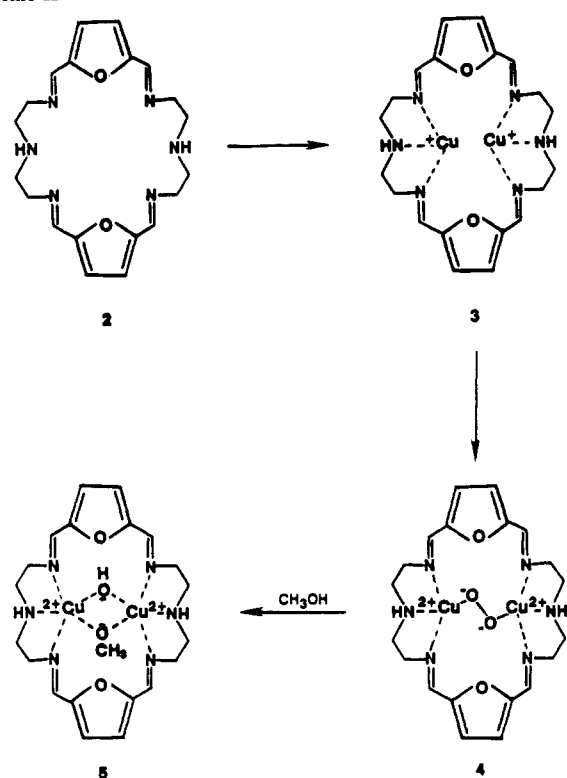
the N_3O_2 ligand donor set. Similar coordination geometries have been found by Kitajima et al.[21,27] in comparable binuclear complexes. Such a mode of coordination may well be a consequence of some strain in the complex imposed by the ligand in addition to the Jahn–Teller distortion.

The overall reaction sequence therefore is illustrated in Scheme II and involves the formation of a binuclear Cu(I) complex of the macrocyclic ligand containing two furan Schiff bases as connecting groups (2). Addition of oxygen to this system produces a furan macrocycle containing two Cu(II)'s separated by a μ-peroxo group indicated in formula 3 which has lifetime of 3–4 h at 5 °C but is eventually converted to a Cu(II) complex containing both hydroxy and methoxy bridging groups with the ligand unchanged throughout the process. The fact that an oxygen complex, albeit of limited lifetime, forms in this case instead of oxygen insertion into the aromatic group is due to the fact that the oxygen of the furan is close to the bridging peroxo group and there is no electron-donating group nearby to react with the coordinated dioxygen, as was the case for the peroxo-bridged binuclear Cu(I) complex containing *m*-xylyl connecting groups in the ligand.

The separation distance between the metal ions is 2.96 Å (Cu⋯Cu). This is significantly shorter that of the binuclear copper site found in *Panulirus interruptus* hemocyanin, where the Cu⋯Cu

distance is about 3.8 Å.[2] There are several other known binuclear complexes of copper that have larger distances of separation between the metal ions.[7,24,29] Therefore, it seems likely that there is some correlation between the metal to metal separations and the structural nature of the ligand that coordinates with these metal ions.

It is interesting to note that O(2)–Cu–O(3) angle at 80° and the N(1)–Cu–N(2) angle at 84° are considerably less than the O(2)–Cu–N(1) and O(3)–Cu–N(2) angles with values of 99.4 and 100.4°, respectively. The bridging angles Cu–O(2)–Cu and Cu–O(3)–Cu are 97.7 and 102.3°, respectively. The Cu–O(2) bond length for the methoxy group, and the Cu–O(3) bond length for the hydroxy group are 1.90 and 1.96 Å, respectively. These values are not significantly different from those observed for other copper(II) complexes with oxygen incorporating bridges.[12,22,31,32] A typical example is the phenoxy- and hydroxy-bridged binulear copper(II) complex of 1,3-bis[*N*-(2-pyridylethyl)formimidoyl]benzene, where the average Cu–O bond lengths involving the hydroxy and the phenoxy group are 1.91 and 1.97 Å, respectively.[31]

Some bond angle deformation is found in the structure. For instance the C(9)–N(3)–C(10) angle is severely distorted, with a value of 139.9°. Other distorted angles include the Cu–N(2)–C(4) angle at 118° and the C(3)–N(2)–C(4) angle at 135°. It is therefore suggested that these distortions are indicative of the extensive degree of steric constraints to which the ligand is being subjected on complex formation, because of its macrocyclic nature. The presence of the bridging linkage between the metallic centers may also be an additional aggravating factor in steric strain increment and consequently bond deformation.

What is clear from these observations is that the way in which the donor set atoms are arranged in a ligand contributes to the strength of interactions between these atoms and the metal ions. In turn, the overall arrangement of the donor atoms is dependent on how well the ligand itself is preorganized. In this case the macrocycle, with donor atoms being at almost fixed positions, has no means by which it can adapt to the coordination preferences of the copper atom as it changes from its univalent to divalent state. The only means of relief from stress from within the complex is therefore through the distortion of bond angles.

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