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Copper-Mediated Hydroxylation of an Arene: Model System for the Action of Copper Monooxygenases. Structures of a Binuclear Cu(I) Complex and Its Oxygenated Product

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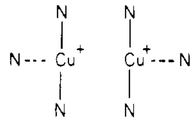
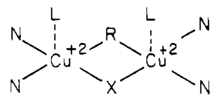
Abstract: A chemical system possessing features that mimic the structures and reactivity of the active sites of the copper oxygen carrier hemocyanin (Hc) and the monooxygenase tyrosinase (Tyr) is presented. When a dinuclear 3-coordinate Cu(I) complex, II, of a binucleating ligand, I, where the two tridentate nitrogen donor groups are separated by a *m*-xylyl bridge is reacted with dioxygen, the specific hydroxylation of the aromatic ring occurs in high yield (>90%). This produces a binuclear pentacoordinate phenolato and hydroxo doubly bridged Cu(II) complex, IIIB. Manometric and mass spectrometric measurements utilizing isotopically labeled $^{18}O_2$ show that the phenolate and hydroxy oxygen atoms in IIIB are derived from dioxygen, making this reaction an excellent biomimic for the action of the copper monooxygenases. Removal of the copper ions from IIIB gives a new phenol, IV, completing the sequence of the copper-mediated hydroxylation of an aromatic ring, I → IV. Crystallographic studies have been completed on both II and III. II crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ and $a = 11.264$ (3) Å, $b = 11.448$ (3) Å, $c = 15.722$ (4) Å, $\alpha = 95.72$ (2)°, $\beta = 102.05°$, $\gamma = 94.77°$. IIIB crystallizes in the monoclinic space group $P2_1/c$, $Z = 4$, with $a = 18.221$ (3) Å, $b = 13.323$ (3) Å, $c = 18.643$ (4) Å, and $\beta = 102.39$ (2)°. The structural features of these complexes are compared to those of other related compounds and to the active sites of the copper proteins. The biological relevance of the monooxygenase model system is also discussed.

Copper compounds have been established to be some of the most versatile and most useful catalysts for oxidation reactions by molecular oxygen in both biological and nonbiological systems. There is considerable interest in the development of chemical model systems which mimic aspects of the biological oxygenases. Studies on nonenzymatic oxygenation reactions as biological mimics can and have contributed to the understanding of the oxygenase-catalyzed reactions.[1-4] Just as important is the use of the concepts derived from the highly efficient enzymes to develop synthetic systems capable of effecting mild selective oxidation or oxygenation by O_2 of organic substrates. The use of molecular oxygen is desirable, since this is the least energy-intensive functionalization agent.[4]

Our biomimetic investigations have focused on the metalloproteins hemocyanin and tyrosinase which contain electronically coupled binuclear copper active centers. Hemocyanins[1,5,6] function as oxygen carriers in the hemolymph of molluscs and arthropods, whereas tyrosinase[1,5,7] is a monooxygenase utilizing O_2 in the hydroxylation of monophenols (monophenol → *o*-diphenol) and further acts as a two-electron oxidase (*o*-diphenol → *o*-quinone). A variety of evidence suggests that in the deoxy form of hemocyanin two[8,10] or three[9,10] imidazole ligands from histidine coordinate to each cuprous ion. Upon oxygenation, substantial changes occur giving rise to tetragonally coordinated Cu(II) ions separated by 3.6 Å and bridged by an exogenous O_2^{2-} ligand (derived from O_2) and an endogenous oxygen-containing group.[8-11] Strong parallels exist between the active sites of hemocyanin and tyrosinase; the latter binds O_2 forming oxy-Tyr which has spectral features nearly identical with oxy-Hc.[12]





In our studies with binuclear Cu(I) and Cu(II) moieties,[13] we have employed the new binucleating ligand *m*-XYLpy$_2$, (I, Figure 1), where two tridentate donor groups are separated by a *m*-xylyl bridge.[13-15] A principal focus of our work has been to isolate,

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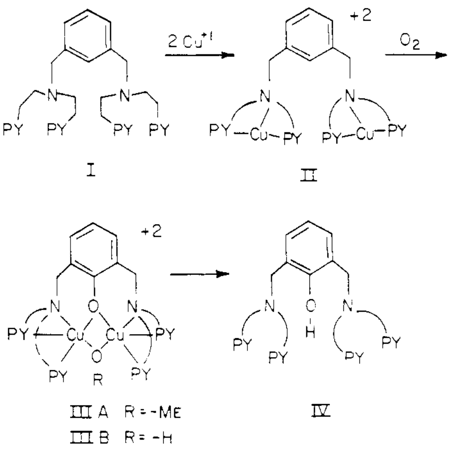

Figure 1. Copper-mediated hydroxylation of an arene: model system for copper monooxygenases. PY = 2-pyridyl.

characterize, and study the reactivities with O_2 of copper(I) complexes containing nitrogen donor ligands. Although there has been increased recent activity in this area, there is a paucity of well-characterized low-coordinate Cu(I) complexes which contain unsaturated nitrogen ligands.[1b,16] Reactions of these with dioxygen are under investigation since the interaction of Cu(I) centers with dioxygen plays an important role in the enzymic systems. Although kinetic studies have been reported,[17-19] lesser attention has been paid to the isolation of reaction products in model systems.[19-21]

Here, we report the synthesis and characterization of a copper complex serving as a mimic for the biological action of the copper monooxygenases. We have communicated the preparation and structure of a novel dicopper(I) complex of *m*-XYLpy$_2$ (I), II, which contains well-separated trigonally coordinated Cu(I) moieties.[15] This complex reacts with dioxygen resulting in the specific hydroxylation of the xylyl ligand producing the phenoxy and hydroxy doubly bridged compound IIIB which we have now characterized structurally by X-ray diffraction. Manometric measurements of O_2 uptake by II and mass spectrometric analyses of the product IIIB prepared by using isotopically pure $^{18}O_2$ show unambiguously that both atoms of dioxygen are incorporated into the oxygenation product. The stoichiometry of this hydroxylation reaction, II → IIIB is directly analogous to that of the copper monooxygenases.[7] The copper ions can be removed from IIIB producing the new phenolic compound IV, completing the sequence involving the copper-mediated hydroxylation of the aromatic ring I → IV (Figure 1).

Experimental Section

Materials and Methods. Reagents and solvents used were of commercially available reagent grade quality. Tetrahydrofuran (THF) was distilled from calcium hydride, methanol from Mg(OMe)$_2$, acetone from anhydrous K_2CO_3, and dichloromethane from CaH_2/K_2CO_3, all under Ar. Anhydrous diethyl ether was freshly dried by passing it through a 60-cm long column of activated alumina and collected under Ar. Dimethylformamide (DMF) was used from freshly opened bottles (glass distilled, MCB Omnisolv) and/or stored over 4-Å molecular sieves.

Preparations and handling of air sensitive compounds were carried out by using standard Schlenk techniques. Deoxygenation of solvents and solutions was carried out by either repeated vacuum/purge cycles or by thorough bubbling (20 min) with Ar. Solid samples were stored and transferred and samples for infrared (IR) and NMR spectra were prepared in a Vacuum/Atmospheres Dry Box filled with argon. All column chromatography of ligands was carried out by "Flash Chromatography"[22] using either silica gel (60–200 mesh, MCB) or alumina (80–200 mesh, MCB). Fractions from column chromatography were monitored by using Baker-Flex 1B-F TLC plates. Purity of ligands was judged by TLC, ^{1}H, and ^{13}C NMR.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN and/or Instranel laboratory Inc., Rensselaer, NY. Infrared and electronic absorption spectra were taken with PE 283 and Cary 14 instruments, respectively. ^{1}H and ^{13}C NMR spectra were taken on a Varian EM 360 60-MHz and a Bruker HX-90 FT NMR spectrometer, respectively. Chemical shifts are reported as δ values downfield from an internal standard of Me$_4$Si.

***m*-XYLpy$_2$ (I).** α,α'-dibromo-*m*-xylene (0.92 g, 3.5 mmol) was added to a solution of bis(2-(2-pyridyl)ethyl)amine (py2)[23,24] (1.59 g, 7.0 mmol) in reagent grade ethyl acetate (75 mL). Diisopropylethylamine (1.34 g, 7.0 mmol) was added to this solution. The mixture was allowed to stir at room temperature for five days. The reaction mixture was filtered, the filtrate was washed with 20% NaOH (aqueous) and extracted with dichloromethane, and the extract was dried over anhydrous MgSO$_4$. Removal of the solvent gave crude oil which was chromatographed on silica gel with methanol as eluant, R_f = 0.5. A total of 1.64 g of pure product was recovered for a total yield of 84%. Purification can also be effected by chromatography on alumina with a methanol:ethyl acetate (1:9) solvent system: R_f = 0.75; ^{1}H NMR (CDCl$_3$) 2.85 (16 H, br s), 3.55 (4 H, s), 6.7–7.0 (12 H, m), 7.1–7.4 (4 H, m), 8.2 (4 H (py-6), br d).

A more efficient method of making I was by direct reaction of an excess of 2-vinylpyridine (58.0 g, 0.55 mol, purified by passing through a short silica gel precolumn using ether solvent, followed by removal of the ether) with *m*-xylylenediamine (7.5 g, 0.055 mol) using acetic acid (16.5 g, 0.27 mol) as the catalyst. The reactants were stirred while heating near reflux in 150 mL of methanol under argon for five days. The MeOH was removed by rotary evaporation and the resulting oil was washed with 150 mL of 15% NaOH (aqueous) and extracted with dichloromethane (3 × 75 mL). The organic layer was dried over MgSO$_4$ and the solvent removed to give 47.6 g of the crude product (containing an excess of 2-vinylpyridine). Typically, 12.0 g was columned on silica gel by using MeOH as eluant to give 6.6 g of the pure product (68% yield based on the diamine).

Cu$_2$(*m*-XYLpy$_2$)(PF$_6$)$_2$ (II). To a suspension of 3.12 g (8.38 mmol) of Cu(CH$_3$CN)$_4$PF$_6$[25] in 75 mL of THF, while stirring, was added dropwise 2.77 g (4.98 mmol) of I in 50 mL of THF. The colorless starting suspension slowly dissolved into solution as a yellow powdery solid started to form. The mixture was stirred further overnight and filtered, and the precipitate was washed first with an acetone/ether (1/2) mixture and then with ether. Drying in vacuo gave 3.29 g (80% yield) of a yellow powder. Anal. Calcd for $Cu_2(C_{36}H_{40}N_6)(PF_6)_2$: C, 44.48; H, 4.14; N, 8.63. Found: C, 45.28; H, 4.17; N, 8.76. Complex II is a yellow-brown crystalline solid which is stable in air as a dry solid for a few minutes. It is soluble in polar organic solvents such as acetone, DMF, and CH$_2$Cl$_2$; in these media it is extremely oxygen sensitive. The complex is diamagnetic as indicated by its sharp ^{1}H NMR spectrum in (CD$_3$)$_2$CO and small shifts compared to the free ligand I: 3.17 (16 H, br db), 3.78 (4 H, s), 7.3–7.6 (12 H, m), 7.7–7.9 (4 H, m), 8.64 (4 H, br db).

$Cu_2C_{36}H_{40}N_6O_2(PF_6)_2$ (Oxygenation Product IIIB). Complex II (300 mg, 0.308 mmol) was dissolved in dimethylformamide (125 mL) under argon. The solution was then exposed to an atmosphere of dry dioxygen overnight, while stirring. Three volumes of dry diethyl ether were then layered on the resulting green solution. The resulting green precipitate was recrystallized twice from dichloromethane/ether (1/3) at 0 °C to give 300 mg of crystalline IIIB (97%). Anal. Calcd for $Cu_2C_{36}H_{40}N_6O_2(PF_6)_2$: C, 42.99; H, 4.01; N, 8.36. Found: C, 42.63; H, 4.16; N, 8.03. IR (KBr) ν (OH) 3605 cm^{-1}; UV-VIS (CH$_3$CN) λ_{max} nm (ϵ, M^{-1} cm^{-1}) 253 (20 600), 280 (sh, 7500), 340 (sh, 2380), 378 (3500), 635 (180) nm. The ^{18}O-labelled IIIB was prepared by the analogous reaction of II in DMF in a closed system with $^{18}O_2$ (Stohler, 99% isotopic purity) with approximately double the volume of dioxygen necessary for completion of the reaction. The dark green solution produced was treated as described above but under an argon atmosphere, to insure against any ^{18}O exchange due to exposure to moisture.

$C_{36}H_{40}N_6O$ (IV). Complex IIIB (1.0 g, 1.0 mmol) was dissolved in 20 mL of CH$_2$Cl$_2$, giving a dark green solution. The solution was filtered and an equal volume of concentrated aqueous ammonia was added. The mixture was stirred vigorously for a few minutes giving a deep blue aqueous layer and a brownish dichloromethane layer. The aqueous layer

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was separated and further extracted with 10 mL of CH_2Cl_2. The organic extracts were combined and the above ammonia treatment and extractions were repeated two additional times to ensure complete removal of copper. The final CH_2Cl_2 solution was washed with water and dried over $MgSO_4$, and the solvent was removed by rotary evaporation and then in vacuo, giving an oily yellow-brown product (0.43 g, 75%): TLC (silica gel, MeOH) $R_f = 0.23$; ^1H NMR ($CDCl_3$) 2.87 (16 H, br s), 3.7 (4 H, s), 6.4–7.0, 7.1–7.4 (15 H, m), 8.25 (4 H, br db). Identification was confirmed by ^1H NMR and field-desorption mass spectrometry which showed a peak at m/z 573 for the protonated molecular ion MH^+ (see below).

Manometry. Quantitative measurement of the uptake of dioxygen by $(Cu_2m\text{-}XYLpy_2)(PF_6)_2$ (II) was done by constant volume (Kontes "Airless Ware" Vacuum Rack) and by constant pressure (modified Warburg apparatus[26]) methods at room temperature. In either method, a solution of complex II was prepared under argon in DMF or CH_2Cl_2 followed by attachment of the flask to the appropriate apparatus. Argon was removed by allowing the solution to boil under reduced pressure with a minimum of solvent loss. When the system had equilibrated at the ambient temperature, an excess of dry dioxygen was introduced and the initial volume or pressure quickly noted. Vigorous stirring of the solution was accompanied by O_2 uptake and measurements were taken after no further changes were apparent over several hours. To correct for the solubility of dioxygen in the solvent, a blank run was taken using pure solvent. It was found that 0.96 ± 0.06 mol of O_2 was absorbed per mole of the binuclear complex (II) ($Cu{:}O_2/2{:}1$).

Mass Spectrometry. Field-desorption (FD) mass specta were obtained through the NIH sponsored Biotechnology Research Resource for Mass Spectrometry (Director: Professor K. Biemann) in the Department of Chemistry at the Massachusetts Institute of Technology (MIT), Cambridge, MA. Sample handling and analysis of data was coordinated through Dr. C. E. Costello, Associate Director. Data were obtained on a MAT 731 double focussing mass spectrometer operated at 8-kV accelerating voltage. Ion source temperature was 80 °C. The emitters were activated 10-μm tungsten wires. The extraction voltage was 5–6 kV.

For m-XYLpy$_2$ (I) the relative abundances for ions m/z 555, 556 (M), 557 (MH), and 558 are 19 ± 5, 100 ± 4, 77 ± 12, and 28 ± 7, respectively (average of 21 determinations with the emitter heating current ranges from 1 mA to 15 mA.

For the binuclear phenoxy- and hydroxy-bridged Cu(II) complex IIIB, the FD spectrum showed that the most abundant species is the (dication + $PF_6)^+$ having a single net positive charge and appearing at m/z 859 (corresponding to isotope $^{63}Cu_2$).[27] Next is the dication itself, which has a charge of +2, and therefore appears at m/z 357. The molecular ion (dication + 2 anions) expected at m/z 1004 is of very low abundance. For IIIB, formed by utilizing $^{18}O_2$, the most abundant ion is m/z 863, corresponding to incorporation of two ^{18}O atoms (m/z, abundance: 861, 31 ± 21; 862, 11 ± 4; 863, 99 ± 2; 864, 50 ± 11; 865, 84 ± 17; 866, 38 ± 12; 867, 26 ± 11).

As stated above, the most abundant peak observed in the FD spectrum of IV corresponds to m/z 573 (MH^+). Other prominent peaks are m/z 467, 347, 330, 227 (py$_2$), and 113.5 (py$_2$ dication). An FD analysis of compound IV isolated from IIIB made by using $^{18}O_2$ showed a shift of the most abundant peak to m/z 575, indicating incorporation of one ^{18}O atom into this phenol.

X-ray Crystallography. Crystallization, Collection, and Reduction of X-ray Diffraction Data. An actone/ether solution of II under Ar yielded clear yellow crystals of $Cu_2(m\text{-}XYLpy_2)(PF_6)_2$ (II) that were suitable for X-ray crystallographic analysis. Dark green X-ray quality crystals of the oxygenation product IIIB were obtained from CH_2Cl_2/diethyl ether. Epoxy-covered crystals (of both II and IIIB) were mounted on a Nicolet R3m four-circle automated diffractometer with a Mo X-ray source equipped with a highly ordered graphite monochromator (λ (Mo Kα) = 0.71073 Å). Automatic centering and least-squares routines were carried out on 25 reflections, for each complex, to obtain the cell dimensions that are given in Table I. A coupled 2θ (crystal) to 2θ (counter) scan mode was employed. The scan length was $(2\theta\ (K\alpha_1 - 1.0))°$ to $(2\theta\ (K\alpha_2 + 1.0))°$. Three check reflections were measured every 197 reflections; these exhibited no significant decay during data collection. The program XTAPE of the SHELXTL package[28] was used to process the data in both complexes. A summary of cell parameters, data collection parameters, and refinement results for complexes II and IIIB is found in Table I.

Table I. Crystallographic Data for Complexes II and IIIB

	complex II	complex IIIb
a, Å	11.264 (3)	18.221 (3)
b, Å	11.448 (3)	13.323 (3)
c, Å	15.722 (4)	18.643 (4)
α, deg	95.72 (2)	90.0
β, deg	102.05 (2)	102.39 (2)
γ, deg	94.77 (2)	90.0
V, Å^3	1961.4 (8)	4420.3 (8)
Z	2	4
D_{calcd}, g/cm^3	1.640	1.51
space group	$P\bar{1}$	$P2_1/c$
crystal dimensions, mm	0.40 × 0.40 × 0.10	0.20 × 0.25 × 0.28
scan rate, deg/min	6.0–30.0	6.0–30.0
scan range, deg	3.0–40.0	0.0–45.0
reflections collected	3643	6347
independent reflections	$2761 \geqslant 6\sigma\lvert F_o\rvert$	$2711 \geqslant 6\sigma\lvert F_o\rvert$
absorption coefficient, cm^{-1}	12.53	12.38
R^a	0.0696	0.0969
$R_w{}^a$	0.0760	0.0971
goodness of fit^b	1.705	2.831

[a] $R = \Sigma[\lvert F_o\lvert F_c\rvert/\Sigma\lvert F_o\rvert]$; $R_w = [\Sigma_w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma_w\lvert F_o\rvert^2]^{1/2}$; $w = 1/\sigma^2(F_o) + g^*(F_o)^2$. [b] GOF = $\langle\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\mathrm{NO} - \mathrm{NV})\rangle^{1/2}$ when NO is the number of observations and NV is the number of variables.

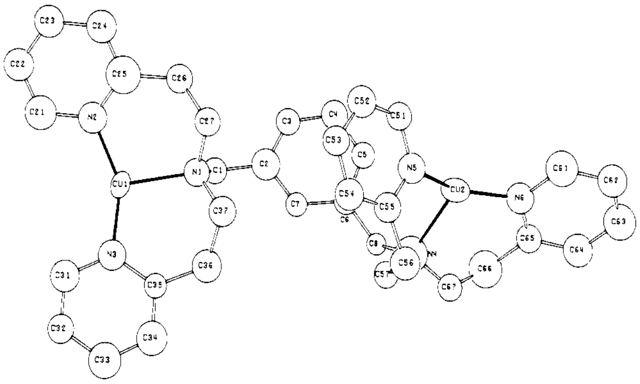

Figure 2. ORTEP diagram for the binuclear copper(I) complex II showing the atom labeling scheme.

Structure Solution and Refinement. In each case, the positional parameters of the copper atoms were determined by the Patterson method. The remaining non-hydrogen atoms were located by subsequent difference Fourier maps and least-square refinements. Atomic scattering factors for neutral atoms were used throughout the analysis. Complex II crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. Each asymmetric unit is found to contain one complete molecule. IIIB crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$. Again, each asymmetric unit contains one complete molecule, with no atoms sitting at special positions. For II, anisotropic refinement was carried out on only the copper atoms and the atoms in the anion. The remaining atoms were refined isotropically. For IIIB, all non-hydrogen atoms were refined anisotropically. In both cases, the hydrogen atoms were included in the final stages of refinement for the complex cation. The carbon–hydrogen bond distance was set at 0.96 Å, with isotropic thermal parameters 1.2 times those of the bonded carbon atoms. The hexafluorophosphate anions that are present in both compounds II and IIIB are unexceptional. No disorder is seen and the bond angles and bond lengths are as expected. The final R factors and refinement data appear in Table I.

Structure factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors are available in the supplementary material for compounds II (Table VI–X) and IIIB (Tables XI–XV).

Description of Structures

$Cu_2(m\text{-}XYLpy_2)(PF_6)_2$ (II). The structure of II consists of one discrete complex dication and two well-separated anions per asymmetric unit. Final positional parameters are given in Table II, and selected bond distances and angles are found in Table III. An ORTEP view of $(Cu_2(m\text{-}XYLpy_2))^{2+}$ is shown in Figure 2, including atom labeling scheme. It consists of two crystallo-

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Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for Complex II

atom	x	y	z	$U_{\text{equiv/iso}}$
Cu(1)	5212 (1)	2327 (1)	4286 (1)	62 (1)[a]
Cu(2)	1655 (1)	2256 (1)	−1357 (1)	61 (1)[a]
N(1)	4688 (6)	2170 (6)	2899 (5)	50 (2)
N(2)	6192 (8)	1033 (8)	4479 (6)	69 (2)
N(3)	4216 (7)	3456 (7)	4675 (5)	55 (2)
N(4)	2012 (6)	3978 (6)	−545 (5)	45 (2)
N(5)	1535 (6)	1284 (6)	−478 (5)	48 (2)
N(6)	1167 (7)	2629 (7)	−2533 (5)	62 (2)
C(1)	5502 (9)	2839 (9)	2441 (6)	56 (3)
C(2)	5136 (8)	2767 (8)	1467 (7)	53 (3)
C(3)	5463 (9)	1884 (9)	907 (7)	71 (3)
C(4)	5120 (10)	1836 (11)	1 (8)	80 (3)
C(5)	4422 (9)	2694 (9)	−353 (7)	64 (3)
C(6)	4070 (8)	3572 (8)	178 (6)	49 (2)
C(7)	4442 (8)	3596 (8)	1068 (6)	51 (2)
C(8)	3295 (8)	4457 (8)	−215 (7)	55 (3)
C(21)	6713 (10)	923 (10)	5331 (8)	78 (3)
C(22)	7347 (10)	−65 (10)	5520 (8)	74 (3)
C(23)	7381 (11)	−908 (11)	4867 (8)	84 (4)
C(24)	6839 (10)	−811 (10)	4033 (8)	76 (3)
C(25)	6253 (9)	184 (9)	3849 (7)	59 (3)
C(26)	5765 (9)	321 (10)	2904 (7)	70 (3)
C(27)	4579 (9)	890 (8)	2640 (7)	60 (3)
C(31)	4223 (9)	3664 (9)	5521 (7)	68 (3)
C(32)	3507 (10)	4382 (9)	5867 (8)	73 (3)
C(33)	2762 (10)	4966 (10)	5316 (7)	75 (3)
C(34)	2691 (10)	4804 (10)	4425 (8)	77 (3)
C(35)	3439 (8)	4013 (8)	4112 (8)	53 (3)
C(36)	3382 (9)	3803 (9)	3157 (7)	61 (3)
C(37)	3430 (8)	2564 (8)	2736 (7)	56 (6)
C(51)	2051 (8)	239 (9)	−401 (7)	62 (3)
C(52)	2050 (9)	−386 (10)	322 (7)	71 (3)
C(53)	1527 (9)	44 (10)	954 (8)	72 (3)
C(54)	990 (9)	1077 (9)	893 (7)	61 (3)
C(55)	1009 (8)	1668 (8)	175 (6)	47 (2)
C(56)	474 (9)	2809 (8)	81 (7)	57 (3)
C(57)	1423 (9)	3863 (9)	212 (7)	59 (3)
C(61)	645 (9)	1756 (10)	−3185 (7)	72 (3)
C(62)	65 (11)	1966 (11)	−3944 (8)	84 (4)
C(63)	−27 (11)	3067 (11)	−4147 (9)	86 (4)
C(64)	473 (10)	3974 (11)	−3519 (7)	77 (3)
C(65)	1071 (9)	3751 (9)	−2702 (7)	58 (3)
C(66)	1680 (9)	4720 (9)	−2025 (7)	67 (3)
C(67)	1341 (9)	4764 (9)	−1132 (7)	62 (3)
P(1)	7047 (4)	2940 (3)	7840 (5)	85 (2)[a]
P(2)	9550 (3)	2036 (3)	3139 (2)	67 (1)[a]
F(1)	6950 (13)	3184 (10)	6887 (6)	198 (7)[a]
F(2)	6004 (12)	3713 (11)	7915 (8)	204 (8)[a]
F(3)	7669 (15)	2104 (14)	7737 (9)	260 (10)[a]
F(4)	7340 (14)	2872 (12)	8827 (7)	221 (8)[a]
F(5)	6215 (15)	1902 (11)	7695 (19)	367 (16)[a]
F(6)	7963 (13)	4063 (13)	8045 (10)	240 (9)[a]
F(7)	9216 (10)	1229 (8)	3804 (6)	149 (5)[a]
F(8)	8687 (8)	2911 (8)	3443 (6)	134 (5)[a]
F(9)	9982 (10)	2877 (8)	2510 (7)	161 (6)[a]
F(10)	10620 (9)	2657 (11)	3861 (7)	192 (6)[a]
F(11)	10441 (8)	1156 (8)	2877 (7)	145 (5)[a]
F(12)	8547 (8)	1409 (13)	2421 (7)	210 (7)[a]

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ii} tensor.

graphically independent cuprous ion coordination environments. Each Cu(I) is three coordinate with ligation from two pyridine and one tertiary amino donor groups.

The bonding distances are typical for three-coordinate Cu(I) with nitrogen donors[21,29,30] while the Cu–N_{py} distances are shorter by ca. 0.08 Å than the bond lengths found in the monomeric tetracoordinate Cu(I) complex containing the same tridentate moiety,[31] Cu(tepa)$^+$ (tepa = tris-2-(2-pyridyl)ethylamine). The cuprous ion polyhedra extend away from each other with Cu(1)···Cu(2) = 8.940 Å.

Table III. Selected Bond Distances and Angles for II

Interatomic Distances, Å			
Cu(1)–N(1)	2.121 (8)	Cu(1)–N(2)	1.937 (9)
Cu(1)–N(3)	1.924 (8)	Cu(2)–N(5)	1.904 (8)
Cu(2)–N(4)	2.196 (7)	Cu(2)–N(6)	1.918 (8)
Interatomic Angles, deg			
N(1)–Cu(1)–N(2)	102.5 (3)	N(1)–Cu(1)–N(3)	104.0 (3)
N(2)–Cu(1)–N(3)	151.4 (4)	N(5)–Cu(2)–N(4)	99.7 (3)
N(5)–Cu(2)–N(6)	150.8 (3)	N(4)–Cu(2)–N(6)	104.4 (3)
Dihedral Angles, deg			
N(1),N(2),N(3)/N(4),N(5),N(6)	48.3		
N(1),N(2),N(3)/N(2)[a]	15.9		
N(1),N(2),N(3)/N(3)[a]	7.1		
N(4),N(5),N(6)/N(5)[a]	46.4		
N(4),N(5),N(6)/N(6)[a]	19.0		

[a] N(X) (X = 2, 3, 5, 6) denotes the best least squares pyridine ring plane containing N(X).

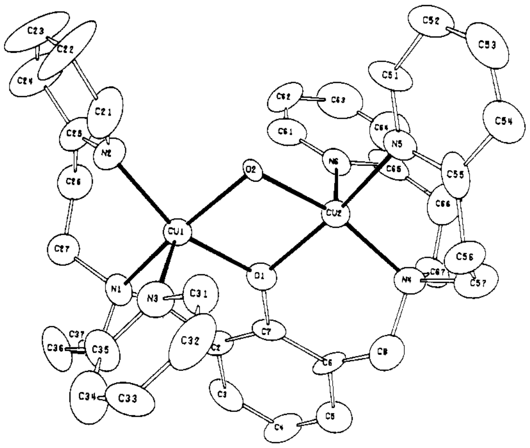

Figure 3. ORTEP diagram for the phenolate-bridged binuclear copper(II) complex IIIB showing the atom labeling scheme.

The chelating tridentate ligands cause considerable distortions from idealized trigonal planar coordination. The N_{amino}–Cu–N_{py} angles (Table III) are acute (99–105°), resulting in large N_{py}–Cu–N_{py} angles of 151.4 (4)° and 150.8 (3)° for Cu(1) and Cu(2), respectively. Some distortion from planarity occurs with Cu1 0.147 Å out of the N(1), N(2), N(3) plane and Cu(2) 0.228 Å out of the N(4), N(5), N(6) plane. The dihedral angle between the best least-squares planes formed by the two "trigonal" copper coordination spheres N(1), N(2), N(3)/N(4), N(5), N(6) is 48.3°. As is found in other related structures,[21,29] the pyridine rings are not coplanar with the copper coordination plane, with the dihedral angles varying between 7.1° and 46.4° (Table III).

The coordination distortions caused by chelation do not greatly affect the bonding of the Cu(I) ions with the pyridine nitrogen lone pairs, the latter being reflected by deviation of the Cu atom position from the best least-squares pyridine plane. The largest distortion is for Cu(2) with the pyridine ring containing N(6). Here, the copper atom lies 0.938 Å out out of the pyridine plane. Judging by a comparison of the Cu–N_{py} distances (Table IV), this deviation has an insignificant effect on the Cu–pyridine bond strength. A considerably larger deviation (0.69 Å out of the py plane) is observed in a Cu(I) complex of a tetradentate N_2S_2 aminoethylpyridine-containing ligand.[32]

Complex IIIB. The structure of the phenolate- and hydroxy-bridged binuclear Cu(II) complex IIIB consists of one discrete

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Table IV. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for Complex IIIB

atom	x	y	z	$U_{equiv/iso}$[a]
Cu(1)	2324 (1)	4467 (2)	4720 (1)	53 (1)
Cu(2)	2979 (1)	6431 (2)	5466 (1)	53 (1)
O(1)	3143 (5)	5444 (8)	4727 (6)	59 (5)
O(2)	2190 (5)	5428 (7)	5462 (5)	49 (4)
N(1)	2440 (7)	3869 (10)	3747 (7)	60 (6)
N(2)	1269 (8)	3991 (12)	4665 (9)	88 (8)
N(3)	3011 (8)	3290 (10)	5438 (8)	70 (6)
N(4)	3985 (7)	7115 (11)	5527 (7)	61 (6)
N(5)	2814 (8)	7030 (10)	6418 (7)	67 (6)
N(6)	2336 (9)	7508 (12)	4731 (8)	64 (7)
C(1)	2676 (9)	4736 (11)	3306 (8)	58 (7)
C(2)	3429 (9)	5127 (12)	3585 (9)	58 (7)
C(3)	3958 (10)	5185 (13)	3153 (10)	75 (8)
C(4)	4642 (10)	5680 (16)	3389 (10)	92 (10)
C(5)	4795 (10)	6084 (13)	4049 (9)	70 (8)
C(6)	4284 (10)	5975 (14)	4518 (10)	56 (8)
C(7)	3617 (9)	5524 (12)	4275 (9)	51 (7)
C(8)	4492 (9)	6344 (15)	5291 (11)	80 (10)
C(21)	1048 (13)	3656 (22)	5317 (11)	145 (14)
C(22)	315 (13)	3514 (31)	5330 (16)	269 (25)
C(23)	−196 (13)	3572 (32)	4736 (14)	253 (26)
C(24)	−6 (14)	3715 (36)	4103 (16)	263 (28)
C(25)	736 (12)	4003 (20)	4032 (11)	107 (11)
C(26)	1050 (9)	4135 (16)	3337 (10)	91 (10)
C(27)	1698 (9)	3485 (14)	3309 (9)	72 (8)
C(31)	3254 (9)	3496 (15)	6176 (9)	78 (8)
C(32)	3677 (10)	2739 (17)	6618 (10)	107 (11)
C(33)	3869 (13)	1906 (14)	6299 (14)	97 (12)
C(34)	3624 (12)	1768 (16)	5576 (11)	85 (10)
C(35)	3199 (12)	2428 (14)	5159 (13)	72 (10)
C(36)	2851 (11)	2272 (14)	4344 (12)	91 (11)
C(37)	2987 (10)	3043 (13)	3838 (10)	69 (8)
C(51)	2121 (12)	7291 (15)	6424 (12)	103 (11)
C(52)	1949 (13)	7638 (16)	7121 (10)	105 (11)
C(53)	2496 (12)	7632 (15)	7726 (10)	99 (10)
C(54)	3211 (12)	7393 (15)	7670 (10)	90 (10)
C(55)	3360 (10)	7080 (15)	7020 (9)	72 (8)
C(56)	4104 (11)	6824 (17)	6876 (9)	95 (10)
C(57)	4315 (10)	7472 (15)	6312 (10)	81 (9)
C(61)	1722 (13)	7237 (18)	4359 (10)	90 (11)
C(62)	1239 (15)	7650 (19)	3910 (14)	155 (16)
C(63)	1366 (14)	8634 (27)	3811 (13)	214 (20)
C(64)	2070 (11)	9085 (16)	4209 (13)	110 (11)
C(65)	2550 (10)	8439 (14)	4653 (10)	76 (8)
C(66)	3332 (10)	8702 (13)	5105 (10)	85 (9)
C(67)	3936 (9)	8040 (11)	5043 (9)	63 (8)
P(1)	4285 (7)	4795 (7)	8518 (7)	201 (7)
P(2)	395 (9)	3764 (11)	7616 (9)	265 (10)
F(1)	4378 (11)	5918 (13)	8626 (9)	209 (11)
F(2)	4004 (16)	4838 (17)	7682 (10)	218 (17)
F(3)	4478 (13)	4560 (18)	9325 (10)	246 (14)
F(4)	4151 (9)	3667 (11)	8442 (12)	183 (11)
F(5)	5084 (8)	4724 (12)	8378 (10)	176 (10)
F(7)	1066 (13)	3757 (13)	8263 (11)	279 (13)
F(8)	760 (14)	3059 (18)	7153 (11)	267 (15)
F(9)	616 (12)	4651 (16)	7265 (14)	239 (14)
F(6)	3439 (15)	4987 (15)	8631 (16)	299 (19)
F(10)	137 (15)	2814 (17)	7872 (18)	354 (22)
F(11)	−108 (20)	4366 (34)	7995 (22)	430 (31)
F(12)	−410 (20)	3679 (31)	6970 (27)	564 (34)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ii} tensor.

Table V. Selected Bond Distances and Angles for IIIB

Interatomic Distances, Å			
Cu(1)-O(1)	1.979 (10)	Cu(1)-O(2)	1.938 (10)
Cu(1)-N(1)	2.034 (14)	Cu(1)-N(3)	2.258 (13)
Cu(1)-N(2)	2.006 (16)	Cu(2)-O(1)	1.972 (11)
Cu(2)-O(2)	1.962 (10)	Cu(2)-N(4)	2.028 (13)
Cu(2)-N(5)	2.027 (14)	Cu(2)-N(6)	2.149 (15)
O(1)-C(7)	1.336 (21)		
Interatomic Angles, deg			
O(1)-Cu(1)-O(2)	76.7 (4)	O(1)-Cu(1)-N(1)	92.4 (5)
O(2)-Cu(1)-N(1)	161.5 (5)	O(1)-Cu(1)-N(3)	97.6 (5)
O(2)-Cu(1)-N(3)	100.0 (5)	N(1)-Cu(1)-N(3)	96.1 (5)
O(1)-Cu(1)-N(2)	157.1 (6)	O(2)-Cu(1)-N(2)	88.8 (6)
N(1)-Cu(1)-N(2)	96.5 (6)	N(3)-Cu(1)-N(2)	102.4 (6)
O(1)-Cu(2)-O(2)	76.3 (4)	O(1)-Cu(2)-N(4)	93.9 (5)
O(2)-Cu(2)-N(4)	163.5 (5)	O(1)-Cu(2)-N(5)	161.3 (5)
O(2)-Cu(2)-N(5)	91.4 (5)	N(1)-Cu(2)-N(5)	94.4 (6)
O(1)-Cu(2)-N(6)	98.3 (5)	O(2)-Cu(2)-N(6)	98.9 (5)
N(4)-Cu(2)-N(6)	95.6 (6)	N(5)-Cu(2)-N(6)	97.6 (6)
Cu(1)-O(1)-Cu(2)	102.5 (5)	Cu(1)-O(1)-C(7)	129.6 (10)
Cu(2)-O(1)-C(7)	127.1 (10)	Cu(1)-O(2)-Cu(2)	104.4 (5)

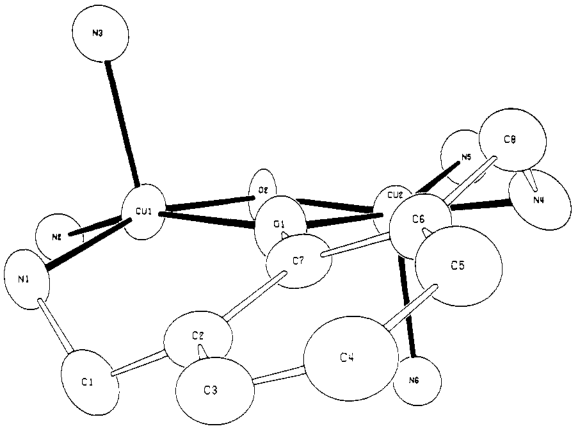

Figure 4. ORTEP diagram for the inner coordination sphere of IIIB showing the orientation of the phenolate group relative to the Cu_2O_2 unit.

dication and two well-separated PF_6^- anions per asymmetric unit. Final positional parameters are given in Table IV; selected bond distances and angles are found in Table V. An ORTEP view with atom labeling scheme is shown in Figure 3.

The structure consists of two crystallographically independent but very similar Cu(II) coordination environments in each binuclear unit. Each copper ion is coordinated to the tertiary amine and two pyridine nitrogen atoms of the tridentate unit py_2. The bridging-phenolate (O(1)) and hydroxide oxygen (O(2)) atoms complete pentacoordination. The geometry around each copper is essentially undistorted from a tetragonal pyramid with N(3) and N(6) pyridines occupying axial positions on opposite sides of the Cu_2O_2 plane. The copper atoms Cu(1) and Cu(2) lie 0.31 and 0.26 Å, respectively, out of their corresponding basal planes towards the apical N_{py} atom. In each case, the $Cu-N_{py-axial}$ vector forms an angle of ca. 87° with its least-squares basal plane.

The Cu_2O_2 unit is essentially planar, with the maximum deviation from the least-squares plane being 0.012 Å. The Cu(I-I)···Cu(II) separation is 3.082 (3) Å. The dihedral angle Cu(1), N(1), N(2)/Cu(1), O(1), O(2) is 25.2° while the corresponding Cu(2), N(4), N(5)/Cu(2), O(1), O(2) dihedral angle is 20.7° (Figure 4). The phenolate ring of the binucleating ligand in IIIB is both twisted and tilted with respect to the planar Cu_2O_2 unit (Figure 4). The dihedral angle between the best least-squares planes of the benzene ring (C(2)–C(7)) and the Cu_2O_2 unit is 28.9°. The tilting is seen by measuring the distances of C(7) and C(4) out from the Cu_2O_2 plane; C(7)/Cu_2O_2 = 0.13 Å and C-(4)/Cu_2O_2 = 0.34 Å).

The Cu(II)–N and Cu(II)–O bond distances (Table V) are in the range expected for this coordination geometry with copper(II). The $Cu-N_{amino}$ bond lengths are both 2.03 (1) Å. This is shorter than is found in other structurally similar binuclear copper(II) complexes[14,21] and in a series of Cu(II) mononuclear complexes with tertiary amine ligands located in the basal plane of a tetragonal pyramid.[31b,33]

As expected, the axially coordinated $Cu-N_{py}$ bond distances are longer than those in the basal plane by 0.14 and 0.25 Å. The two distances differ significantly, with Cu–N(3) = 2.26 (1) Å, and Cu–N(6) = 2.15 (2) Å. The basal $Cu-N_{py}$ bond lengths

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(33) Karlin, K. D.; Hayes, J. C.; Juen, S.; Hutchinson, J. P.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 4106–4108.

average 2.02 Å, which is typical. Equatorially coordinated pyridine ligands have Cu–N bond lengths very close to this value; these distances seem to be independent of the oxidation state of copper (Cu(I) or Cu(II)) for tetra- or pentacoordination.[31-33] A significant Cu–$\mathrm{N_{py}}$ bond lengthening occurs on going from 3-coordination (in complex II) to 5-coordination.[21,34]

It is interesting to note that while the Cu–$\mathrm{N_{py}}$ distances increase upon increasing coordination number and oxidation state, the Cu–$\mathrm{N_{amino}}$ bond lengths decrease significantly.[21] This may reflect an appreciable amount of Cu(I)–$\mathrm{N_{py}}$ π back bonding present in the Cu(I) complexes,[21,35] which is absent in the Cu(II) compounds.

Results and Discussion

Ligands. Pyridine donors are useful mimics for ligating groups at the enzyme active sites because they are good donor atoms for both the cuprous and cupric oxidation states,[31b,35a] potentially allowing for reversible redox chemistry. Pyridine also approximates the imidazole group of the protein binding sites in its pK_a value more closely than do other donors such as pyrazole.[21,36]

Incorporating the py$_2$ tridentate moiety into the xylyl binucleating ligand[37] to form I yields just one ligand in a large series which allows for systematic studies.[13] By varying the donor groups (pyridine or others), the number of methylene groups between ligating termini and the connectivity between the tridentate donors (xylyl group, alkyl, etc.), the structural and redox properties of the metal ion(s) and the effective metal···metal distance may be controlled. In monomeric Cu(I)–Cu(II) systems including complexes possessing the py$_2$ moiety, we have already shown that the chelate ring size has a dramatic effect upon the structural and redox properties of its copper ion chelates.[31b,32,33,40]

Binuclear Cu(I) (II). The paucity of well-characterized low-coordinate complexes of Cu(I) containing unsaturated nitrogen ligands warrants the current extensive investigations in this area.[15] To our knowledge, only two other compounds have been reported[21,29] which contain 3-coordinate Cu(I) with all nitrogen ligands and no Cu(I)–Cu(I) interactions. While in the past the tendency for disproportionation and extreme lability have made the synthesis of Cu(I) compounds difficult, it is seen that chelating ligands containing "soft" nitrogen donors can help overcome these difficulties.[34] Compounds of Cu(I) with coordination numbers varying from 2[11c,41] to 5[42] are known, depending primarily on such ligand constraints.[34]

Complex II is stable indefinitely under inert atmosphere and it is soluble in polar organic solvents. It undergoes an extensive addition chemistry,[15] reacting with a variety of donors L such as CO, phosphines, phosphites, olefins, and sulfides to form tetracoordinate complexes formualted as $\mathrm{Cu_2}(m\text{-XYLpy}_2)\mathrm{L_2}^{+2}$. The structure for L = $\mathrm{PPh_3}$ has been determined;[43] each Cu(I) atom is in a pseudotetrahedral environment with coordination to the py$_2$ unit and to L; the copper(I) ions are well separated, Cu···Cu = 9.925 Å.

It is of interest to compare the Cu(I)–$\mathrm{N_{heterocyclic}}$ (heterocycle = derivatives of imidazole, pyrazole, pyridine, or pyrazolylborate) bonding distances found in a variety of complexes of Cu(I) including II, in which Cu(I) is 2-, 3-, or 4-coordinate. A survey of these complexes indicates very definite ranges for the Cu(I)–N distances. Thus, Cu–N bond lengths fall in the range 1.86–1.88 Å[11c,41] in nearly linear 2-coordinate Cu(I) complexes, 1.88–2.02 Å[21,29,30,34,44,45] in 3-coordinate compounds, and 1.98–2.04 Å[21,31b] in 4-coordinate complexes. EXAFS studies indicate that the average Cu–N bond distance in deoxy Hc (where there are at least two imidazole nitrogen ligands[9,46-48]) is 1.95 (±0.02–0.03) Å.[8-10] Comparison of this bond length with the coordination compound ranges cited suggests the likelihood of 3-coordinate Cu(I) (rather than 2[8-10]) in deoxy Hc. Also supporting this hypothesis is the observed ability of deoxy Hc to bind CO, which is consistent with the findings that while 2-coordinate Cu(I) complexes fail to bind CO, 3-coordinate Cu(I) compounds do.[11c,44b,c]

Reaction of II with Dioxygen. II is a 3-coordinate binuclear Cu(I) moiety where two of the three donors are aromatic nitrogen ligands, thus mimicking some of the established coordination properties of the protein active centers. Also, the stoichiometry of its reaction with $\mathrm{O_2}$ and the products are highly reminiscent of the copper monooxygenases.[7]

The product of the reaction is the binuclear Cu(II) complex IIIB, where two atoms of O have been incorporated. One atom of O is a phenolate oxygen, which bridges the two Cu(II) ions in the oxygenated product. Thus, the aromatic ring (connecting the two py$_2$ tridentate groups) of the XYL binucleating ligand has been hydroxylated, formally an insertion of an O atom into the aromatic C–H bond. The other O atom in the product is part of a hydroxide bridging ligand, where the formal oxidation state of the oxygen atom is −2. Thus, the overall stoichiometry of the reaction involves a two-electron process and can be described as

$$\mathrm{XYL{-}H + 2Cu^{+} + O_2 \rightarrow 2Cu^{+2} + OH^{-} + XYL{-}O^{-}}$$

where XYL–H is the binucleating ligand I and –H is the site of hydroxylation.[49] As in the copper monooxygenases, this stoichiometry implies that the source of the phenolic oxygen is dioxygen. This is proven for the transformation II → IIIB by studying the stoichiometry of the reaction by manometric measurement of the $\mathrm{O_2}$ uptake and by mass spectrometric analysis of the product IIIB made by using labelled $^{18}\mathrm{O_2}$.

The oxygenation of II in acetone, DMF, or dichloromethane by the introduction of $\mathrm{O_2}$ to the yellow-brown solution or sus-

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pension of II results in a rapid color change to a give a soluble dark green product, IIIB, which can be isolated in high yield (>90%). Manometric measurements indicate that the stoichiometry of dioxygen uptake is one mole of O_2 per mole of binuclear complex II (Cu:O_2/2:1) which is strongly indicative that both atoms of oxygen in IIIB come from dioxygen. Field desorption mass spectrometric measurements on IIIB also demonstrate incorporation of two ^{18}O atoms per molecule of the binuclear complex (Experimental Section). One atom of ^{18}O is found in the isolated free phenol IV (Figure 1). Thus, dissolution of IIIB in dichloromethane followed by extraction with aqueous ammonia removes the copper ions producing IV, whose identity is confirmed by its ^1H NMR spectrum and mass spectrometry (Experimental Section).

Properties of IIIB. The synthesis and characterization of copper complexes of binucleating ligands containing a phenolate donor has become popular in recent years.[30,50–52] The focus of attention has been the use of these and related systems to model the type 3 binuclear sites of the copper proteins.[1b,51a]

The structure of the phenolate- and hydroxy-bridged binuclear Cu(II) compound IIIB (Figures 3 and 4) is nearly identical with the corresponding methoxy-bridged complex IIIA which we previously reported.[14] They both contain tetragonally coordinated Cu(II) ions, with phenolate and X (X = OH^-, OMe^-) double bridging. In both cases, the Cu_2O_2 unit is essentially planar and Cu···Cu $\cong$ 3.1 Å, thus the bridging angles about Cu and O are very similar. The UV–VIS absorption spectra of IIIA and IIIB in CH_3CN solution (see Experimental Section) exhibit charge transfer (CT) bands at 340 (Cu(II) $\leftarrow$ OH^- LMCT[53,56b]), and 378 (Cu(II) $\leftarrow$ ^-OPh) LMCT[21,54]), and 635 nm (d–d transitions).

As outlined above, spectroscopic evidence including EXAFS studies on oxy or met-Hc derivatives point to tetragonal tetra- or pentacoordination about Cu(II) ions which are bridged by the endogenous phenolate (or OR^-) ligand, two or three imidazole donors, and an exogenous ligand X. The only feature of III not conforming to the model proposed for the protein centers is the shorter Cu···Cu distance. This separation is suggested to be in the range of 3.4$\sim$3.65 Å for Hc complexes of the ligands X = O_2^{2-}(oxy), N_3^-, F^-, and H_2O.[10] Only one-atom bridging is possible for ligands such as H_2O and F^-, and at the Cu···Cu distances observed, this would lead to unreasonably long Cu–X bond distances and/or nonbonded contacts between X and the phenolate oxygen atom.[10] Thus, these ligands are presumed to be terminally coordinated with only the endogenous bridge remaining. For 1,2-peroxide or 1,3-azide which would give two-atom or three-atom bridging, respectively, the Cu···Cu distances given by EXAFS analysis are reasonable. This is also in accord with a model system recently described by Reed and co-workers,[55] where a doubly bridged binuclear Cu(II) complex with 1,3-bound azide has a Cu···Cu distance of 3.61 Å, close to that of met-azido Hc.[10]

In a number of singly hydroxy-bridged binuclear Cu(II) complexes,[39b,56] the Cu···Cu distances are 3.38[56c] and 3.57–3.65 Å.[39b,56a,b] These values are close to those found in the Hc derivatives mentionzed above[10] and suggest that these coordination complexes might accomodate a second two-atom or three-atom bridging ligand.[55] When there is a second one-atom bridging ligand, the Cu···Cu distance is always 3.1 Å or less, as is found in numerous complexes containing $Cu_2(OR)_2$ (R = H, alkyl, aryl)[57] or for $Cu_2(OH)(H_2O)$.[58] We suggest that in the active site of Hc, it is possible for the protein backbone structure to control the stereochemistry of the ligating groups such that the Cu(II) ion centers are not capable of closer approach than about 3.4 Å, even with the endogenous bridge. At these distances, only ligands capable of 1,2- or 1,3-interactions can have stable bridging coordination. Perhaps, the binding and/or reactivity of a reduced dioxygen species is controlled by such coordination constraints.

In IIIB, the bridging OH^- ligand can be substituted by other ligands and we have characterized some of these by X-ray diffraction. Thus, IIIB reacts with HX (X = N_3^-, Cl^-) to form X-bridged complexes.[59] In the case of the azide complex, 1,1-bridging is observed, consistent with the structural features discussed above.

Biological Relevance and Conclusions. The development and characterization of the systems I $\rightarrow$ IV had led to a unique chemistry with possible relevance to (i) the active site chemistry in the oxygen carrier Hc and the monooxygenase tyrosinase and (ii) the development of synthetic systems which utilize O_2 for the oxygenation of organic substrates. The system has significant potential in leading to the determination of (a) mechanisms of Cu-mediated hydroxylation, (b) the nature of Cu–O_2 intermediates, and (c) those coordination and electronic factors necessary for O_2 activation. Although, other examples of copper-mediated monooxygenation are known,[4,20,60–62] in most of the systems reported the yields are low, structural information is lacking, and oxygen incorporation from molecular O_2 has not been clearly established.

It is interesting to note that a complex exactly corresponding to II in all features, except containing pyrazole (instead of pyridine) donors, failed to effect introduction of oxygen into the organic ligand.[21] We and others[19–21] have found that oxygenations of most Cu(I) complexes result in the formation of hydroxy-bridged Cu(II) complexes. These findings indicate that the oxygenation of organic substrates by copper–oxygen species may require a very fine tuning of the coordination geometry and/or electronic environment of the copper[21] in order to produce the proper "active" oxygenation agent.[63] Since, in some runs we also get small amounts of unidentified oxidized products in which the ligand is not hydroxylated, there is probably a delicate kinetic balance between the possible courses of reaction.[64]

The development of the model monooxygenase system presented here demonstrates the validity of the model approach in the biochemistry of copper and the field of biomimetic chemistry.[2–4,65] The aim is not necessarily to duplicate all of the chemical and physical characteristics that a particular biological target system possesses. Rather, by careful design and systematic studies of

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systems where one or more pertinent features (e.g., spectral, structure, ligand type required, redox behavior expected, etc.) can be examined in detail, one strives to elucidate those factors contributing to the observed unique characteristics possessed by the natural system. From this point of view, it may be expected that the model approach will yield certain kinds of information unavailable directly from studies of the proteins.[1]

Further chemical investigations of I–IV and their analogues are in progress, in order to identify Cu–O_2 intermediates and elucidate those structural and electronic factors required for this copper ion mediated oxygenation.

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Registry No. I, 79854-06-1; II, 82731-39-3; IIIB, 86593-51-3; IV, 89017-39-0; $Cu(CH_3CN)_4PF_6$, 64443-05-6; α,α′-dibromo-*m*-xylene, 626-15-3; bis(2-(2-pyridyl)ethyl)amine, 15496-36-3; diisopropylethylamine, 7087-68-5; 2-vinylpyridine, 100-69-6; *m*-xylylenediamine, 1477-55-0; oxygen, 7782-44-7; monooxygenase, 9038-14-6.

Supplementary Material Available: Listings of structure factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for compounds II (Tables VI–X) and IIIB (Tables XI–XV) (48 pages). Ordering information is given on any current masthead page.

Addition of Fluorenylidene to 1,2-Dichloroethylenes. Effects of Additives and the Question of Spin-State Equilibrium[†]

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Abstract: The photolysis of diazofluorene in *cis*- and *trans*-1,2-dichloroethylene has been studied. While cyclopropanation of the trans isomer is >92% stereospecific, the stereoselectivity of addition to the cis isomer is less than 86%. In the presence of styrene or butadiene the degree of stereoselectivity increases, and both the absolute and relative yields of an adduct formed via rearrangement of a diradical intermediate, 9-(2,2-dichloroethylidene)fluorene, decrease. An opposite trend both in stereoselectivity and yield of rearrangement product is observed when reaction mixtures are diluted with hexafluorobenzene. Other diluents, trichlorotrifluoroethane, perfluoromethylcyclohexane, tetramethylsilane, and benzene, have little effect on the stereoselectivity of cyclopropanation. In the presence of the highly reactive substrate methanol, the stereoselectivity of cyclopropane formation from *cis*-1,2-dichloroethylene is also unperturbed. It is suggested that both singlet and triplet fluorenylidene are present as reactive intermediates, singlet reacting with dichloroethylene exclusively by stereospecific cis addition and triplet fluorenylidene yielding stereoisomeric cyclopropanes and rearrangement product via a diradical adduct. Interconversion of these carbene spin states seems to be rapid compared to their reactions with dichloroethylene and methanol, but not so rapid as the reactions of triplet fluorenylidene with styrene and butadiene. The effect of hexafluorobenzene may be to form a carbenoid that can mimic triplet fluorenylidene.

The addition of carbenes to olefins yielding cyclopropanes is a reaction both preparatively and mechanistically useful.[1] Traditionally the stereospecificity of cyclopropane formation has been the most frequently employed means to distinguish the spin states of reacting carbenes.[2] Quantitative assay of the ratio of singlet and triplet carbenes undergoing reaction has been difficult, however, because the ratio of stereoisomeric cyclopropanes formed from the triplet carbene is generally not known.[3] This problem does not exist for a reagent that gives quite different products from singlet and triplet carbenes.[4]

It has been reported that the 1,2-dichloroethylenes react to give products of different structure from the lowest singlet and triplet states of carbenes.[5–7] Singlet $:CBr_2$,[5] $:CCl_2$,[5] $:C(CO_2CH_3)_2$,[6] and $:C(C_6H_5)_2$[7] undergo addition to the *cis*-olefin with a high degree of stereospecificity (>90%) to yield *cis*-1,2-dichlorocyclopropanes, while triplet $:C(CO_2CH_3)_2$[6] and $:C(C_6H_5)_2$[7] give products of addition with rearrangement, $R_2C{=}CHCHCl_2$ (see Scheme I). That an organometallic carbenoid formed from $:CBr_2$ also gives a product of addition with rearrangement[8] injects a note of caution but does not lessen the utility of the 1,2-dihaloethylenes as reagents for mechanistic studies of carbenes, and their use has enabled us to present new evidence for the establishment of a mobile singlet–triplet equilibrium in the reactions of diphenylmethylene.[7]

The key step that avoids the formation of cyclopropanes from the reactions of previously studied triplet carbenes with 1,2-dichloroethylenes is believed to be a rearrangement by chlorine atom migration of diradical intermediate I in Scheme I. It is assumed that spin is conserved in the initial carbene additions, and therefore thermochemistry dictates that intersystem crossing must precede ring closure of I. Intersystem crossing must also then be a discrete step in the rearrangement sequence, but may occur after chlorine migration.

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