A Minimalist Approach to C–H Activation by Copper

by **Anita Kuebel-Pollak**[a]), **Stéphane Rüttimann**[a]), **Nichola Dunn**[a]), **Xavier Melich**[a]), **Alan F. Williams***[a]), and **Gérald Bernardinelli**[b])

[a]) Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, 30 quai Ernest Ansermet, CH-1211 Genève 4 (phone: +41 22 379 64 25; fax: +41 22 379 68 30; e-mail: Alan.Williams@chiam.unige.ch)

[b]) Laboratory of X-Ray Crystallography, University of Geneva, 24 quai Ernest Ansermet, CH-1211 Genève 4

Dedicated to Professor *Andreas Zuberbühler* on the occasion of his retirement

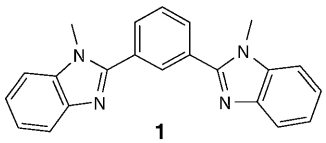
The complex $[Cu_2(\mathbf{1})_2]^{2+}$ (**1** = 1,3-bis(1-methyl-1*H*-benzimidazol-2-yl)benzene) undergoes slow oxidation by dioxygen in DMF solution to give the hydroxylated product $[Cu_2(\mathbf{2}\text{-H})_2]^{2+}$ (**2** = 2,6-bis(1-methyl-1*H*-benzimidazol-2-yl)phenol) characterized by an X-ray crystal-structure analysis. The oxidation occurs much faster when Cu^{II} is mixed with **1** in the presence of H_2O_2, with 80% hydroxylation observed within a few minutes. The mononuclear complex formed with 1-methyl-2-phenyl-1*H*-benzimidazole (**3**) shows no hydroxylation under these conditions. It is concluded that the hydroxylation requires the presence of a ligand capable of stabilizing a binuclear species, but no special coordinative activation of the copper is required.

Introduction. – Although the C–H bond is traditionally regarded as difficult to oxidize in the laboratory, Nature has developed a large number of enzymes capable of activating the C–H bond in an efficient and controlled way. The enzyme tyrosinase is a good example of this and uses a dicopper centre to transform the phenol of tyrosine to an *ortho*-catechol [1][2]. Tyrosinase is structurally similar to the oxygen-carrying protein hemocyanin [3], and both have been the subject of intensive modelling with low-molecular-weight coordination compounds. Hydroxylation of a model complex of Cu^I containing a ligand with two tridentate centres separated by a *meta*-xylyl spacer was reported as long ago as 1981 by *Karlin et al.* [4], and some years later *Feringa* and co-workers showed a similar effect using a bis-bidentate ligand [5]. Since then, a number of other workers have published similar results using a variety of bis-tridentate ligands [6][7] and bis-bidentate ligands [8–10].

In most cases, molecular oxygen acts as the source of the O-atom, although *Karlin* and co-workers have shown that H_2O_2 will also effect hydroxylation of a dicopper(II) complex where the Cu^I complex shows oxygenase activity [11]. The mechanism has been studied in some detail by *Karlin*, *Zuberbühler* and co-workers showing the initial formation of a dicopper(II) peroxo-species which then hydroxylates the ligand [12]. In a detailed study, they showed the presence of a NIH shift which suggested that the μ-(η^2:η^2)-peroxo complex carries out an electrophilic attack on the aromatic spacer, and this was confirmed by the effect of substituents on the aromatic ring [13]. This hypothesis is generally accepted for peroxo complexes. The pressure dependency was meas-

ured recently [14], and *Casella et al.* have shown that these complexes may also promote hydroxylation of exogeneous substrates [6][15][16]. *Casella* and co-workers have shown recently that H_2O_2 can induce the double hydroxylation of a system containing two tridentate binding sites separated by a 1,3-dimethylenephenyl spacer, and have deduced from spectroscopic data that a μ-1,1-hydroperoxo species is formed and is the active species [17]. Such a species has since been characterized by X-ray crystallography by *Suzuki* and co-workers [18].

We have previously studied the binuclear copper(I) complex $[Cu_2(\mathbf{1})_2]^{2+}$ in connection with the formation of helicates [19][20] and observed that it slowly turned green upon standing in DMF solution. In the present manuscript, we characterize the product, show it to be the result of ligand hydroxylation, and present qualitative observations on the mechanism. We discuss their significance for the hydroxylation of aromatic C–H bonds.



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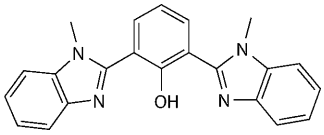

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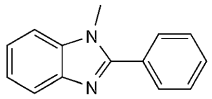
Results. – *Synthesis.* For the purpose of comparison with the ligand **2** produced by hydroxylation, a purely organic route to **2** was developed (*Scheme*) using the nitro amine reduction method of *Piguet et al.* [21]. Ligands **3** and **4** were synthesized from benzene-1,2-diamine, and benzoic acid and salicylic acid, respectively, followed by methylation involving deprotonation with NaH and treatment with MeI. For ligand **4**, the anisole group thereby formed was deprotected with BBr_3. The complex $[Cu_2(\mathbf{2}\text{-H})_2](TsO)_2 \cdot 3\,H_2O$ was prepared by mixing stoichiometric amounts of ligand, copper(II) *p*-toluenesulfonate, and Et_3N.



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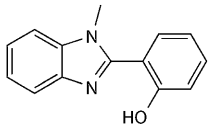

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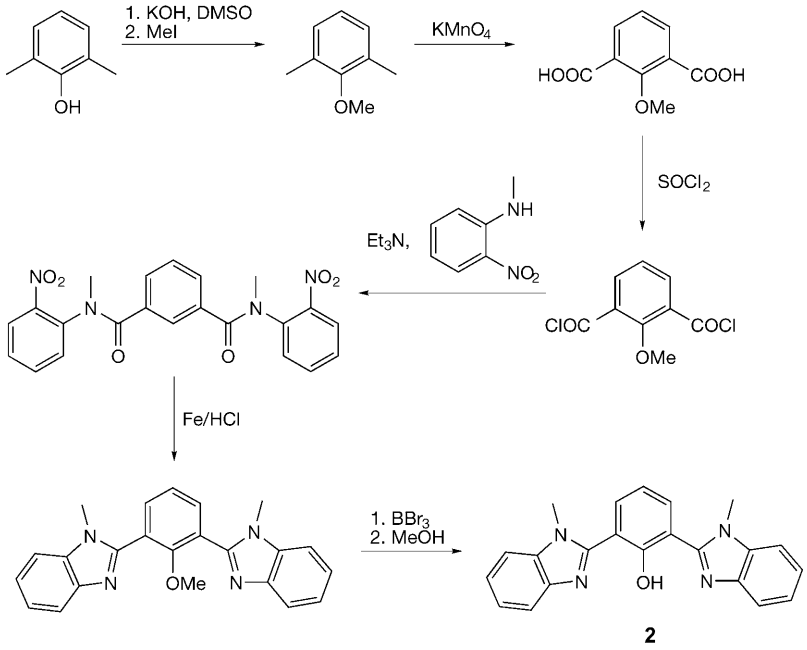
Characterization of the Hydroxylated Product. The oxygenated product was initially formed by stirring a solution of $[Cu_2(\mathbf{1})_2]^{2+}$ in DMF at 80° under O_2 for 18 h. Evaporation of the solvent gave the product as a green solid, which could be recrystallized from DMF by vapor diffusion of Et_2O. The crystals were suitable for X-ray crystallography, and showed the complex to be $[Cu_2(\mathbf{2}\text{-H})_2(DMF)_2](ClO_4)_2 \cdot 2$ DMF. The complex could equally be prepared by using stoichiometric amounts of ligand **1** and copper(II) perchlorate under the same conditions.

The electrospray mass spectrum (ES-MS) shows the peaks expected for the complex $[Cu_2(\mathbf{2}\text{-H})_2(DMF)_2]^{2+}$ with adduct anions and with loss of weakly bound DMF. The isotopic distribution corresponds to a dinuclear copper species. The UV/VIS spectrum of the hydroxylated product is quite characteristic. Ligand **1** shows essentially only

Scheme. *Synthesis of Ligand* **2**



one band in the UV at 300 nm (ε 35500 cm^{-1} M^{-1}), but in ligand **2** the spectrum shows two bands at 284 nm (ε 21500 cm^{-1} M^{-1}) and 324 nm (ε 20400 cm^{-1} M^{-1}). In the hydroxylated complex $[Cu_2(\mathbf{2}\text{-H})_2(DMF)_2]^{2+}$, the second band is shifted into the visible 353 nm (ε 16000 cm^{-1} M^{-1}) and is responsible for the strong green color of the solution. This band has been attributed by *Casella et al.* to a ligand-based transition to which some ligand-to-metal charge-transfer character is added [8]. The band is slightly blue-shifted in EtOH solution. This band is a useful marker of hydroxylation and has been used to follow the reaction. Not surprisingly, in view of the double phenolate bridge, which would be expected to give rise to strong antiferromagnetic coupling, the complex is EPR-silent. A ^{1}H-NMR spectrum in (D_7)DMF may be observed in the range 0–21 ppm, but the peaks are severely broadened and could not be assigned.

Structure of $[Cu_2(\mathbf{2}\text{-}H)_2(DMF)_2](ClO_4)_2 \cdot 2\ DMF$. The structure of the complex cation shows two Cu^{II} ions linked by two ligands which have been hydroxylated and deprotonated, with the phenolate functions bridging the two metals (*Fig. 1*). The cation lies on a crystallographic centre of inversion, and so the two Cu sites are identical, with square pyramidal coordination (*SPY-5*). The base of the pyramid is formed by two N-atoms of benzimidazoles and two bridging phenolate functions; the apex of the pyramid is formed by the O-atom of a coordinated DMF molecule. The Cu–N bond distances of 1.952(4) and 1.951(4) Å are slightly shorter than the Cu–benzimidazole distances observed for another square pyramidal copper(II) complex (2.04 Å [22]), but longer than the bonds to two-coordinate copper(I) in $[Cu_2(\mathbf{1})_2]^{2+}$ (1.89 Å) [19]. The copper-phenolate distances of 1.974(3) and 2.009(3) Å are slightly longer than those observed by *Karlin et al.* [4] and *Casella et al.* [8] in complexes where there is only

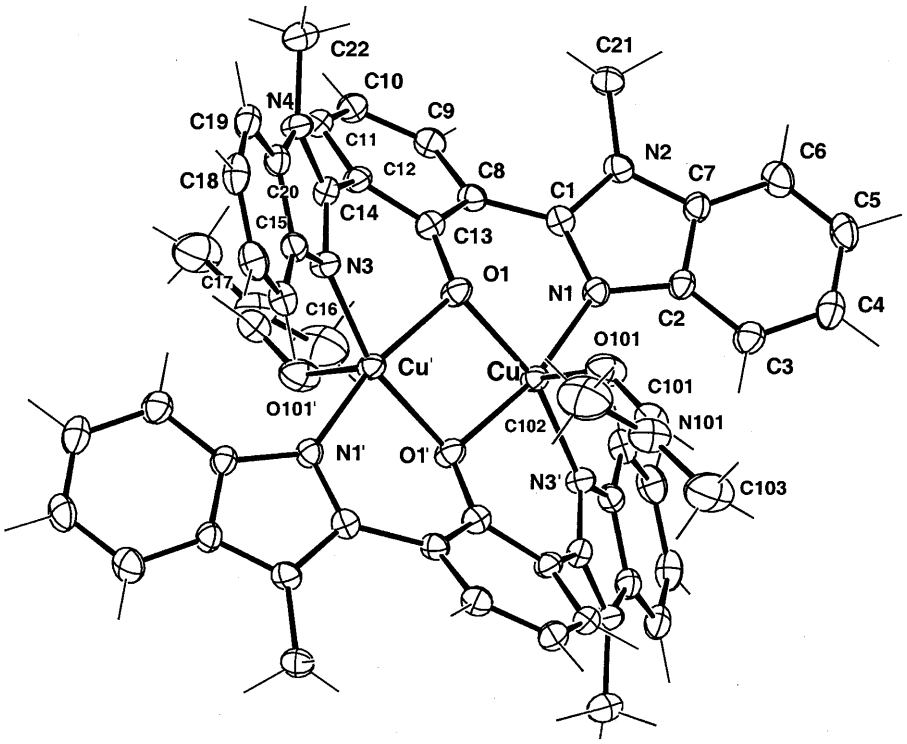


Fig. 1. *View of the cation* $[Cu_2(\mathbf{2}\text{-}H)_2(DMF)_2]^{2+}$. There is a crystallographic centre of inversion between the two Cu^{II} ions. Ellipsoids are drawn at 40% probability.

one bridging phenolate. The axial Cu–O(DMF) distance of 2.271(3) Å is, as expected for Cu^{II}, much longer. The Cu–Cu distance of 3.0489(7) Å is less than half that observed in $[Cu_2(\mathbf{1})_2]^{2+}$ (7.140 Å) [19]. The conformation of the ligands is interesting: the phenolate moiety is significantly distorted from planarity, and may be regarded as slightly folded about the axis of the C–O bond. In consequence, the two atoms on the axis lie roughly 0.08 Å above the least-squares plane, and the others 0.01–0.06 Å below it. The two benzimidazole moieties are twisted at *ca.* 42° to the phenolate plane. The ligand as a whole appears to be curved, and the plane of the phenol is inclined by *ca.* 47° with respect to the Cu_2O_2 plane (*Fig. 2*).

The cations form layers parallel to the *bc* plane and show stacking interactions between benzimidazole moieties of neighboring complexes as observed previously in benzimidazolonium salts [23]. The perchlorate anions and included DMF molecules show no features of interest and lie in sheets in between the layers of cations.

The Hydroxylation Reaction. The observation of hydroxylation of $[Cu_2(\mathbf{1})_2]^{2+}$ in DMF solution was somewhat surprising since the two Cu^{I} ions are over 7 Å apart in this complex [19], and the Cu^{I} is in no way activated for dioxygen binding. The initial preparation used quite concentrated solutions (0.025M) and heating. If the procedure was repeated at room temperature and followed by UV/VIS spectroscopy, the formation of hydroxylated product was very slow, with only 30% conversion after 3 weeks. It

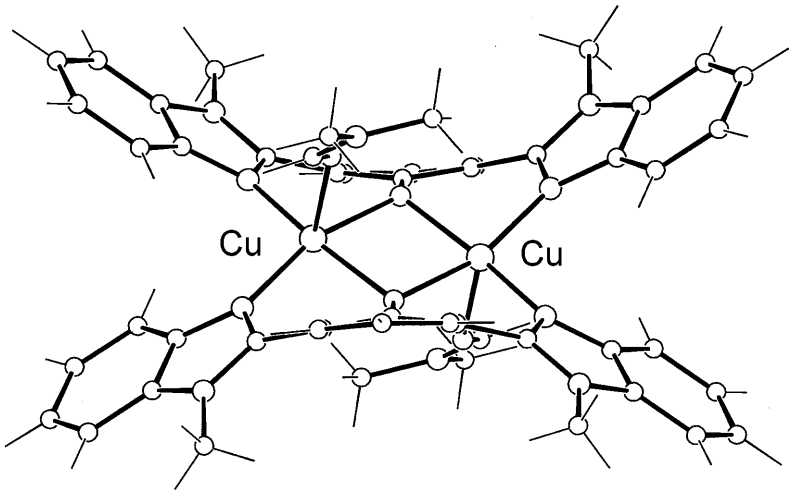


Fig. 2. *Another view of* $[Cu_2(\mathbf{2}\text{-}H)_2(DMF)_2]^{2+}$ *roughly along the C–O bonds of the phenolate moiety showing the distortion of the phenolate and its inclination to the* Cu_2O_2 *plane*

could be speeded up somewhat by addition of an acetate buffer, and stopped by addition of 2,6-lutidine. Measurement of the oxygen uptake showed that the volume of O_2 necessary to oxidize completely the Cu(I) to Cu(II) was taken up over a timescale of minutes, but that the hydroxylated product was formed much more slowly. In MeCN solution, no oxidation was observed at all. The slowness of the reaction in DMF, coupled to the apparent rapid oxidation to Cu^{II} deduced from the O_2-uptake experiment, led us to suspect that partial decomposition of the solvent (to CO and Me_2NH) might be involved.

We then studied the effect of H_2O_2 as an oxidant on a mixture of Cu^{II} and ligand **1**. The hydroxylation was much faster in this case. In DMF with a concentration of **1** around 10^{-3} M, a 20% excess of Cu^{II}, and 10 equiv. of H_2O_2, 60% conversion, as judged by the absorbance, was achieved in under 1 h. The yield could be increased slightly to *ca.* 80% in the presence of a lutidine buffer. *Fig. 3* shows the growth of the band at 350 nm and a clean isosbestic point. The reaction could also be effected in EtOH, although the low solubility of the product in this solvent forces the use of lower concentrations to avoid precipitation of the product. A clean reaction with an isosbestic point is again observed. The hydroxylation reaction using H_2O_2 should in principle lead to the liberation of protons according to *Eqn. 1*.

$$2\,Cu^{2+} + 2\,\mathbf{1} + 2\,H_2O_2 \rightarrow [Cu_2(\mathbf{2}\text{-}H)_2]^{2+} + 2\,H_3O^+ \quad (1)$$

The pH of the solution does indeed fall upon addition of H_2O_2, and titration of the resulting solution with lutidine suggests that 1 equiv. of protons is liberated per mol of copper. The presence of lutidine slightly increases the yield by preventing protonation of free ligand.

The nature of the species formed in solution by Cu^{II} and **1** is not clear. Ligand **1** is not chelating and may act as a monodentate or as a bis-monodentate ligand in a binu-

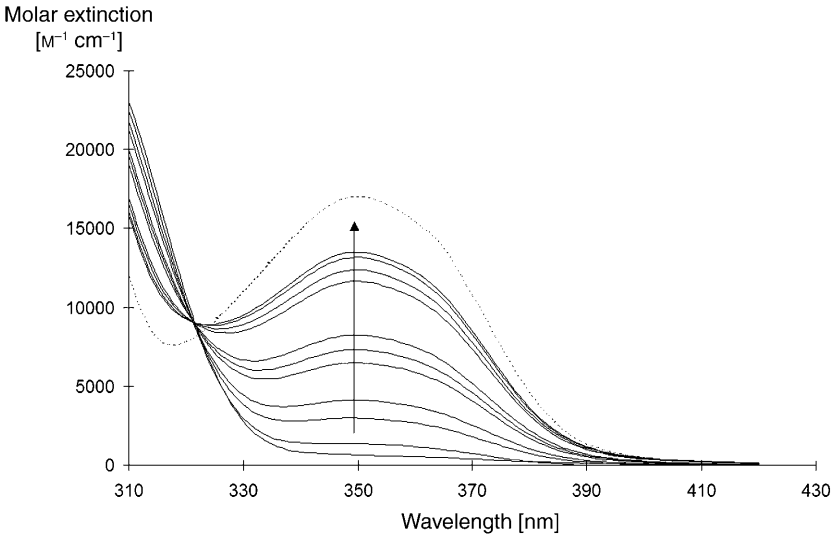


Fig. 3. *Spectral changes with time in a solution of* $[Cu(TsO)_2] = 9.6 \cdot 10^{-4}$ M, $[\mathbf{1}] = 8 \cdot 10^{-4}$ M *in DMF* (lutidine buffer 0.025M) *to which a tenfold excess of* H_2O_2 *is added.* The growth of the transition at 350 nm is clearly visible. The dashed line is that of a solution containing $[Cu(TsO)_2] = 9.6 \cdot 10^{-4}$ M and $[\mathbf{2}] = 8 \cdot 10^{-4}$ M.

clear complex. A monodentate benzimidazole moiety is not expected to be a strongly binding ligand with a typical stability constant of 10^3 [24]. Under the conditions used for hydroxylation, only partial complexation of copper would be expected. Electrospray mass spectra confirmed this showing peaks due to free ligand, [Cu(**1**)] and [Cu(**1**)$_2$]. Spectroscopic titrations, either adding ligand to Cu^{II} or Cu^{II} to ligand suggested the formation of [Cu(**1**)] and [Cu(**1**)$_2$] with log β values of 2.9(2) and 7.0(1), respectively, but these values should only be considered as indicative since the absorbance changes were small.

The final experiment was to investigate whether a more simple ligand such as **3** could be hydroxylated under the same conditions. Ligand **3** has an aromatic C–H bond in the same position with respect to the coordination site of the benzimidazole, but cannot form a binuclear complex in the way that ligand **1** can. Oxidation of ligand **3** was attempted in four ways: *a*) by simple reaction with 0.5 or 1 equiv. of Cu^{II} in DMF in air; *b*) as for *a* but with 0.5 equiv. of copper only for 5 h at 60°; *c*) as for *b*, but in presence of 3 equiv. of AcOH for 4 h at 80°; *d*) as for *a* but in presence of 5 equiv. of H_2O_2. In no case was the band at 356 nm expected for hydroxylation observed, although ligand **1** would have been at least partially hydroxylated under these conditions. The expected product of hydroxylation **4** was synthesized directly, and reacted with Cu^{II}. One equiv. of Cu^{II} reacted with 2 equiv. of ligand **4** and 2 equiv. of Et_3N in DMF solution showed the intense band expected for the phenolato complex at 356 nm (ε_{max} 11000 cm^{-1} M^{-1}). We may, therefore, deduce that **3** is not oxidized under these conditions.

Discussion. – Although the hydroxylation of aromatic substrates catalyzed by copper is by now well-established, the work described here shows a number of unusual features. The traditionally studied systems contain two good complexation sites for the Cu^{I} ions, usually bidentate or tridentate, which lower the redox potential of the Cu^{II}/Cu^{I} couple, and thereby favor reaction with O_2, together with a suitable bridging unit linking the two coordinate sites. In this work, ligand **1** is a simple bis-monodentate ligand, which complexes Cu^{I} only weakly [20] giving a linear coordination of the copper in $[Cu_2(\mathbf{1})_2]^{2+}$ [19] which is not favourable for Cu^{II}. $[Cu_2(\mathbf{1})_2]^{2+}$ does not in fact react with oxygen in MeCN solution. Furthermore, complexation of Cu^{II} by ligand **1** has also been shown to be weak.

The benzene-1,3-diyl bridge does not appear suitable for dioxygen activation since the Cu–Cu distance in $[Cu_2(\mathbf{1})_2]^{2+}$ is over 7 Å, but examination of models and the results presented here show that rotation about the benzimidazol-phenyl bonds will bring copper ions bound to the benzimidazoles much closer to each other. Such conformational reorganization is now well-established for *m*-xylyl bridges in the tyrosinase model systems. The conformational change will approach the dicopper site to the C–H bond which is to be hydroxylated. This will of course be energetically costly, but can be compensated by the binding of a peroxide between the two coppers. Since **1** is only weakly complexed by Cu^{II}, we may assume that the formation of the bridging peroxide group (which is well-precedented) also plays an important role in stabilizing the dinuclear complex. The binding of the peroxide to two copper ions enhances its electrophilicity [25], and the aryl C–H bond is brought close to the now electrophilic peroxide by the conformational rearrangement of the bridging ligand. The way is thus opened for a rapid hydroxylation, as we observe. The need for peroxide to stabilize the dinuclear complex would also explain the greatly increased rate in the reaction with H_2O_2.

The mononuclear ligand **3** does not show this hydroxylation, presumably since the ligand bridge which brings the C–H bond close to the peroxide is no longer present. It may be noted that a bridging ligand is not essential for the stabilization of a peroxide [26–28], especially when the Cu-coordination sphere is such as to favor electron transfer to dioxygen, but this is not the case with ligand **3**.

The initial observation of the hydroxylation with $[Cu_2(\mathbf{1})_2]^{2+}$ remains somewhat mysterious. The O_2-uptake experiments showed that the copper was oxidized to Cu^{II} quite rapidly, and long before the characteristic band of the hydroxylated product was observed. The long timescale and the fact that this reaction is only seen in DMF leads us to associate it with partial decomposition of the solvent. DMF is well-known to have reducing properties, and may thereby generate trace amounts of Cu^{I} which can then generate traces of peroxide by reaction with O_2. This may then react as for the Cu^{II}/peroxide system discussed above. We may also note that dicopper products similar to those of the reactions presented here have been shown to accelerate the hydrolysis of DMF to formate [29].

Finally, we may note that kinetic studies of these reactions were inconclusive. Since the complexes are relatively weak and are substitutionally labile, the speciation in solution is a non-trivial matter. Both the reaction of $[Cu_2(\mathbf{1})_2]^{2+}$ with dioxygen, and that of Cu^{II} with **1** and hydrogen peroxide are non-complementary, in that the first requires 6 and the second 4 oxidizing equiv. to reach the product $[Cu_2(\mathbf{2}\text{-H})_2]^{2+}$, while the oxidizing

agents supply 4 and 2 equiv., respectively. We, therefore, suspect that $[Cu_2(\mathbf{2}\text{-H})_2]^{2+}$ is to be regarded as the final, thermodynamic product, and that it is not the initial product of the hydroxylation reaction. It would be more logical for one ligand at a time to be hydroxylated.

In conclusion, the results presented here show that efficient hydroxylation may be observed in systems where the copper is not specifically activated for dioxygen binding, and indeed where the copper complex involved in hydroxylation is not very stable. On the other hand, the fact that the ligand positions the C–H bond close to the postulated bridging peroxide does appear to be important as shown by the different reactivity of **1** and **3**.

We thank the *Swiss National Science Foundation* for their support of this work.

Experimental Part

General. Solvents and starting materials were purchased from *Fluka AG* (CH-Buchs) and were used without further purification unless otherwise stated. DMF was distilled from CaH_2. UV/VIS Spectra: *Cary IE* or *Perkin-Elmer Lambda-5* UV/VIS/NIR spectrometers; quartz cells of 1- or 0.1-cm path lengths; λ_{max} (ε) in nm. Spectroscopic titrations were carried out using a *J&M* diode array spectrometer (*Tidas* series) connected to an external computer. Data were analyzed using the SPECFIT program [30]. IR Spectra: *Perkin-Elmer Spectrum-One* or *883* instruments, KBr discs; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Varian Gemini-300* or *Bruker Advance-400* at 300 or 400 (^1H), and 74.44 MHz (^{13}C) at 22°; chemical shifts δ in ppm with respect to Me_4Si, *J* in Hz. MS: electron impact (EI) at 70 eV with *VG 7000E* and *Finnigan 4000* instruments, electrospray ionisation (ESI) with *Finnigan Mat-SSQ7000* instrument of the Mass Spectrometry Laboratory, University of Geneva; in *m*/*z* (rel.%). Elemental analyses were performed by Dr. *H. Eder,* University of Geneva.

*Synthesis of Ligands. 1,3-Bis(1-methyl-1*H*-benzimidazol-2-yl)benzene* (**1**) was obtained according to the procedure described in [19].

2,6-Dimethylanisole (=*2-Methoxy-1,3-dimethylbenzene).* KOH (85%; 21.08 g, 0.32 mol, 4 equiv.) was added to 120 ml of DMSO. 2-Hydroxy-*m*-xylene (9.76 g, 0.08 mol) was added, and the soln. was stirred for 5 min. The flask was cooled in ice, and when the temp. reached 0°, 12.26 ml of MeI (0.19 mol, 2.4 equiv.) were added. After 15 min, the flask was taken out of the ice and allowed to warm to r.t. H_2O (100 ml) was added, and the product was extracted with CH_2Cl_2. The fractions of CH_2Cl_2 were collected and washed with H_2O to eliminate the remaining DMSO. The product, which is a liquid, was purified by column chromatography (CC) (SiO_2 (200 g); CH_2Cl_2). The final product was then distilled under reduced pressure: 8.8 g (0.065 mol; 81%) of liquid product. B.p. 170–171°. IR(KBr): 2943v*s*, 1475v*s*, 1416*m*, 1262*s*, 1214v*s*, 1170*m*, 1091*s*, 1017v*s*, 811*m*, 768v*s*. ^1H-NMR ($CDCl_3$, 300 MHz): 2.26 (*s*, 6 H); 3.69 (*s*, MeO); 6.86–6.91 (*dd*, 1 arom. H); 6.97–6.99 (*d*, 2 arom. H). EI-MS: 136 (100, M^+), 121 (97), 105 (17), 91 (47), 77 (50), 65 (13), 51 (14).

2-Methoxyisophthalic Acid (=*2-Methoxybenzene-1,3-dicarboxylic Acid*). 2,6-Dimethylanisole (8.8 g, 0.056 mol) was dissolved in 120 ml of H_2O and heated to 60° with mechanical stirring. $KMnO_4$ (43 g, 0.273 mol, 4.2 equiv.) was added in two portions. The first portion was added, and, when the violet colour disappeared, the rest was poured into the soln. The soln. was left overnight at 60° and filtered while still warm. The black precipitate (MnO_2) was washed with hot H_2O. The filtrate was concentrated to *ca.* 100 ml, then neutralized with HCl 4M to pH 3.3. A precipitate formed, and it was filtered and dried: 5.72 g (0.029 mol, 52%). The product is soluble in MeOH and H_2O, insoluble in CH_2Cl_2. M.p. 184°. IR: 3100–2400v*s* (br.), 1669v*s* (br.), 1583*s*, 1504*m*, 1468*s*, 1400*s*, 1296v*s*, 1240v*s*, 1168*m*, 1139*m*, 1092*s*, 1000*s*, 955*m,* 884*m*, 846*m*, 781*m*, 713*m*, 683v*s*. ^1H-NMR (CD_3OD, 300 MHz): 3.87 (*s*, Me); 7.18–7.23 (*t*, 1 arom. H); 7.86–7.89 (*d*, 2 arom. H). EI-MS: 196 (22, M^+), 179 (15), 178 (83), 166 (12), 165 (65),

150 (16), 149 (100), 148 (38), 147 (67), 138 (18), 133 (17), 132 (51), 122 (15), 121 (39), 120 (82), 119 (45), 105 (41), 104 (23), 93 (10), 92 (34), 91 (30), 79 (23), 77 (30), 76 (32), 75 (15), 74 (16), 65 (51), 64 (17), 63 (57), 62 (24), 53 (30), 52 (27), 50 (24), 45 (17).

N,N′-*Dimethyl*-N,N-*bis(2-nitrophenyl)benzene-1,3-dicarboxamide*. 2-Methoxyisophthalic acid (1.6 g, 0.008 mol) was poured into 150 ml of CH_2Cl_2, the soln. was dried with CaH_2, and a few drops of DMF were added to the soln. $SOCl_2$ (11 ml; 0.15 mol, 20 equiv.) was mixed with the soln. It was allowed to reflux protected by a tube of $CaCl_2$ for 90 min, until the product had completely dissolved. The solvent, the HCl, and the $SOCl_2$ which had not reacted were evaporated, and the flask was dried for 1 h under vacuum. The resulting solid was slightly beige. The acid chloride is not very stable, and the synthesis was continued without its isolation.

A soln. of 2.5 equiv. of *N*-methyl-2-nitroaniline (3 g, 0.02 mol) and 8 equiv. of Et_3N (8.9 ml, 0.064 mol) was prepared in 30 ml of dried CH_2Cl_2. The acid chloride was dissolved in 150 ml of dried CH_2Cl_2 and added dropwise into the first soln. The addition must last at least 15 min. The soln. was then allowed to stay 15 h at r.t. with stirring. The solvent was evaporated, and the solid was put into a mixture of 300 ml of CH_2Cl_2 and 200 ml of a aq. sol. of half-sat. NH_4Cl. The aqueous phase was washed with two 100 ml portions of CH_2Cl_2. The org. phases were assembled, dried (Na_2SO_4), and then the solvent was evaporated. The solid was purified by CC (SiO_2; initially 3% hexane/97% CH_2Cl_2 then 100% CH_2Cl_2, and finally 5% MeOH/95% CH_2Cl_2): 2.07 g (4.46 mmol, 56%) of the product. M.p. 92–95°. IR: 3075*w*, 2950*s*, 1727*s*, 1657v*s* (br.), 1601*s*, 1526v*s*, 1464*s*, 1417*s*, 1350*s*, 1292*m*, 1237*m*, 1140*m*, 1079*m*, 1043*m*, 998*m*, 851*m*, 837*m*, 816*m*, 784*m*, 756*m*, 705*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.7 (*s*); 3.2 (*s*); 3.25 (*s*); 3.32 (*s*); 3.37 (*s*); 3.45 (*s*); 3.53 (*s*); 3.85 (*s*); 3.95–3.99 (*dd*); 7.0–7.12 (*m*, 1 H); 7.3–7.53 (*m*, 7 H); 7.69–7.74 (*m*, 1 H); 7.89 (*m*, 1 H); 8.02–8.05 (*m*, 1 H). The NMR spectrum of this compound shows a series of *s*s between 2.7 and 3.99 ppm because of blocked rotation around the OC–N, C(aryl)–CO, and N–C(aryl)NO_2 bonds at r.t. ES-MS: 487 (68, M^++23 (Na)), 146 (100).

*2-Methoxy-1,3-bis(1-methyl-1*H*-benzimidazol-2-yl)benzene*. *N,N′*-Dimethyl-*N,N′*-bis-(2-nitrophenyl)benzene-1,3-dicarboxamide (1.4 g, 3 mmol) was dissolved in a soln. containing 600 ml of EtOH, 150 ml of H_2O, and 18.9 ml of HCl (37%; 0.226 mol, 75 equiv.). Activated Fe (30 equiv., 5.05 g, 0.09 mol) were then poured into the mixture. The soln. was left in an atmosphere of N_2 and allowed to reflux for 20 h. The soln. was colourless after 1 h, but, after 20 h, it became red brown, and no more iron powder remained in suspension. H_2O (120 ml) was added to the soln., and EtOH was then evaporated. The soln. was poured into 600 ml of CH_2Cl_2, then 30 g of [Na_2H_2(edta)] dissolved in 120 ml of H_2O was mixed in. The pH was brought to 8.5 with NH_4OH (12%). [Na_2H_2(edta)] complexes Fe^{III} more strongly than Fe^{II}. Therefore, 6 ml of H_2O_2 (30%) were added, under vigorous stirring, to oxidize the remaining Fe^{II}. After 15 min of stirring, the org. phase was collected, and the aq. phase was washed twice with 300 ml of CH_2Cl_2. The product was purified by CC (SiO_2; CH_2Cl_2/MeOH: 100% → 93%/0% → 7% eluent: 0.55 g (1.5 mmol, 50%) of the product. M.p. 185°. IR: 3060*m*, 3050*m*, 2945*m*, 1668*m*, 1651*m*, 1610*m*, 1600*m*, 1506*m*, 1458v*s*, 1441*s*, 1426*s*, 1413v*s*, 1386v*s*, 1325*s*, 1282*s*, 1254*m*, 1234*m*, 1177*w*, 1155*w*, 1127*w*, 1098*w*, 1081*m*, 1054*m*, 1019*w*, 996*s*, 960*w*, 903*w*, 869*m*, 819*m*, 748v*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.26 (*s*, MeO); 3.78 (*s*, 2 MeN); 7.34–7.40 (*m*, 3 H); 7.43–7.47 (*m*, 3 H); 7.79–7.82 (*dd*, ^3J=7.65, 2 H); 7.85–7.88 (*m*, 3 H). EI-MS: 369 (20, [M+1]$^+$), 368 (91), 367 (100), 353 (37), 351 (28), 337 (21), 207 (16), 184 (26), 77 (21).

*2,6-Bis[1-methyl-1*H*-benzimidazol-2-yl]phenol* (**2**). 2-Methoxy-1,3-bis(1-methyl-1*H*-benzimidazol-2-yl)benzene (0.5 g, 1.3 mmol) was dissolved in 200 ml of dry CH_2Cl_2 (distilled on CaH_2). The flask was put into ice, and 5 equiv. (6.5 ml) of BBr_3 were added to the mixture. The flask was kept in ice until it melted and was left 15 h at r.t. under N_2 while being stirred magnetically. The BBr_3 was then hydrolyzed with 100 ml of MeOH, the soln. stirred for 10 min, the solvent was evaporated, and the solid was dried 1 h in low vacuum. The solid was mixed into 100 ml of H_2O, as a suspension, and the pH was neutralized to 6 with 2M NaOH. The precipitate was filtered, and the aq. phase was washed with CH_2Cl_2. The org. phase was dried, and the solvent was evaporated. The beige solid was purified by CC (SiO_2; 99.5% CH_2Cl_2/0.5% MeOH). 0.30 g (0.87 mmol, 67%) of **2**. The compound is soluble in CH_2Cl_2, DMF, $CHCl_3$, MeOH, EtOH, MeCN; insoluble in Et_2O, hexane, H_2O. M.p. >190°. UV (DMF): 324 (20400), 284 (21500). UV (EtOH): 283 (21000), 324 (18500). IR: 3473–3418*m* (br.), 3062*m*, 2929*m*, 2875*m*, 2366*m*, 1629*m*, 1515*m*, 1501*m*, 1490v*s*, 1430*m*, 1407*s*, 1385*s*, 1324*m*, 1270*s*,

1260*s*, 1151*m*, 1118*m*, 1097*m* (sh), 1055*m*, 1003*m*, 931*w*, 864*m*, 799*m*, 624*m*, 604*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.98 (*s*, 2 Me); 7.14–7.18 (*t*, ^3J = 7.7, 1 H); 7.31–7.39 (*m*, 4 H); 7.44–7.47 (*dd*, ^3J = 7.08, ^4J = 1.7, 2 H); 7.79–7.81 (*dd*, ^3J = 6.75, 2 H); 7.83–7.86 (*d*, ^3J = 7.8, 2 H). EI-MS: 353 (100), 337 (10), 250 (8), 207 (10), 193 (10), 177 (30), 133 (15), 104 (15), 92 (13), 90 (13), 77 (100), 65 (26), 63 (30), 51 (66).

*2-Phenyl-1*H*-benzimidazole.* Benzene-1,2-diamine (2.03 g, 0.018 mol) and 3.31 g (0.027 mol) of PhCOOH were mixed in 50 ml of H_3PO_4 (85%). The soln. was heated 2 h at 90° and then 4 h at 200° under mechanical stirring. The mixture was poured into 200 ml of H_2O and neutralized to pH 6 with 2M NaOH. The precipitate was filtered and suspended in 200 ml of an aq. soln. containing 10% of Na_2CO_3. The suspension was heated to 60° for 1 h under magnetic stirring. The pink solid was then dried under vacuum at 90°. It was dissolved in MeOH and treated with charcoal for 1 h. The solid was then recrystallized in MeOH: 2.44 g (0.0125 mol, 70%) of the product. M.p. >190°. ^{1}H-NMR (CD_3OD, 300 MHz): 7.2–8.1 (*m*, 9 H). EI-MS: 194 (100, M^+), 97 (100), 90 (10), 77 (100), 63 (10).

*1-Methyl-2-phenyl-1*H*-benzimidazole.* 2-Phenyl-1*H*-benzimidazole (1.12 g, 5.7 mmol) was dissolved in 50 ml of dry DMF (distilled over CaH_2). The flask was then put into ice before 492 mg (*ca.* 10 mmol) of NaH (50–60%) were added to the soln. The mixture was allowed to return to r.t. under magnetic stirring. It stood for 1 h before 0.55 ml (8.8 mmol) of MeI was added. The soln. was kept under magnetic stirring at r.t. for one night. During all the manipulations, the flask was kept under N_2. The solvent was then evaporated, the solid was dried and purified by CC (SiO_2; CH_2Cl_2/MeOH 97:3). Yield: 60%. Soluble in MeOH, EtOH, DMF, MeCN, acetone, CH_2Cl_2, $CHCl_3$, and toluene; insoluble in Et_2O, H_2O, and hexane. M.p. 92–93°. UV/VIS (DMF): 286 (15300). IR: 3060*m*, 2947*m*, 1943*w*, 1901*w*, 1777*w*, 1680*w*, 1610*m*, 1523*m*, 1466*s*, 1440*s*, 1380v*s*, 1327*s*, 1275*m*, 1250*w*, 1240*m*, 1177*w*, 1155*m*, 1126*m*, 1100*m*, 1076*m*, 1058*m*, 1020*m*, 1002*m*, 973*w*, 927*m*, 876*w*, 850*w*, 817*m*, 778*s*, 754v*s*, 700*s*, 679*m*, 540*m*, 484*m*. ^{1}H-NMR (CD_3OD, 300 MHz): 3.88 (*s*, Me); 7.38–7.27 (*m*, 2 arom. H); 7.54–7.61 (*m*, 4 arom. H); 7.66–7.69 (*m*); 7.76–7.79 (*m*, 2 arom. H). EI-MS: 208 (75, M^+), 207 (100), 129 (6), 104 (19), 90 (16), 77 (22), 63 (9), 51 (13).

*2-(1*H*-Benzimidazolyl-2-yl)phenol.* Benzene-1,2-diamine (4 g, 0.037 mol) and 5.5 g (0.04 mol) of salicylic acid were dissolved in 50 ml of H_3PO_4 (85%). The salicylic acid sublimes below 140°; therefore, a slight excess is needed. The soln. was heated 1 h at 180° and 2 h at 230°. It was then allowed to cool and poured into 200 ml of H_2O. It was neutralized to pH 6 with 5M NaOH. The black precipitate was filtered and suspended in 100 ml of an aq. soln. containing 40% Na_2CO_3. The mixture was heated at 60° for 1 h. The solid was then treated with charcoal in MeOH and recrystallized from a mixture of EtOH and H_2O. Yield: 12%. M.p. >180°. IR: 3260*m*, 2918*m*, 1628*w*, 1588*m*, 1532*m* 1513*s*, 1486*s*, 1458*s*, 1434*s*, 1414*m*, 1395*s*, 1368*m*, 1317*m*, 1294*m*, 1276*s*, 1257*s*, 1223*m*, 1188*m*, 1157*m*, 1142*m*, 1129*m*, 1112*m*, 1081*m*, 1036*w*, 1003*w*, 960*w*, 904*w*, 839*m*, 820*m*, 798*s*, 738v*s*, 697*m*. ^{1}H-NMR (CD_3OD, 300 MHz): 6.93–7.02 (*m*, 2 H); 7.22–7.27 (*m*, 2 H); 7.3–7.35 (*m*, 1 H); 7.57–7.69 (*m*, 2 H); 7.82–7.89 (*dd*, 1 H). EI-MS: 210 (100, M^+), 182 (52), 156 (10), 143 (8), 129 (4), 105 (9), 91 (28), 68 (20), 65 (24), 63 (20), 51 (12).

*1-Methoxy-2-(1-Methyl-1*H*-benzimidazol-2-yl)benzene.* 2-(1*H*-Benzimidazol-2-yl)phenol (0.5 g, 2.38 mmol) was dissolved in 40 ml of dry DMF (distilled over CaH_2). The flask was put into ice and 0.21 g (*ca.* 5 mmol) of NaH (50–60%) were added. The soln. was allowed to return to r.t. under magnetic stirring. After 1 h, the soln. was again put into ice, and 0.74 g (5 mmol) of MeI was added. The mixture warmed up to r.t. and left for a further 2 h under magnetic stirring. The product was purified by CC (SiO_2; initially 100% of CH_2Cl_2 and then with CH_2Cl_2/MeOH 99.5:0.5). Yield: 58%. M.p. 98–100°. IR: 3381*s*, 3062*s*, 2945*s*, 2845*s*, 1647*m*, 1602*s*, 1577*s*, 1552*m*, 1520*s*, 1485*s*, 1457*s*, 1430*s*, 1380v*s*, 1324*s*, 1276*s*, 1252v*s*, 1235*s*, 1177*s*, 1149*m*, 1130*m*, 1120*m*, 1094*s*, 1053*s*, 1022v*s*, 1004*m*, 969*m*, 951*m*, 928*m*, 823*m*, 799*m*, 781*s*, 750v*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.66 (*s*, MeN); 3.88 (*s*, MeO); 7.05–7.l (*d*, 1 H); 7.29–7.33 (*m*, 2 H); 7.39–7.42 (*m*, 1 H); 7.48–7.51 (*m*, 1 H); 7.57–7.6 (*dd*, 1 H); 7.81–7.84 (*m*, 1 H). EI-MS: 238 (95, M^+), 237 (73), 209 (14), 208 (17), 207 (100), 77 (24), 51 (13).

*2-(1-Methyl-1*H*-benzimidazol-2-yl)phenol.* 1-Methoxy-2-(1-methyl-1*H*-benzimidazol-2-yl)benzene (0.338 g, 1.4 mmol) was dissolved in 40 ml of dry CH_2Cl_2 (distilled over CaH_2). The flask was put into ice, and 7 ml (7 mmol) of a soln. of BBr_3 1M in CH_2Cl_2 were added dropwise to the soln. The flask was left, under magnetic stirring, until the ice melted and the H_2O warmed to r.t. It was kept under magnetic stirring over night. The excess of BBr_3 was first hydrolyzed with MeOH (puriss.) and stirred for 10 min. The solvent was then evaporated, and the solid was dried 1 h under vacuum. H_2O (60 ml) was then poured onto the solid, and the mixture was neutralized to pH 6 with 2M NaOH. The product was then

extracted from this aq. soln. with CH_2Cl_2. The solid was purified by CC (SiO_2; 100% with CH_2Cl_2 at first until a first product eluted, then CH_2Cl_2/MeOH increasing gradually from 100 : 0 to 90 : 10, until the product came out: 78 mg (0.348 mmol, 25%) of the product. M.p. 157–158°. UV/VIS (DMF): 286 (17050), 324 (15600). IR: 2552*s* (br.), 2360*s* (br.), 1825*s*, 1729*m*, 1691*m*, 1680*m*, 1632*m*, 1610*s*, 1586*s*, 1555*m*, 1518*s*, 1502*m*, 1453v*s*, 1383v*s*, 1326*s*, 1292*s*, 1265*s*, 1236*s*, 1162*m*, 1129*m*, 1112*m*, 1099*m*, 1060*m*, 1030*m*, 1004*m*, 969*w*, 942*m*, 908*m*, 838*w*, 801*m*, 764*m*, 752v*s*, 667*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 4.07 (*s*, Me); 6.96–7.01 (*t*, ^3J = 7.17, 1 H); 7.34–7.42 (*m*, 6 H); 7.72–7.79 (*m*, 2 H). EI-MS: 225 (16, $[M+1]^+$,), 224 (96 M^+), 223 (100), 222 (11), 208 (9), 207 (55), 195 (15), 169 (9), 78 (10), 77 (20), 63 (10), 51 (14).

*Synthesis of Complexes. Bis[2,6-bis(1-methyl-1*H*-benzimidazol-2-yl)phenolate]dicopper(II)* p-*Toluenesulfonate* ($[Cu_2(\mathbf{2}\text{-H})_2](TsO)_2 \cdot 3\,H_2O$). 2,6-Bis[1-methyl-1*H*-benzimidazol-2-yl)phenol (18 mg, 0.05 mmol), 25 mg (0.05 mmol) of $Cu(TsO)_2 \cdot 5.5\,H_2O$, and 0.05 mmol of Et_3N were dissolved in a minimum of DMF and placed into an atmosphere of Et_2O; the soln. was green. After 3 d, 14 mg of a pale green precipitate were formed on the bottom of the flask (0.011 mmol, 46%), the soln. was colorless. The precipitate was dried 5 h at 40° under vacuum. UV/VIS (DMF): 286 (26000), 353 (16000), 755 (108). UV/VIS (EtOH): 285 (26500), 346 (17000), 726 (180). IR: 3364*m*, 3057*m*, 2952*m*, 1675*m*, 1609*m*, 1569*m*, 1521*m*, 1479*s*, 1421*s*, 1280*s*, 1213*s*, 1185*s*, 1118*s*, 1087*m*, 1030*m*, 1008*s*, 931*w*, 875*w*, 859*w*, 819*w*, 749*s*, 712*w*, 678*s*. ^{1}H-NMR ((D$_7$)DMF, 400 MHz; 293 K): 3.74 (*s*); 3.95 (*s*); 6.56 (*s*); 6.91 (*s*); 7.25 (*s*); 7.33 (*s*); 9 (v. br.); 15.2 (*s*); 20.5 (*s*). All peaks are broadened by paramagnetic relaxation, and the feature around 9 ppm corresponds to several signals. ES-MS (in DMF): 1187.5 (22), 1185.5 (18, $[Cu_2(\mathbf{2}\text{-H})_2(TsO) \cdot 2\,DMF \cdot 2\,H_2O]^+$), 1004.9 (80), 1002.9 (74, $[Cu_2(\mathbf{2}\text{-H})_2(TsO)]^+$), 879 (14), 877 (13), 490 (35) 489 (52, $[Cu_2(\mathbf{2}\text{-H})_2(DMF)_2]^{2+}$), 453.9 (63), 452.9 (70, $[Cu_2(\mathbf{2}\text{-H})_2DMF]^{2+}$), 417.5 (5), 416.3 (20, $[Cu_2(\mathbf{2}\text{-H})_2]^{2+}$). Anal. calc. for $[Cu_2(\mathbf{2}\text{-H})_2](TsO)_2 \cdot 3\,H_2O$ ($C_{58}Cu_2H_{54}N_8O_{11}S_2$; 1230.32): Cu 10.33, C 56.62, H 4.42, N 9.10, S 5.21; found: Cu 10.12, C 56.80, H. 4.49, N 9.12, S 5.05.

The compound could also be synthesized from ligand **1**. *1,3-Bis-(1-methyl-1*H*-benzimidazol-2-yl)benzene* (**1**; 170 mg, 0.5 mmol) and $Cu(ClO_4)_2 \cdot 6\,H_2O$ (180 mg, 0.5 mmol) were dissolved in DMF (20 ml). The flask was filled with O_2 and heated to 80° for 2 d. The soln. turned from pale green to dark green and the perchlorate salt bis[2,6-bis[1-methyl-1*H*-benzimidazol-2-yl)phenolate]bis(dimethylformamide)dicopper(II) diperchlorate dimethylformamide solvate could be isolated as dark green crystals by slow diffusion of Et_2O vapor. Synthesis using H_2O_2 replaced the saturation with O_2 by the dropwise addition, under stirring, of 250 µl of H_2O_2 (30%), followed by the addition of 50 µl of Et_3N in five aliquots. The formation of $[Cu_2(\mathbf{2}\text{-H})_2]^{2+}$ was established by the UV/VIS and ES mass spectra.

Oxygen-uptake experiments were performed in a thermostated room. The apparatus consisted of a flask containing DMF and a magnetic stirrer, solid $[Cu_2(\mathbf{1})_2](ClO_4)_2$ in a sidearm, a 20-ml burette (*Metrohm*), and a U-tube manometer. The apparatus was flushed with O_2 and closed. The reaction was started by tipping the $[Cu_2(\mathbf{1})_2](ClO_4)_2$ into the DMF and stirring. As the reaction progressed, the pressure was maintained constant (as measured by the manometer) by advancing the piston of the burette. The soln., initially colourless, turned light green within a few min. Absorption was essentially complete within 1 h, and the volume of O_2 absorbed corresponded to that required to oxidize the Cu^I into Cu^{II}. The volume required to form $[Cu_2(\mathbf{2}\text{-H})_2]^{2+}$ would be three times larger, and the formation of this complex could equally be ruled out by the UV/VIS spectrum.

*X-Ray Crystal-Structure Determination: Bis[2,6-bis(1-methyl-1*H*-benzimidazol-2-yl)phenolate]bis-(dimethylformamide)dicopper(II) Diperchlorate Dimethylformamide Solvate.* Crystals were obtained by vapor diffusion of Et_2O into a DMF soln., $Cu_2(C_{22}H_{17}N_4O)_2(ClO_4)_2(C_3H_7NO)_6$, M_R 735.8, dark green crystal, 0.154 × 0.21 × 0.26 mm, monoclinic, $P2_1/c$, a = 13.0308(9), b = 15.7813(12), c = 15.9187(11) Å, β = 100.112(8)°, V = 3222.7(4) Å^3, Z = 2, μ = 0.823 mm^{-1} (T_{min} = 0.8115, T_{max} = 0.8950), D_x = 1.516 g cm^{-3}. Intensities were measured at 200 K on a *Stoe IPDS* diffractometer with MoK_α radiation (λ = 0.7107 Å) and corrected for absorption. 37210 reflections were measured of which 6529 were unique (R_{int} = 0.098). The structure was solved by direct methods using MULTAN [31], and all other calculations were performed with XTAL system [32] and ORTEP [33] programs. Full-matrix least-squares refinement based on $|F|$ using weight of $1/(\sigma^2(F_o) + 0.00015(F_o^2))$ gave final values R = 0.042, ωR = 0.38, and S = 1.18(1) for 449 variables and 3403 contributing reflections. The H-atoms were placed in calculated positions.

CCDC-284148 contains supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the *Cambridge Crystallographic Data Centre,* 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk)).

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