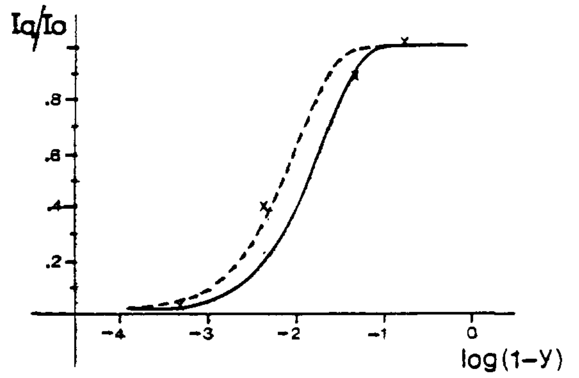

Figure 3. Proportion of fluorescence quenching (I_q/I_0) as a function of the logarithm of the concentration of quencher B, ($1 - y$), into A (m/m) for a ^{1}D randomly distributed system. Solid line: $n_c/2 = 25$; dashed line: $n_c/2 = 50$ (see eq 3).

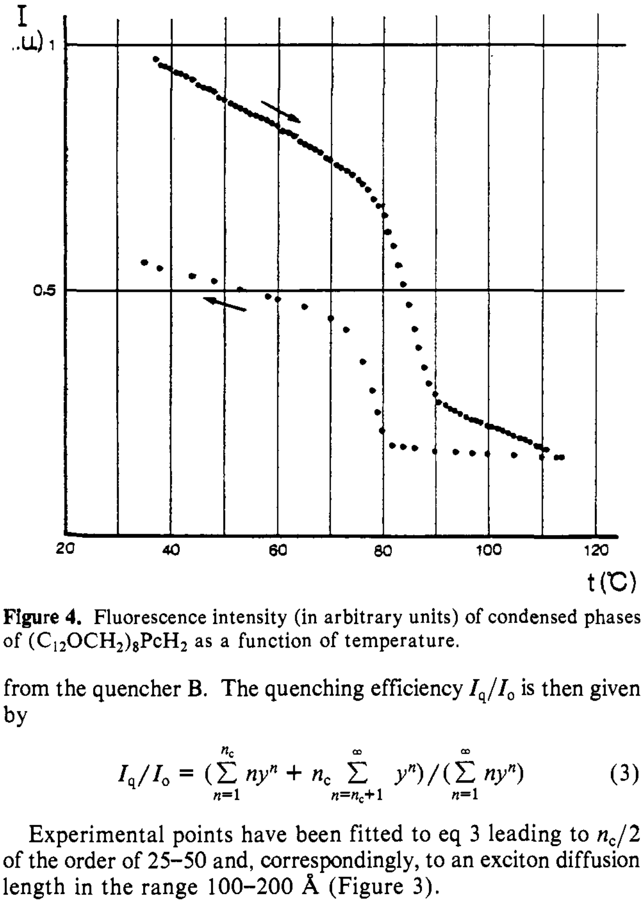

Figure 4. Fluorescence intensity (in arbitrary units) of condensed phases of $(C_{12}OCH_2)_8PcH_2$ as a function of temperature.

from the quencher B. The quenching efficiency I_q/I_0 is then given by

$$I_q/I_0 = \left(\sum_{n=1}^{n_c} ny^n + n_c \sum_{n=n_c+1}^{\infty} y^n\right)\Big/\left(\sum_{n=1}^{\infty} ny^n\right) \qquad (3)$$

Experimental points have been fitted to eq 3 leading to $n_c/2$ of the order of 25-50 and, correspondingly, to an exciton diffusion length in the range 100-200 Å (Figure 3).

The luminescence of $(C_{12}OCH_2)_8PcH_2$ has been studied as a function of temperature (Figure 4) indicating a strong fluorescence decrease when going from the solid to the mesophase. A hysteresis effect is observed by cooling down from the mesomorphic state and the characteristics of the solid are restored only after a few weeks. The effect of the incorporation of copper complex in the liquid crystal domain could not be accurately studied because of the low intensity of fluorescence. Luminescence properties of $(C_{12}OCH_2)_8PcH_2$ and the corresponding unsubstituted derivatives were studied in different phases: monomer or aggregates in solution, thin films, single crystals; these studies demonstrate that the least-ordered states yield to the lowest luminescence quantum yields. The low intensity of fluorescence in the mesophase is therefore probably related to a more disorganized state.[10]

In the present publication, the energy migration processes involved in ^{1}D molecular materials have been studied. This is a first step toward molecular superlattices in which two different molecular materials would be periodically alternated. Since the mean free path of charge carriers is of the order of 10 Å at room temperature in the case of molecular materials,[11] the superlattice period must be of the same order of magnitude.[14] Polymeric phthalocyanine derivatives have been synthetized for this purpose.[12]

Acknowledgment. This work was supported by C.N.R.S., M.R.E.S., C.N.E.T., and E.E.C. M. Bernard is acknowledged for technical assistance and D. Markovitsi for helpful discussions.

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Dioxygen-Copper Reactivity: Hydroxylation-Induced Methyl Migration in a Copper Monooxygenase Model System

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In this report, we describe a system in which a copper-ion mediated hydroxylation of an arene exhibits a mechanistic similarity to that known for the iron-dependent monooxygenases such as phenylalanine hydroxylase and cytochrome P-450. The overall process of hydroxylation-induced migration is reminiscent of the "N.I.H. shift"[1-3] and suggests that the reaction proceeds by the electrophilic attack of a $Cu(I)_n/O_2$ derived species upon the aromatic substrate.

We have previously described a chemical system in which an aromatic ring, which is part of a dinucleating ligand, is hydroxylated.[4,5] Here, the dinucleating ligand, *m*-XYL (**1**), in which two tridentate PY2 units (PY2 = bis[2-(2-pyridyl)ethyl]amine, **9**) are connected by a *m*-xylyl group, is employed. The three-coordinate dinuclear copper(I) complex **2** reacts with dioxygen, resulting in the oxygenation of the ligand and concomitant formation of the phenoxo- and hydroxo-bridged dinuclear Cu(II) complex **3**. The free phenol **4** can be isolated by leaching out the copper ions using a base extraction procedure.[4] The hydroxylation reaction, **2** + O_2 → **3**, is analogous to the reactions mediated by the copper monooxygenases such as tyrosinase[6,7] and dopamine *β*-hydroxylase[6b-8] since labeling studies on the enzymes and this

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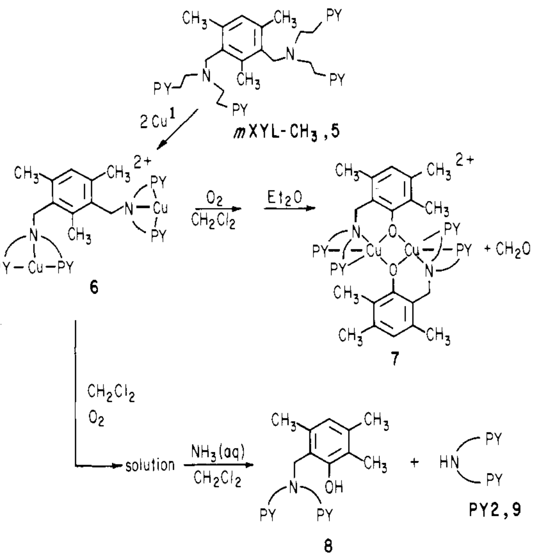
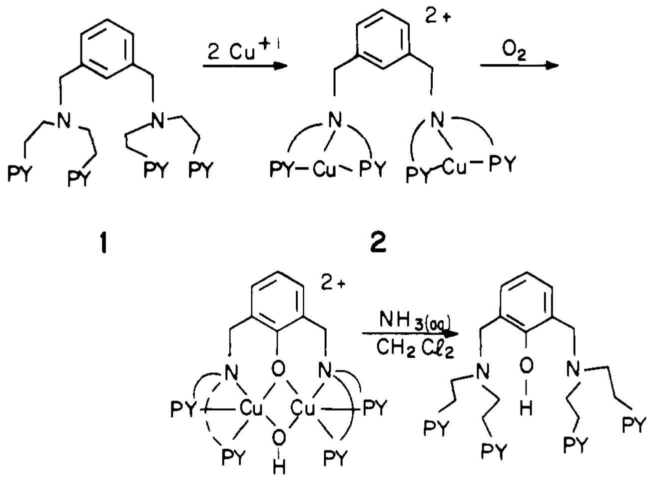


Figure 1. Scheme indicating the reactivity of $[Cu_2(m\text{-XYL-CH}_3)]^{2+}$ (**6**) with dioxygen, showing the hydroxylation-induced migration of a methyl group of the *m*-XYL-CH_3 ligand (**5**) to give either a dimeric phenoxo-containing Cu(II) complex **7** or the free phenol **8**. The other products of this reaction are the amine PY2 (**9**) and formaldehyde. Note that PY = 2-pyridyl. See text for further explanation.

model system show that one atom of O_2 is incorporated into the organic substrate and the stoichiometry of the reaction is Cu:O_2 = 2:1.



Here, we describe the case where a methyl group is placed in the 2-position of the *m*-xylyl dinucleating ligand, i.e., *m*-XYL-CH_3,[9] **5** (Figure 1). The addition of O_2 to $[Cu_2(m\text{-XYL-CH}_3)]^{2+}$ (**6**) results in hydroxylation of the *m*-XYL ligand with the concomitant migration of the methyl group on the aromatic ring; the loss of one PY2 arm (**9**) of the *m*-XYL-CH_3 ligand and the generation of formaldehyde (CH_2O) accompany this reaction (Figure 1).

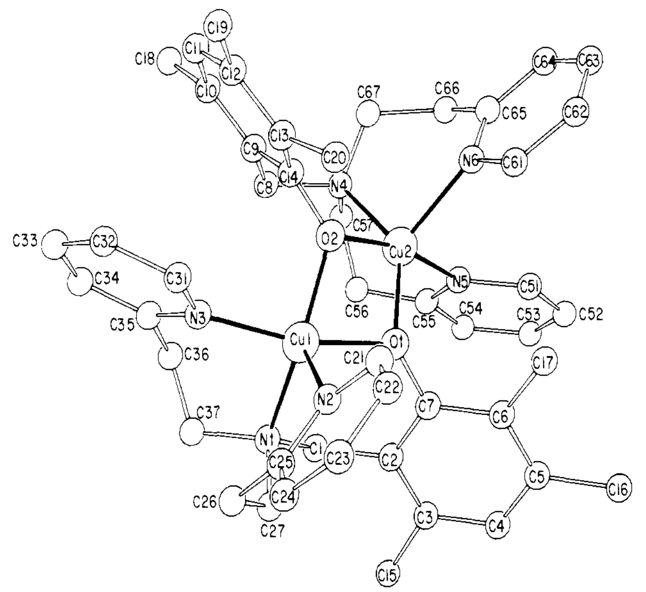


Figure 2. ORTEP diagram of the dicationic portion of complex **7** showing the atom labeling scheme. Selected bond lengths (Å) and angles (deg) are as follows: Cu···Cu 3.091; Cu1-O1, 1.908 (8); Cu1-O2, 2.051 (9); Cu2-O1, 2.037 (9); Cu2-O2, 1.924 (8); Cu1-N1, 2.112 (11); Cu1-N2, 2.183 (9); Cu1-N3, 1.953 (9); Cu2-N4, 2.157 (12); Cu2-N5, 1.959 (9); Cu2-N6, 2.159 (10); O1-Cu1-O2, 73.7 (3); O1-Cu1-N1, 93.8 (4); O1-Cu1-N2, 100.0 (3); O1-Cu1-N3, 162.6 (4); O2-Cu1-N1, 147.3 (4); O2-Cu1-N2, 118.4 (3); O2-Cu1-N3, 91.7 (4); N1-Cu1-N2, 93.2 (4); N1-Cu1-N3, 93.7 (4); N2-Cu1-N3, 95.3 (3); O1-Cu2-O2; 73.7 (3); O1-Cu2-N4, 138.8 (4); O1-Cu2-N5, 93.7 (4); O1-Cu2-N6, 126.4 (4); O2-Cu2-N4, 92.5 (4); O2-Cu2-N5, 165.9 (4); O2-Cu2-N6, 97.7 (4); N4-Cu2-N5, 93.1 (4); N4-Cu2-N6, 93.3 (4); N5-Cu2-N6, 94.9 (4); Cu1-O1-Cu2, 103.1 (3); Cu1-O2-Cu2, 102.0 (4).

The ligand *m*-XYL-CH_3 (**5**) is reacted with $Cu(CH_3CN)_4PF_6$[11] in CH_2Cl_2 under argon to produce the dicationic dicopper(I) complex $[Cu_2(m\text{-XYL-CH}_3)]^{2+}$ (**6**),[12] possessing two three-coordinate Cu(I) centers.[13] Complex **6** reacts with O_2 in dichloromethane (Cu:O_2 = 2:1, manometry[14]) to give a purple-brown product solution; when the copper ions are stripped from the complexed organic products by extraction with aqueous ammonia,[4] chromatographic isolation and separation (alumina, ethyl acetate/MeOH) provides the hydroxylated cleavage product **8** (68% isolated yield, field desorption, *m*/*z* 376, MH^+) and PY2 (**9**) (>40% isolated yield, field desorption, *m*/*z* 228, MH^+) (Figure 1).[15] The phenol oxygen atom in **8** was shown to be derived from dioxygen by carrying out the experiment with use of $^{18}O_2$ (>70% ^{18}O incorporation). The detection of CH_2O was made difficult by using this base extraction procedure (39% yield, with use of the Nash method[16]). However, when diethyl ether was added to the reaction product mixture of $[Cu_2(m\text{-XYL-CH}_3)]^{2+}$ (**6**) plus O_2, a dimeric copper complex **7** (>68% yield[17]), containing the

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(9) This dinucleating ligand was synthesized by the reaction of 2,4-bis(chloromethyl)mesitylene (Lancaster) with PY2[10] (**9**) in the presence of a base, followed by column chromatography.

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(12) Anal. for $[Cu_2(m\text{-XYL-CH}_3)](PF_6)_2\cdot 1.25CH_2Cl_2$ (**6**-$(PF_6)_2$). Calcd for $C_{40.25}H_{48.5}Cl_{2.5}Cu_2F_{12}N_6P_2$: C, 43.06; H, 4.36; N, 7.49. Found: C, 43.07; H, 4.41; N, 7.75. A ^1H NMR spectrum of **6**-$(PF_6)_2$ confirms the presence of the CH_2Cl_2 solvent of crystallization.

(13) We presume that **6**-$(PF_6)_2$ contains two three-coordinate Cu(I) centers since we have synthesized and crystallographically characterized several such examples of Cu(I) which contain the PY2 tridentate unit. See, for example, ref 4 and Blackburn et al. (Blackburn, N. J.; Karlin, K. D.; Concannon, M.; Hayes, J. C.; Gultneh, Y.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1984**, 939–940).

(14) The yields of products reported correspond to conditions where the reaction is allowed to proceed on a manometer setup until the dioxygen absorption reached a value of Cu:O_2 = 2:1. There appears to be some followup oxidation reaction occurring in this system, since when the oxygenation is allowed to proceed to completion, the dioxygen uptake is Cu/O_2 = 1:1. However, we have not detected any other products under such conditions, and the yields of **8** and PY2 (**9**) are comparable. The reaction is seen to be incomplete if O_2 is allowed only to be taken up in the ratio of Cu/O_2 = 4:1.

(15) A small but detectable amount of methylbis[2-(2-pyridyl)ethyl]amine was also isolated from the reaction by this procedure: field desorption, *m*/*z* 242 (MH^+).

(16) Nash, T. *Biochem. J.* **1953**, *55*, 416.

(17) Anal. Calcd for **7**-$(PF_6)_2\cdot CH_2Cl_2$, $C_{49}H_{58}Cl_2Cu_2F_{12}N_6O_2P_2$: C, 47.02; H, 4.68; N, 6.72. Found: C, 47.36; H, 4.69; N, 6.65. A ^1H NMR spectrum of a solution of **7**-$(PF_6)_2\cdot CH_2Cl_2$ which was reduced in situ with an excess of KCN in CD_3NO_2 confirmed the presence of the dichloromethane solvent.

deprotonated phenol **8**, was precipitated, and formaldehyde was detected in good yield (81%).

The X-ray crystallographic determination of the structure of **7** confirms the formation of the hydroxylated arene **8** and the regiochemistry of the methyl and hydroxyl groups in this compound. The structure of the dication **7** is shown in Figure 2.[18,19] The complex is a noncentrosymmetric dimer composed of distorted square-based pyramidal Cu(II) coordination spheres, which are joined by basal-edged (i.e., equatorial) μ-phenoxo ligands. Pentacoordination is completed by an amino (N1 or N4) and one pyridyl nitrogen atom (N3 or N5) in the remaining basal positions; the other pyridine nitrogen atoms (N2 or N6) occupy the axial sites and possess significantly longer $Cu-N_{py}$ bond lengths. The Cu···Cu distance is 3.091 Å.

We have already presented some evidence for the intermediacy of a peroxo–dicopper(II) complex in the hydroxylation reaction $\mathbf{2} + O_2 \rightarrow \mathbf{3}$.[20] Here, the observed methyl migration provides support for the notion that in the reaction of **2** or **6** with O_2 an electrophilic copper–oxy species (derived from the dicopper(I) complex plus O_2) attacks the arene, which then collapses to the observed products. Thus, in the reaction of **2** with O_2, it is suggested that the 2-H atom undergoes a 1,2-migration and is then lost as H^+ (probably to the resulting μ-hydroxy group[4]) during the rearomatization of an oxygenated intermediate (e.g., arene oxide[1–3,23] or carbenium ion intermediate[1–3,23]). Rather than lose CH_3^+ for the case of $\mathbf{6} + O_2$, the lone pair on one amine nitrogen atom can be seen to "assist" with resulting loss of the iminium ion, $[(PYCH_2CH_2)_2N{=}CH_2]^+$ (PY = 2-pyridyl), and formation of the copper complex derivative of **8** (**7**). The former product could readily undergo hydrolysis to give PY2 (**9**) and CH_2O under the reaction conditions employed.[24]

The transformation of *m*-XYL-CH_3 (**5**) to **8** represents the first example of a hydroxylation-induced migration of an alkyl group (i.e., "N.I.H. shift") involving copper ions.[25,26] For phenylalanine hydroxylase, examples of 1,2-shifts in 4-deuterio-,[27,28] 4-tritio-,[27a,28] 4-X- (X = halogen),[29,30] and 4-methyl-substituted[31] phenylalanines are established, and hydroxyl group migration has also been suggested[31] to account for the products observed in such reactions. The results described here for this copper monooxygenase model system also provide support for previous suggestions[32,33] that copper monooxygenases such as tyrosinase (and perhaps the copper-dependent phenylalanine hydroxylase[7]) proceed via electrophilic attack on the aromatic substrates.

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Supplementary Material Available: Listings of atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors (13 pages). Ordering information is given on any current masthead page.

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(18) Complex **7**-$(PF_6)_2 \cdot CH_2Cl_2$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.294$ (4) Å, $b = 22.347$ (7) Å, $c = 20.415$ (4) Å, $\beta = 98.98$ (2)°, $V = 5540$ (3) Å^3, and $Z = 4$. A Nicolet R3m diffractometer was used in the ω-scan mode to collect 5782 data ($0° \leq 2\theta \leq 40°$) of which 2675 data with $F_o \geq 6\sigma|F_o|$ were used in the solution and refinement. The positional parameters of the copper atoms were determined by the Patterson method. The remaining non-hydrogen atoms were located on difference Fourier maps. Hydrogen atoms were calculated and fixed at 0.96 Å from carbon; the phenyl and pyridyl rings were refined as rigid hexagons (d(C–C(N)) = 1.395 Å). The structure was refined to the current residual values of $R = 0.0786$ and $R_w = 0.0811$ (Mo Kα, $\lambda = 0.71069$ Å).

(19) Supplementary Material.

(20) (a) When a dicopper(II) species containing **1** is reacted with hydrogen peroxide, high yields of **3** are also obtained. See article cited in ref 13. (b) We also observed that when a 2-fluoro-substituted *m*-xylyl ligand is used (i.e., *m*-XYL-F, in which a fluorine atom is placed in the position that is hydroxylated), little or no hydroxylation occurs in the reaction of $[Cu_2(m\text{-XYL-F})]^{2+}$ with O_2. At low temperature, a spectrum of the adduct identified as $[Cu_2(m\text{-XYL-F})(O_2)]^{2+}$ (peroxo–dicopper(II) complex[21]) is observed.[22]

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Asymmetric Synthesis of Achiral Molecules: Meso Selectivity†

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In contemplation of a synthesis of the naturally occurring meso compound teurilene (**1**),[2] we were intrigued by the possible and unique advantage that asymmetric reactions might offer in the preparation of achiral molecules. To be specific, we wondered whether the chiral diepoxy diol ***d,l*-2** would give ***meso*-3**, a potential precursor to **1**, by way of an "end-to-end" reaction pathway involving base-catalyzed Payne rearrangement (***d,l*-2** → **4**), intramolecular epoxide opening (**4** → **5**), and bimolecular epoxide opening by hydroxide ion (**5** → ***meso*-3**). The sequence of stereoselective preparation of ***d,l*-2** followed by conversion to ***meso*-3** would constitute an example of what could be called a meso-selective process; it is of conceptual note that the optical purity of the sample of chiral precursor used in such a ploy would be irrelevant. Examples of the Payne rearrangement with substrates which require internal nucleophilic attack on a tertiary epoxide center are rare[3] and can require forcing conditions.[3a] Thus, an alternative "inside-out" pathway via initial bimolecular attack by $^{-}$OH (***d,l*-2** → **6**) and subsequent internal epoxide opening (**6** → ***d,l*-3**) was considered to be a potentially viable (albeit definitely undesirable, since it results in the *d,l*-diastereomer which is useless

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† Dedicated to Professor Harold W. Heine on the occasion of his 65th birthday.

(1) Fellow of the Alfred P. Sloan Foundation.

(2) Suzuki, T.; Suzuki, M.; Furusaki, A.; Matsumoto, T.; Kato, A.; Imanaka, Y.; Kurosawa, E. *Tetrahedron Lett.* **1985**, *26*, 1329.

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