siderable improvements in behavior should be possible with this system, since no attempts were made to optimize parameters such as film thickness and clay/PVA ratio in the present work. Experiments with different clay types and incorporated substances are also in progress. Finally the strategy employed here should be applicable to other types of materials of interest, such as zeolites[13] and silicas.[14]

Acknowledgment. We thank Dr. M. Krishnan for many helpful suggestions and for carrying out the film-thickness measurements; the support of the National Science Foundation (CH7903729) is gratefully acknowledged.

Registry No. Fe(bpy)$_3^{2+}$, 15025-74-8; TMAFe(Cp)$_2^+$, 86527-05-1; Ru(NH$_3$)$_6^{3+}$, 18943-33-4; Ru(bpy)$_3^{2+}$, 15158-62-0; SnO$_2$, 18282-10-5; Pt, 7440-06-4; C, 7440-44-0; PVA, 9002-89-5; MV^{2+}, 4685-14-7; montmorillonite, 1318-93-0.

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Dicopper Complexes of a Macrocyclic Ligand as Models for Type 3 Copper Proteins

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Recent chemical and physical studies on hemocyanin[1] and tyrosinase[2] derivatives allow the identification of certain basic requirements in synthetic models for these and probably other type 3 copper proteins. These include (i) a binucleating capability on the part of the synthetic ligand that permits a relatively close approach (3–4 Å) of the copper ions, (ii) accessibility of both Cu(I) and Cu(II) oxidation states, (iii) coordinative unsaturation of the metal ions in the reduced state, and (iv) a coordination polyhedron for each metal ion that includes two (or three) nitrogen donors. The provision of a bridging group that mediates antiferromagnetic coupling between the Cu(II) ions may also be important. Recently, several synthetic dicopper complexes that incorporate some or all of these features have been described[3] including some that exhibit (partially) reversible O$_2$-binding activity[3a,3b] (cf. hemocyanin) and monooxygenase[3f] or oxidase activity[3c,i,k,l] (cf. tyrosinase, laccase, etc.). We here report on the structures and properties of some dicopper(I) and dicopper(II) complexes of a macrocyclic ligand that also satisfy the requirements noted above and that, additionally, function as catalysts for the oxidation of several organic substrates, including catechols, in the presence of oxygen.

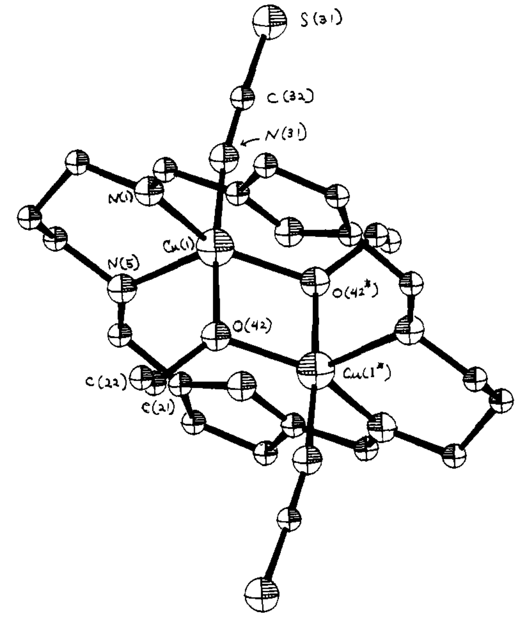
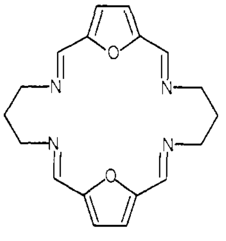


Figure 1. Structure of [Cu$_2$L(OEt)$_2$(NCS)$_2$]. Selected bond distances (Å): Cu(1)–N(1) = 2.108 (18); Cu(1)–N(5) = 2.282 (19); Cu(1)–O(42) = 1.943 (14); Cu(1)–N(31) = 1.919 (23).

The macrocycle L (1) was synthesized as the complex BaL(ClO$_4$)$_2$·EtOH from 2,5-diformylfuran and 1,3-diaminopropane by use of Ba^{2+} ion as a template.[4] Replacement of Ba^{2+} by Cu^{2+} led to a series of diCu(II) complexes including Cu$_2$L(OH)$_2$(ClO$_4$)$_2$·H$_2$O (2), [Cu$_2$L(OR)$_2$(MeCN)$_2$][BPh$_4$]$_2$ (3), and [Cu$_2$L(OR)$_2$(NCS)$_2$] (4) (R = Me, Et, *n*-Pr). The structure[5] of [Cu$_2$L(OEt)$_2$(NCS)$_2$] (4) is shown in Figure 1. Each Cu(II) ion is bonded to two imino nitrogens of the macrocycle, the nitrogen of one (terminally bound) thiocyanate ion, and to two bridging ethoxide groups in an approximate trigonal-bipyramidal geometry. The two metal ions are displaced by 0.57 Å on opposite sides of the roughly planar macrocycle so that each bridging ethoxide occupies an axial site in the coordination sphere of one metal ion and an equatorial site of the other. The Cu···Cu separation is 3.003 (4) Å. The furan oxygens are not coordinated (Cu···O > 2.95 Å).



(1)

The complexes (3) have nearly identical ligand field spectra with those of 4 (λ_{max} 715, 1070 nm) and therefore undoubtedly have closely similar structures. The spectrum of 2 is different

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(5) All complexes gave satisfactory C, H, and N analyses for the formulae indicated: data supplied to referees.

(6) Crystal data: monoclinic, a = 15.356 (9) Å, b = 10.239 (11) Å, c = 18.662 (10) Å; β = 102.5 (1)°; Z = 4; space group $I2/c$; Mo Kα radiation; 1023 independent reflections above background refined to R 0.073.

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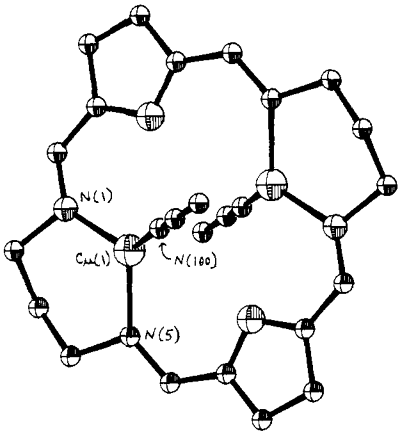


Figure 2. Structure of the $[Cu_2L(MeCN)_2]^{2+}$ cation. Selected bond distances (Å) and angles (deg): Cu(1)-N(1) = 1.958 (18); Cu(1)-N(5) = 1.971 (19); Cu(1)-N(100) = 1.919 (16); N(1)-Cu(1)-N(5) = 101.4 (8); N(1)-Cu(1)-N(100) = 129.7 (7); N(5)-Cu(1)-N(100) = 124.7.

(λ_{max} 680 nm) and suggests a tetragonal type of coordination. In both series of bis(μ-alkoxo) complexes **3** and **4** the pairs of Cu(II) ions are strongly antiferromagnetically coupled with $2J$ in the range -600 to -700 cm^{-1}; the dihydroxo complex is less strongly coupled, however.[7]

All the dicopper(II) complexes undergo reduction simply by heating their solutions in MeCN. For **4** the product is $[Cu_2L(SCN)_2]$ (**5**) previously shown[8] to contain two tetrahedrally coordinated Cu(I) ions, 2.796 (8) Å apart, intramolecularly linked via the sulfur atoms only of the thiocyanate ions. For **2** and **3** the reduction product is the diamagnetic complex $[Cu_2L(MeCN)_2]Y_2$ [Y = ClO_4 or BPh_4 (**6**)] in which each three-coordinate Cu(I) ion is bonded to two macrocycle nitrogen donors and to the nitrogen of one MeCN molecule (Figure 2). The stereochemistry is distorted trigonal planar with the Cu(I) ions displaced 0.23 Å, on opposite sides, from the N_3 planes.[9] The Cu···Cu separation is 3.35 Å.

In the presence of certain substrates the reduction of **2** or **3** is accompanied by substrate oxidation according to eq 1. Thus,

$$Cu^{II}(OH)_2Cu^{II} + H_2X_2 \text{ (or 2HX)} = Cu^{I}\cdots Cu^{I} + X_2 + 2H_2O \qquad (1)$$

for example, PhSH, PhC≡CH, hydrazobenzene, catechols, hydroquinone, and ascorbic acid afford respectively PhSSPh, PhC≡CC≡CPh, azobenzene, *o*-quinones, *p*-quinone, and dehydroascorbic acid, together with **6** or other dicopper(I) complexes. When carried out in dimethylformamide solution in the presence of O_2, several of the oxidations proved to be catalytic in **2** or **3** but not **4**, with, as shown by O_2-uptake measurements, a O_2/substrate (H_2X_2 or 2HX) stoichiometry of 0.5 ± 0.02 (see Figure 3 for typical results on the oxidation of 3,5-di-*tert*-butylcatechol).[10] No induction period was observed and the catalytic oxidation was equally successful whether the catalysts were the diCu(II) complexes **2** or **3** or the dicopper(I) complex **6**. The inactivity of complex **4** reflects the need for coordinative unsaturation in the reduced state while the very poor activity of (mononuclear) $Cu(ClO_4)_2\cdot 6H_2O$ indicates the importance of a "built-in" dicopper site.

A significant observation was the consumption by (**6**) of only 0.5 ± 0.03 mol O_2 per dicopper(I) unit in the *absence* of substrate.

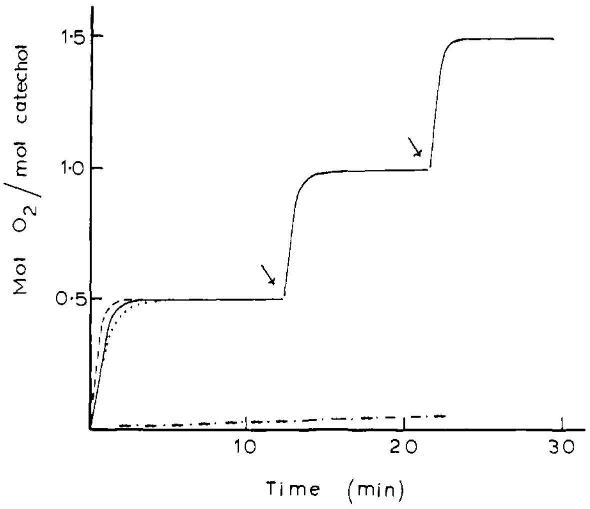


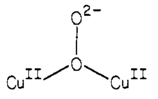
Figure 3. Uptake of O_2 (1 atm initial pressure) by solutions of 3,5-di-*tert*-butylcatechol in dry dimethylformamide (7×10^{-3} M) containing different copper complexes (3.5×10^{-4} M) at 30 °C: $Cu_2L(OH)_2(ClO_4)_2\cdot H_2O$ (—); $[Cu_2L(OEt)_2(MeCN)_2][BPh_4]_2$ (- - -); $[Cu_2L(MeCN)_2][BPh_4]_2$ (···); $Cu(ClO_4)_2\cdot 6H_2O$ (7×10^{-4} M) (-·-·-). The arrows denote fresh additions of catechol.

This contrasts with the 1:1 O_2/Cu_2 stoichiometry found for hemocyanin[1] and tyrosinase[2] as well as other model compounds[3b,j] including the dicopper(I) complex[3c] of a related, but larger, macrocycle and suggests that each O_2 molecule is associated in its reduction, with four copper atoms rather than two. Such a situation could occur if the initial coordination of O_2 by **6** is followed, in the absence of substrate, by a fast bimolecular two-electron transfer with a second molecule of **6** to generate the μ-oxo species[11] **8** (eq 2 and 3), this possibly having an aggregate (dimeric)

$$\underset{\mathbf{6}}{Cu^{I}\cdots Cu^{I}} + O_2 \rightarrow \underset{\mathbf{7}}{Cu^{II}—(O_2)^{2-}—Cu^{II}} \qquad (2)$$

$$\underset{\mathbf{7}}{Cu^{II}—(O_2)^{2-}—Cu^{II}} + \underset{\mathbf{6}}{Cu^{I}\cdots Cu^{I}} \rightarrow \underset{\mathbf{8}}{[Cu^{II}—O—Cu^{II}]_2} \qquad (3)$$

structure such as found for the complexes $[Cu_4L_2(C{\equiv}CPh)]^{3+}$[12] and $[Cu_6L_3(SPh)_2]^{4+}$[13] of the same macrocycle. Aggregate structures containing oxo-bridged Cu(II) ions have been described previously.[14] The occurrence in **4**, **5**, and **6** of Cu···Cu distances (2.80–3.35 Å) significantly smaller than those proposed for hemocyanin (~3.6 Å) leads to the speculation of a μ-1,1-$[O_2]^{2-}$ bridge structure (**9**) for the initially formed adduct as an alter-



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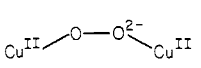

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native to the two-atom μ-1,2-$[O_2]^{2-}$ bridge (**10**) believed to occur in the natural systems. A μ-1,1-$[O_2]^-$ superoxo bridgc between Al(III) ions has recently been reported.[15]

Registry No. 2, 86497-55-4; **3** (R = Me), 86497-57-6; **3** (R = Et), 86497-61-2; **3** (R = *n*-Pr), 86507-89-3; **4** (R = Me), 86497-58-7; **4** (R = Et), 86507-87-1; **4** (R = *n*-Pr), 86497-59-8; **5**, 78809-10-6; **6** (Y = ClO_4), 86507-91-7; **6** (Y = BPh_4), 86527-01-7; PhSH, 108-98-5;

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[7] The magnetic data for **2** (μ_{eff} = 1.37 μ_B at 293 K, 0.70 μ_B at 93 K) do not conform to that required for coupled *pairs* of $S = {}^1/_2$ spins, possibly because of additional intermolecular interactions between metal ions of adjacent macrocyclic units (see subsequent discussion).

[8] Nelson, S. M.; Esho, F.; Drew, M. G. B. *J. Chem. Soc., Chem. Commun.* **1981**, 388.

[9] Crystal data for $[Cu_2L(MeCN)_2][BPh_4]_2$: monoclinic, a = 10.45 (1) Å, b = 13.72 (1) Å, c = 18.08 (1) Å; β = 97.0 (1)°; Z = 2; space group $P2_1/n$; Mo Kα radiation; 1212 independent reflections above background refined to R 0.075.

[10] Parallel results were obtained for the oxidation of hydroquinone, ascorbic acid, and PhSH.

[11] Attempts to isolate this material in a pure form have not so far been successful; present indications are that it is very easily hydrated/hydrolyzed to re-form **2**.

[12] Drew, M. G. B.; Esho, F.; Nelson, S. M. *J. Chem. Soc., Chem. Commun.* **1982**, 1347.

[13] Drew, M. G. B.; Esho, F.; Nelson, S. M., unpublished results. In this "triple-decker" structure each four-coordinate sulfur atom is bonded to two Cu atoms of one macrocyclic unit and to one Cu atom of a second.

[14] Davies, G.; El-Shazly, M. F.; Rupick, M. W.; Churchill, M. R.; Rotella, F. J. *J. Chem. Soc., Chem. Commun.* **1978**, 1045.

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PhC≡CH, 536-74-3; 1,2-benzenediol, 120-80-9; hydrazobenzene, 122-66-7; hydroquinone, 123-31-9; ascorbic acid, 50-81-7.

Supplementary Material Available: Listing of atomic coordinates, thermal parameters, and molecular dimensions for **4** and **6** (15 pages). Ordering information is given on any current masthead page.

Photochemical H_2 Generation by Visible Light. Sensitization of TiO_2 Particles by Surface Complexation with 8-Hydroxyquinoline

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The surface modification of large band gap semiconductors such as TiO_2 and SnO_2 by adsorbed or covalently linked photoactive dyes is a subject of increasing investigation[1,2] in view of potential applications to solar energy conversion. In both photoelectrochemical cells[1] and H_2-generating photochemical systems,[2] the phenomenon of photosensitized charge injection is used to effect charge separation with light of less than band gap energy. We wish to report here our preliminary results concerning the surface modification of anatase TiO_2 by the prototype dye 8-hydroxyorthoquinoline (HOQ) and the ability of such modified TiO_2 powders to generate H_2 in a sacrificial water reduction system using visible light. Initial evidence for H_2 production via a charge injection mechanism will be presented.

When powdered TiO_2 is introduced into aqueous solutions of HOQ (solubility $\leq 4 \times 10^{-3}$ M), a bright yellow orange color develops on the powder while the supernatant absorption spectrum shows simply a decrease in free HOQ.[3] No pH change accompanies this process. We believe that the color change is due to the formation of surface Ti(IV)-OQ complexes, most likely through the so-called "esterification" of surface hydroxyl groups with concomitant loss of water. Such reactions between TiO_2 and other alcohols are well documented.[4] Our evidence for this reaction is twofold. First, color development in samples where HOQ is added to optically transparent TiO_2 colloid[5] is quite slow and is considerably slower in base than in acid. HOQ (10^{-4} M) adsorption onto 1 g/L TiO_2 is complete in 1 h at pH 2.5 and in 5 days at pH 12.8. Second, the spectrum of the HOQ-modified colloidal TiO_2 differs greatly from that of either free HOQ, OQ^-, or H_2OQ^+ (Figure 1). Both the position and intensity of the 380-nm absorption band are very similar to that observed for $M(OQ)_n$ complexes where M is a closed d-shell metal ion. This transition has been assigned as a ligand localized transition for all such complexes.[6,7]

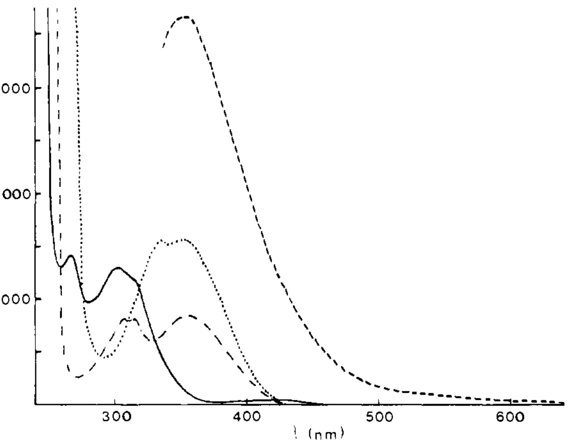

Figure 1. Optical absorption spectra of HOQ: (—) in neutral H_2O; (···) pH 10, (----) pH 1.6, (- - -) on colloidal TiO_2 (1 g/L) at pH 2.5 (vs. colloidal TiO_2 reference).

Table I. Comparison of the Sensitizing Ability of HOQ and a Surfactant Ruthenium Bipyridyl Complex for Different Anatase TiO_2 Powders in a Sacrificial H_2-Generating System

	μL H_2/h[a]
HOQ on TiO_2	
Degussa P-25	300-420
Bayersol	800-1220
TiO_2-U	750-1000
TiO_2-U without Pt[b]	310-350
$Ru(bpy)_2(4,4'\text{-tridecyl-}2,2'\text{-bpy})^{2+}$	
Degussa P-25	700-840
Bayersol	700-800
TiO_2-U without Pt[b]	800-1080

[a] In a 5-mL sample, 5-mL headspace. Range of values is the total obtained from 6-8 repeats. [b] H_2-generating catalyst in this case is 0.2% RuO_2 initially present on the TiO_2.

Complexation between HOQ and anatase TiO_2 powder was compared for three powders, Degussa P-25 (surface area 55 m^2/g), Bayer "Bayersol" (surface area 180 m^2/g), and Montedison TiO_2-U, an anatase powder doped with 0.4% Nb and loaded with 0.2% RuO_2 by weight (surface area ~ 200 m^2/g). In saturated aqueous solutions of HOQ containing 1 g/L TiO_2, HOQ uptake was found to be 300 μequiv/g for Degussa P-25, 800 μequiv/g for Bayersol, and 1000 μequiv/g for TiO_2-U. These data are consistent with a previous report of 200 μequiv/g for uptake of HOQ by Degussa P-25 from benzene solution[3] and indicate that complexation is roughly proportional to surface area. Emission, typically an easily detectable property of HOQ and closed d-shell $M(OQ)_n$ complexes,[6,7] could not be detected from either solid samples of HOQ modified TiO_2 powder or modified colloidal TiO_2 at room temperature using a Perkin-Elmer MPF 44A spectrofluorimeter. Nanosecond flash photolysis[8] of HOQ-modified TiO_2 colloid showed no emission or transients, indicating that the excited state lifetime or the surface Ti(IV)-OQ complex is less than the 11-25 ns typically observed for emissive $M(OQ)_n$ complexes in DMF.[7] Exaustive photolysis of the same samples with ≥435-nm light resulted in no photodecomposition after 17 h.

HOQ-modified TiO_2 powder proved to be an excellent photosensitizing agent in the following sacrificial water reduction system. Samples, 5 mL, were made up containing 10^{-3} M HOQ equilibrated with 5 mg of TiO_2 powder, 2×10^{-2} M EDTA as a sacrificial electron donor, and 10 mg/L Pt (0) sol.[9] For comparison, analogous samples were made up in which 10^{-4} M surfactant $Ru(bpy)_2(4,4'\text{-tridecyl-}2,2'\text{-bpy})^{2+}$ was physisorbed onto the TiO_2, and HOQ was omitted. At these concentrations, light absorption by the insoluble ruthenium complex is 2-6 times that of the HOQ-modified TiO_2, depending on the surface area of the TiO_2 used, and light absorption ≥435 nm by free HOQ is negligible.

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[8] Laser flash equipment is described in: Rothenburger, G.; Infelta, P.; Grätzel, M. *J. Phys. Chem.* **1981**, *85*, 1850-1856.

[9] See: Brugger, P. A.; Cuendet, P.; Grätzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 2923-2927, for Pt preparation. Centrifugation and supernatant analysis confirmed that complete deposition of Pt onto the TiO_2 particles takes place. Platinization of TiO_2 by sol deposition prior to complexation by dye results in a system with slightly less activity but with similar stability.

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