# Dioxygen Activation Using Schiff Base Macrocyclic Dinuclear Copper(I) Complexes: Structurally Characterized Dioxygen Reaction Products

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Schiff-base condensation of diethylenetriamine with a series of dialdehydes [isophthalaldehyde (**2a**), 5-*tert*-butylisophthalaldehyde (**2b**), 2-methylisophthalaldehyde (**2c**), and *p*-phthalaldehyde (**2d**)] affords four hexaaza macrocyclic ligands [$L^{H,H}$ (**3a**), $L^{tBu,H}$ (**3b**), $L^{H,Me}$ (**3c**), $L^{p\text{-}H,H}$ (**3d**)] bearing different substituents on the aromatic units that connect the two metal ion binding sites. The dinuclear copper(I) complexes $[L^{H,H}Cu_2(MeCN)_2](ClO_4)_2$ (**4a**), $[L^{tBu,H}Cu_2(MeCN)_2](ClO_4)_2$ (**4b**), $[L^{H,Me}Cu_2(MeCN)_2](ClO_4)_2$ (**4c**), and $[L^{p-H,H}Cu_2(MeCN)_2](CF_3SO_3)_2$ (**4d**) are obtained in good yields by reaction with $Cu^I$ salts. X-ray diffraction studies performed on **4a** and **4d** reveal a distorted tetrahedral coordination geometry around each $Cu^I$ ion, which is constructed by three nitrogen donors of the macrocyclic ligand and one acetonitrile solvent molecule. Treatment of these complexes with molecular dioxygen shows that their reactivity can be fine-tuned by the nature of the aromatic unit of the dialdehyde building blocks. Thus two different dinuclear $Cu^{II}$ complexes resulting from the reaction of **4a** and **4b** with dioxygen were isolated and characterized by single crystal X-ray diffraction, XPS and magnetic measurements. The introduction of a methyl group in the 2-position of the aromatic spacers in **4c** hinders such oxygen transfer reactions but may allow the characterization of stable dioxygen binding species.


## Introduction

The study of copper-dioxygen interactions and reactivity is of great interest in chemical systems that involve redox activity or oxidative transformations. In biological systems copper proteins are known to provide a variety of functions including dioxygen transport by hemocyanin (Hc), oxygenation and dehydrogenation of substrates combined with the transformation of $O_2$ to either $H_2O_2$ or water.[1−3] With the hope of mimicking the mild and selective biological oxygenation reactions,[4−10] a great variety of mononuclear[11−15] and dinuclear[16−21] copper(I) complexes ligated by polydentate N-ligands (containing amine or imine groups) have been synthesized and investigated. In most cases, two interacting copper centers were found to be included in dioxygen binding and activation process just as hemocyanins and tyrosinases do in the natural systems.[4,10,22]

Tolman and co-workers[22−25] suggested an equilibrium between $Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo})$ and $Cu_2(\mu\text{-oxo})_2$ cores using mono- or binucleating 1,4,7-3R-1,4,7-triazacyclonoanes ligands (R = alkyl or aryl), which was strongly influenced by ligand geometry, solvent donor ability and temperature. It was further found that either of the cores might be responsible for oxygenation of substrates. Karlin and coworkers thoroughly investigated the reaction of dioxygen with a series of dinuclear $Cu^I$ complexes ligated by alkyl- or aryl-bridged bis[2-(pyrid-2-yl)ethyl]amine.[26−30] The alkyl bridge afforded in some cases the reversible binding of dioxygen to the copper centers, identified by UV/Vis or resonance Raman spectroscopy.[26−28] The replacement of the alkyl bridge by an aryl group, however, usually resulted in hydroxylation at the 2-position of the arene spacer, leading to $[Cu_2^{II}(R-XYL-O^-)(OH^-)]^{2+}$ (XYL: *m*-xylylene) species.[20,29,30] Surveying back the development of copper(I) complexes used in the oxygenation reaction, much of the research work has been focused on the use of "open" (non-macrocyclic) ligands. Only a few macrocyclic copper com-

[‡] X-ray diffraction (**4a**, **5a** and **5b**).
[‡‡] X-ray diffraction (**4d**).

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plexes have been reported for oxygenation reactions during the past several decades.[31−35]

According to the active sites of type III copper proteins (hemocyanins, tyrosinases), two copper ions coordinated by two or three nitrogen ligands per Cu unit and a suitable copper-copper distance for dioxygen binding are necessary aspects for the formation of stable copper-dioxygen adducts.[1−3] In our opinion, Schiff-base macrocyclic ligands fulfil these requirements. At the same time, a freely adjustable Cu···Cu distance can be realized by designing ligands of various sizes. Martell, Schindler et al. reported the first example of oxygenation reaction of a copper(I) complex ligated by a Schiff-base macrocyclic ligand. A possible oxygenation mechanism[32] and kinetic details[34] were provided in their work. However, they did not provide structural characterization of $Cu^{I}$ or $Cu^{II}$ complexes, leaving many structural and mechanistic questions unanswered. It is found that a minor modification of the ligand environment around the copper center will lead to a dramatic variation in oxygenation activity of the copper(I) complexes.[26,27] For a better understanding of the relation between a complex's structure and its reactivity towards dioxygen, we report here a series of Schiff-base macrocycles of different size and substitution, which provide structural insight into a tyrosinase model system.

## Results and Discussion

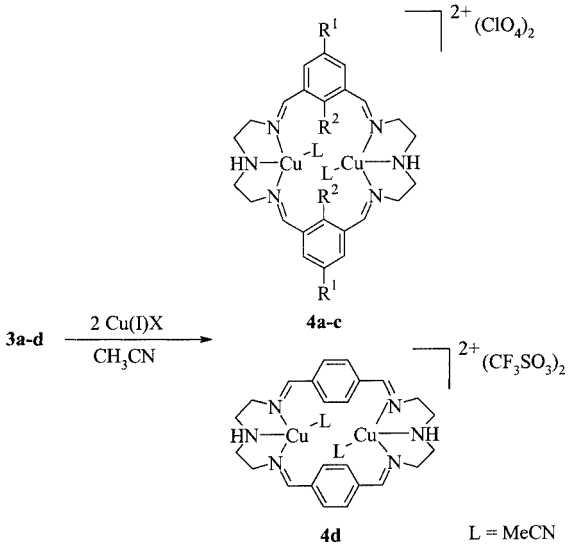
### Syntheses of Ligands

The macrocyclic compounds used in our investigations (Scheme 1) were prepared by a Schiff-base condensation reaction of diethylenetriamine (**1**) with four different aromatic aldehydes (**2a**−**d**) under dilute conditions.[36]

The dropwise addition of aldehydes in acetonitrile to a solution of amine in the same solvent affords the formation of macrocycles, which precipitate as white crystalline solids. This one step procedure gives all [2+2][37] cycles in good to quantitative yields. The products were characterized by a combination of different MS techniques (CI, FAB, MALDI-Tof: size distribution), by elemental analysis, and by IR and NMR spectroscopy. The $^{1}H$ NMR spectra of the macrocycles **3a**−**c** suggest the existence of isomers in solution. This can be explained by a facile nucleophilic attack of an NH group to one of the neighboring imine fragments, leading to the reversible formation of 18-membered diimine imidazolidine macrocycles.[33] According to $^{1}H$ and $^{13}C$ NMR spectroscopy at 25 °C, **3b** exists predominantly in the form of the bisimidazolidine isomer, while for **3a** and **3c** no preference can be found.

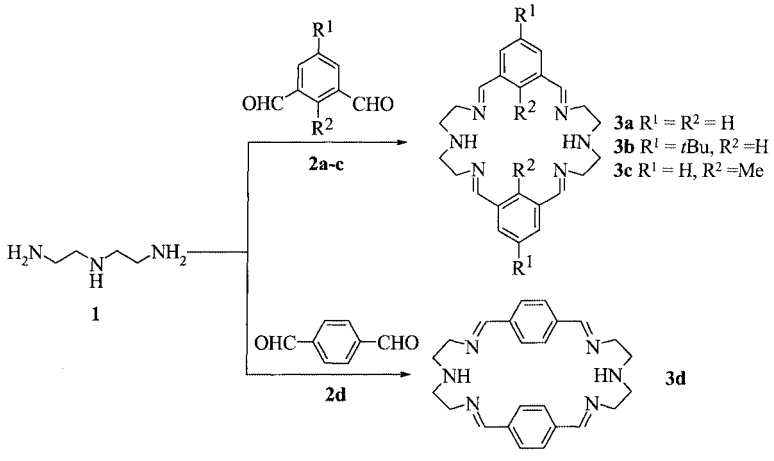
### Syntheses and Characterization of Copper(I) Complexes

$Cu^{I}$ complexes of the macrocycles **3a**−**d** were obtained by an addition of in situ generated $Cu^{I}$ perchlorate[38] or $Cu^{I}$ triflate to the ligand solution in dichloromethane (Scheme 2).




Scheme 2. Formation of dinuclear $Cu^{I}$ complexes

The yellow to red crystalline compounds obtained were isolated and in selected cases characterized by single-crystal X-ray analysis. Suitable crystals of **4a** and **4d** were obtained by diffusion of diethyl ether into an acetonitrile solution




Scheme 1. Reaction of diethylenetriamine (**1**) with dialdehydes **2a**−**d** to form macrocyclic ligands **3a**−**d**

Table 1. Crystallographic data overview for **4a** and **4d**

| | **4a** | **4d** |
|---|---|---|
| Empirical formula | $C_{28}H_{36}Cl_2Cu_2N_8O_8$ | $C_{30}H_{36}Cu_2F_6N_8O_6S_2$ |
| Formula mass [g/mol] | 810.65 | 909.87 |
| Crystal size [mm] | 0.61 × 0.38 × 0.27 | 0.52 × 0.48 × 0.42 |
| Crystal color | yellow | red |
| Crystal system | monoclinic | monoclinic |
| Space group | *I*2/*a* | $P2_1/n$ |
| *a* [Å] | 19.085(2) | 13.178(2) |
| *b* [Å] | 11.416(1) | 11.505(2) |
| *c* [Å] | 31.613(4) | 25.048(3) |
| β [°] | 95.09(2) | 97.340(10) |
| *V* [Å$^3$] | 6860.5(14) | 3766.5(10) |
| *Z* | 8 | 4 |
| $D_{calcd.}$ [g/cm$^3$] | 1.570 | 1.605 |
| μ [mm$^{-1}$] | 1.46 | 1.32 |
| Temperature [K] | 220(2) | 193(2) |
| θ range [°] | 2.08−25.93 | 2.56−25.26 |
| Refl. collected | 23000 | 7104 |
| $R_{int}$ | 0.076 | 0.020 |
| Refl. unique | 6337 | 6792 |
| Refl. observed [$I > 2\sigma(I)$] | 4762 | 5309 |
| *R*1, *wR*2 [$I > 2\sigma(I)$] | 0.038/0.084 | 0.0409/0.0954 |
| *R*1, *wR*2 (all data) | 0.054/0.088 | 0.0603/0.1016 |
| Goodness-of-fit on $F^2$ | 0.99 | 1.031 |
| Largest diff. peak and hole [e Å$^{-3}$] | 0.50 and −0.37 | 0.63 and −0.41 |

of the complex. The crystallographic analysis of **4a** and **4d** (Table 1) confirms in both cases the coordination of two copper atoms to the hexadentate macrocycle. Additionally, a coordinated acetonitrile molecule completes the distorted tetrahedral coordination geometry of the copper centers (Figures 1 and 2). In the case of **4a** the *meta*-substituted aromatic spacer units afford a $C_2$-symmetric arrangement of both copper(I)-containing subunits relative to each other leading to a short Cu···Cu distance of 4.28 Å, which is indeed similar to that found in tyrosinase (ca. 3.6 Å) and in the solid state of oxygenated and deoxygenated haemocyanin (3.6 and 4.6 Å).[1−3] Thereby the two copper centers are pointing towards each other, enforced by a pocket-like orientation of the macrocyclic ligand array (Figure 1).

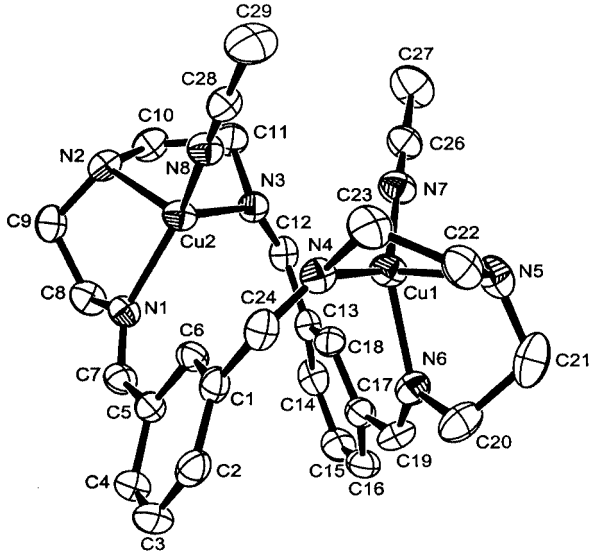



Figure 1. An ORTEP view of $[L^{H,H}Cu_2(MeCN)_2](ClO_4)_2$ (**4a**); hydrogen atoms and anions are omitted for clarity

Compound **4d** contains two tridentate metal binding sites that are separated by *para*-substituted aromatic spacer units. This leads to a "linear" arrangement of the two copper sub-structures with a larger Cu···Cu distance (relative to **4a**) of 6.86 Å. The two triflate anions show no direct interaction with the metal centers. In contrast to a recently published crystal structure of a similar complex with perchlorate anions,[35] the metal centers in **4d** are oriented to the same side of the plane defined by the macrocycle (Figure 2).

### Reaction of Copper(I) Complexes with $O_2$

The dinuclear copper(I) complexes **4a**−**d** were exposed to oxygenation reactions.[39] Dioxygen was bubbled directly via a gas releasing apparatus into the solution of **4a** in a mixture of acetonitrile, dichloromethane and methanol at room temperature. A clear green solution developed gradually. After workup, green prismatic crystals of **5a** could be isolated by recrystallization from acetonitrile. Single crystal analysis indicates **5a** to be a dinuclear bis(μ-methoxy)-copper complex still bearing the initial macrocyclic ligand (Scheme 3). This is a clear difference to the bis(μ-hydroxo)dicopper(II) complex or the aromatic hydroxylation $Cu^{II}$ complex proposed by Menif et al.[32,34] Complex **5a** displays sharp signals for the aromatic units of the ligand in the $^1$H NMR spectrum. A broad peak appears at δ = 5−6 ppm which could be assigned to the bridging methoxy groups. Thus the existence of two strongly-coupled copper(II) centers is suggested for **5a**. This hypothesis is further supported

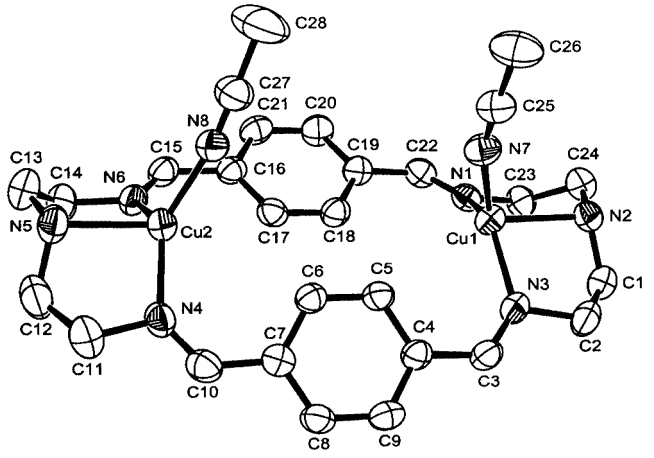
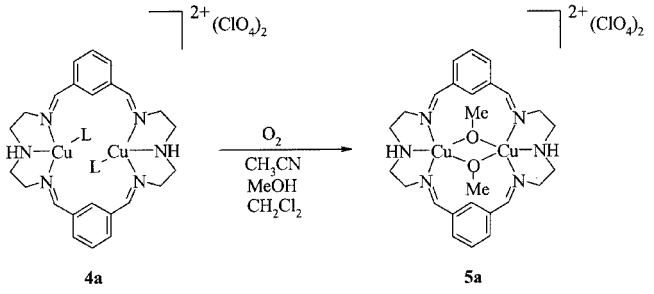


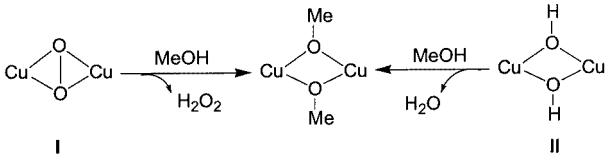

Figure 2. An ORTEP view of $[L^{p\text{-}H,H}Cu_2(MeCN)_2](CF_3SO_3)_2$ (**4d**); hydrogen atoms and anions are omitted for clarity




Scheme 3

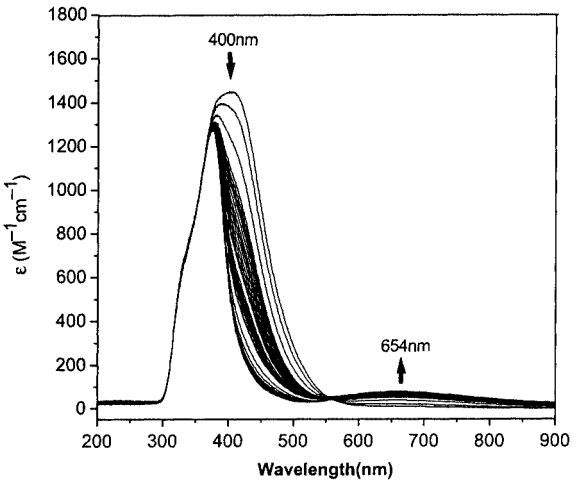
by temperature-dependent magnetic susceptibility measurements and by X-ray photoelectron spectroscopy.

Compound **5a** is not the first example of a methoxy-bridged $Cu^{II}$ complex. The isolation of similar $Cu^{II}$ species from the reaction of $Cu^{I}$ precursors bearing noncyclic ligands with dioxygen has been reported by other groups [7,16,40,41]. However, the formation process is still not understood. We assume here that the formation of **5a** occurs most likely via the reaction of the oxygenated species [either the dioxygen-binding species **I** or the bis(μ-hydroxo)dicopper complex **II**, Scheme 4] with solvent molecules.[42] Unfortunately, we were not able to demonstrate the formation of hydrogen peroxide or water. Direct synthesis of the bis(μ-hydroxo)dicopper(II) species from $Cu^{II}$ salts also failed due to the decomposition of the Schiff-base ligands in the presence of water or a base.

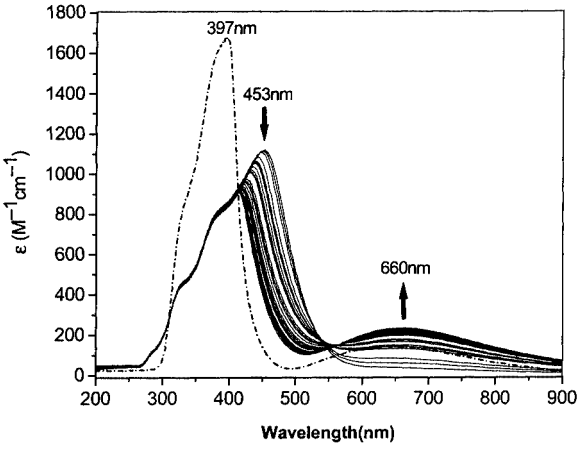



Scheme 4

To gain a better understanding, the reaction of **4a** with dioxygen was further investigated by UV/Vis spectroscopy in *N*,*N*-dimethylformamide. A single absorption at 400 nm is displayed initially for **4a**. By bubbling dioxygen into this




(A)

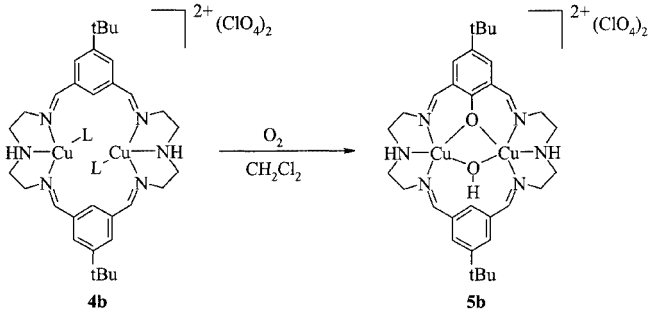



(B)

Figure 3. Reaction of (A) $[L^{H,H}Cu_2(MeCN)_2](ClO_4)_2$ (**4a**), (B) $[L^{tBu,H}Cu_2(MeCN)_2](ClO_4)_2$ (**4b**) with dioxygen in dry *N*,*N*-dimethylformamide; the initial trace shows the electronic spectrum of **4a** or **4b**; the subsequent traces were obtained upon adding dioxygen continually at room temperature for 2 h; the dashed line in (B) is the spectrum of $[(L^{tBu,H}O)Cu_2(\mu\text{-}OH)](ClO_4)_2$ (**5b**) in DMF

solution continually, this absorption shifts gradually to shorter wavelength with decreasing intensity. At the same time, a new absorption around 650−700 nm appears with lower intensity [Figure 3 (A)]. The final trace (after oxygenation is complete) shows a strong absorption at 375 nm and a weak one at 654 nm, which are only slightly different from the data reported by Menif (362 nm and 620 nm).[32] However, it suggests the formation of phenoxo- hydroxo-bridged dinuclear copper(II) complexes in DMF.[1,17,27,32] The absorption at 375 nm can be assigned to the ligand to metal charge transfer transition (from phenoxide to the $Cu^{II}$ center). The high wavelength absorption at 654 nm is due to the d-d transition band, which is characteristic for $Cu^{II}$ complexes.[1,7] The existence of the proposed bis(μ-hydroxo)dicopper complex[32−34] could not be identified definitely, however, the deviation of the low energy absorption (654 nm instead of 620 nm) might indicate its formation.

The reaction of **4b** with dioxygen in dichloromethane proved to be even faster than **4a**. Complex **5b**, which was




Scheme 5

isolated from this reaction in high yield, is the product of an intramolecular oxygen transfer and bears the dioxygen molecule after reductive O−O bond cleavage (Scheme 5, Figure 6). Such aromatic hydroxylation products obtained from noncyclic $Cu^{I}$ precursors and dioxygen are already well known.[29,30] However, to the best of our knowledge, **5b** is the first characterized structure obtained from the reaction of a Schiff-base macrocyclic $Cu^{I}$ complex and $O_2$.

An electrophilic attack of the μ-$\eta^2$:$\eta^2$-peroxo moiety to the aryl part of the ligand is proposed for the formation of such hydroxylation products.[29,30] This suggestion is supported by our observation that *tert*-butyl substitution at the 5-position of the aromatic spacer unit increases the rate of the C−H activation process in the 2-position and leads to higher yields of the insertion product **5b**. It is further found that a lower reaction temperature or addition of toluene inhibits the hydroxylation reaction. However, the presence of benzyl alcohol[43] increases the ratio of **5b** to the rest of oxidation products up to 88%. This is consistent with the result of Casella et al.[44] whereby the increase of the proton donor ability of the reaction medium favors the formation of the hydroxylation products (Table 2).

The UV spectrum of **4b** in the presence of dioxygen displays a similar reactivity to complex **4a**. The initial absorption at 453 nm of **4b** is gradually replaced by new absorptions at 397 nm and 660 nm, indicating the formation of the phenoxo- hydroxo-bridged dicopper complex **5b** [Figure 3, (B), solid lines)]. Nevertheless, the proposed dioxygen adduct intermediates which are responsible for the formation of **5b**, are again undetectable due to fast subsequent oxygen transfer.[1−10,14] By comparing the UV spectrum of pure **5b** [isolated crystals, Figure 3 (B), dashed line] with the final trace of **4b** after oxygenation, a good agreement is obtained except for the low energy region. Compound **5b** displays a d-d transition band at 640 nm (in contrast to the absorption at 660 nm of the reaction mixture), indicating most probably the formation of some other $Cu^{II}$ species during the oxygenation reaction. One suitable suggestion might be the formation of bis(μ-hydroxo)dicopper(II) complexes. This is supported by the findings of Karlin and co-workers on dinuclear $Cu^{I}$−dioxygen reaction products ligated by substituted pyridine ligands.[19,20,29,30]

The reaction of **4c**, bearing methyl substituents on the aromatic rings of the macrocyclic frame, with dioxygen shows a completely different reactivity than **4a** and **4b** (Figure 4 vs. Figure 3). The initial absorption at 433 nm shifts gradually to *longer* wavelength with *increasing* intensity and a weaker absorption appears at ca. 550 nm. Furthermore the intensity of this new absorption ($\varepsilon \approx 800$ $M^{-1}cm^{-1}$) is significantly higher than the comparable d-d bands in Figure 3 ($\varepsilon < 200$ $M^{-1}cm^{-1}$). This suggests the formation of new species [instead of phenoxo- hydroxo-bridged dicopper complex or bis(μ-hydroxo)dicopper complex] by reaction with dioxygen.[1,11]

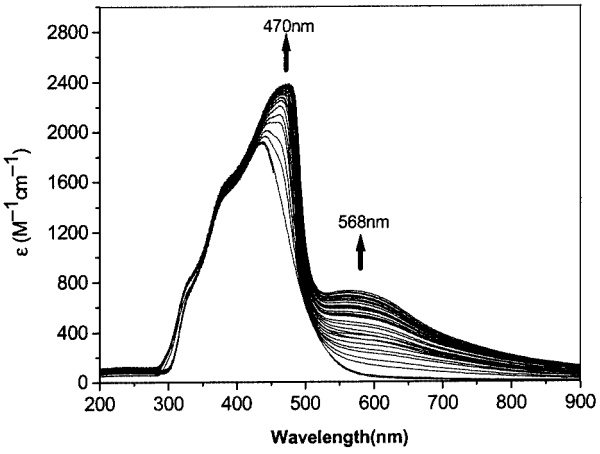



Figure 4. Reaction of $[L^{H,Me}Cu_2(MeCN)_2](ClO_4)_2$ (**4c**) with dioxygen in dry *N*,*N*-dimethylformamide; the initial trace shows the electronic spectrum of **4c**; the subsequent traces were obtained upon continuous addition of dioxygen at room temperature for 2 h

The features depicted in Figure 4 are more similar to what was reported for μ-peroxo-bridged complexes. These species show absorptions near 550 nm with moderate molar

Table 2. Aspects influencing the reaction of **4b** with $O_2$

| | Conc. [mM] | Solvent | BzOH (BzOH/Cu) | Temp. [°C] | Time [h] | **5b**[a] (%) |
|---|---|---|---|---|---|---|
| **1** | 0.58 | $CH_2Cl_2$/toluene (20:1) | - | -80/25 | 5/15 | 13 |
| **2** | 3.09 | $CH_2Cl_2$/toluene (20:1) | - | 25 | 20 | 44 |
| **3** | 3.60 | $CH_2Cl_2$ | - | 25 | 20 | 50 |
| **4** | 1.45 | $CH_2Cl_2$ | 1:1 | -80/25 | 5/15 | 70 |
| **5** | 1.45 | $CH_2Cl_2$ | 1:1 | 25 | 20 | 88 |
| **6** | 10 | $CH_2Cl_2$ | 1:1 | 25 | 24 | 80[b] |
| **7** | 10 | $CH_2Cl_2$ | 2:1 | 25 | 24 | 79[b] |

[a] Determined after hydrolysis of the reaction mixture by the ratio of hydroxylated dialdehydes to their nonhydroxylated counterparts.[32] [b] Dioxygen was bubbled for 1 min.

absorbance of about 1000 $M^{-1}cm^{-1}$ ,[42] which is similar to the observed absorption at 568 nm. The absorption at ca. 470 nm (ca. 2000 $M^{-1}cm^{-1}$) after oxygenation of **4c** is again assigned to a ligand to metal charge transfer transition. The relatively low intensity[42] of this band can result either from a generally low absorption of our macrocyclic ligands or − most probably − from a low concentration of the peroxo species, which seems to be stable for hours even at room temperature.

The reaction of **4c** with dioxygen was also performed on a synthetic scale in dichloromethane at room temperature. The color of the solution changed gradually to yellow-greenish and a solid of the same color precipitated. No pure green color developed as in the cases of **4a** and **4b**. After workup, a yellow-greenish powder was isolated, which shows the existence of a $[L^{H,Me}Cu_2(O_2)]^{2+}$ fragment by means of MS spectrometry. Unfortunately, all attempts to purify the products by crystallization failed, due to the poor solubility in suitable solvents. The analysis of products obtained after hydrolysis by addition of 4 N HCl and subsequent extraction with dichloromethane gave the original dialdehyde, 4-hydroxy-2-methylisophthalaldehyde, and a tetraaldehyde coupling product (Scheme 6).[45] Thus, the introduction of 2-methyl substituents in **4c** has not blocked the binding of dioxygen but has effectively inhibited the intramolecular hydroxylation reactions. The formation of 4-hydroxy-2-methylisophthalaldehyde might be explained by assuming that an intermolecular hydroxylation process occurs. If an electrophilic attack is suggested for this process,[29,40,46] the hydroxylation should happen in the 5-position of the aromatic unit. Thus 4-hydroxy-2-methylisophthalaldehyde and even the coupling product are most likely formed via a free radical process before or during acidic decomposition.[47]

Compared to the oxygenation activity of **4a**−**c**, the *para*-subsituted $Cu^I$ complex **4d** is completely inert to dioxygen. No oxygenation or even decomposition was observed in solution or in the solid state after exposure to dioxygen.[35] This surprising effect becomes clear by comparing the Cu···Cu distances in the *meta*-bridged complex **4a** and the "linear", *para*-bridged complex **4d**. The *para*-substituted aromatic units restrict the free location of the two $Cu^I$ centers relative to each other and leads to a separation of the Cu centers (Cu···Cu: 6.86 Å). This implies that no dioxygen can be activated. The *meta*-aromatic bridges force the two copper(I) centers into a chiral, "pocket-like" arrangement (cf. Figure 1) with a short Cu···Cu distance (4.28 Å) allowing both copper centers to bind and activate the dioxygen molecule simultaneously.[4−10]

## Characterization of Copper(II) Complexes

### Solid State Structures

Single crystals of dinuclear copper(II) complexes **5a** (Figure 5) and **5b** (Figure 6) were obtained and characterized

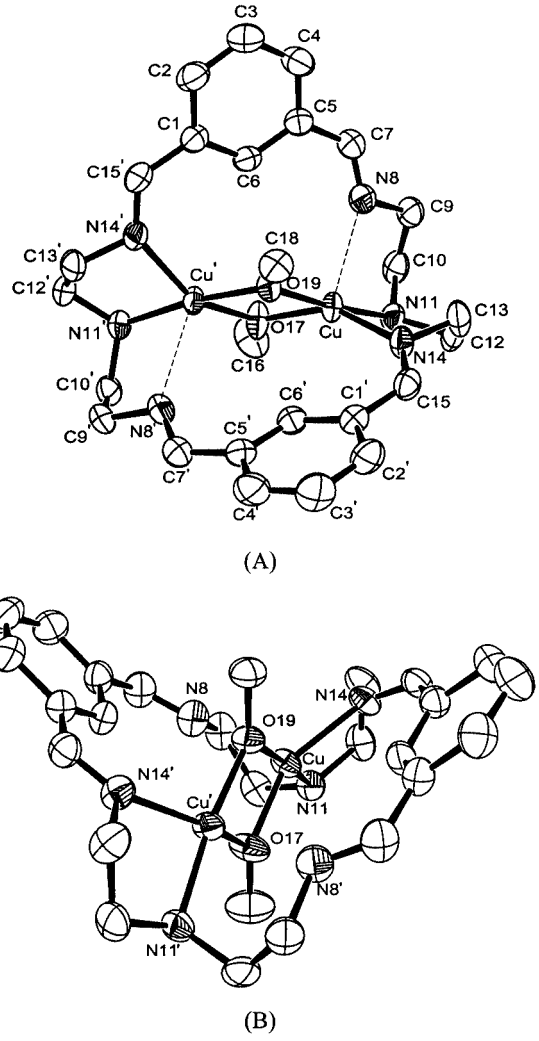
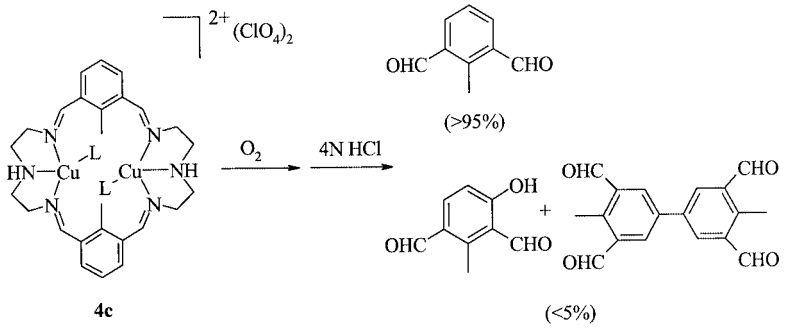



Figure 5. Two ORTEP views of $[L^{H,H}Cu_2(\mu\text{-}OMe)_2](ClO_4)_2$ (**5a**); hydrogen atoms and anions are omitted for clarity




Scheme 6

by X-ray diffraction (Table 3). The dicationic portion of **5a** shows a chiral, $C_2$-symmetric coordination around the dinuclear $Cu^{II}$ core in the solid state. Compared to the quasi-tetrahedral coordination adopted by **4a**, the coordination geometry around each $Cu^{II}$ ion in **5a** is most likely distorted square planar with a Cu···Cu separation of about 3.03 Å. This distance is typical for dinuclear copper complexes containing two single-atom bridging ligands.[23,27] The $Cu-N_{imine}$, $Cu-N_{amine}$ distances in **5a** do not differ from each other and are in the expected region for nitrogen-coordinated copper complexes of that type (Table 4).[10,11,22,27]

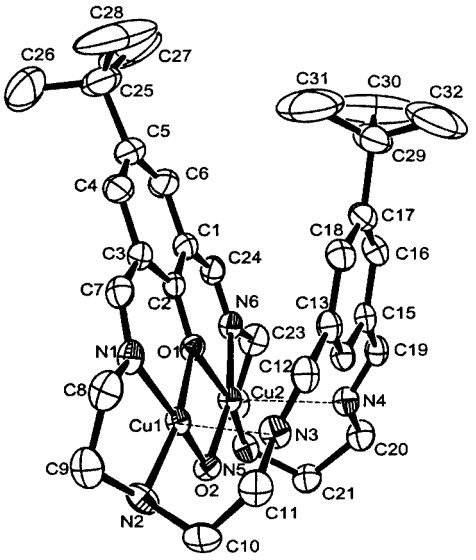



Figure 6. ORTEP view of $[(L^{tBu,H}O)Cu_2(\mu\text{-}OH)](ClO_4)_2$ (**5b**); hydrogen atoms and anions are omitted for clarity

However, the imine nitrogen atoms N8 (N8′) are also relatively close to the respective copper centers (N8−Cu, N8′−Cu′: 2.62 Å), thus a distorted square pyramidal environment can be assumed for both Cu centers[29,30] [Figure 5 (A)]. The $[Cu_2(\mu\text{-}OMe)_2]^{2+}$ core unit forms an ideal plane (torsion angle O19−Cu−O17−Cu = 0°), which is located perpendicular to the "macrocyclic pocket" structure [Figure 5 (B)] and N8, N8′ are disposed *anti* relative to it.

The nonsymmetric complex **5b** is the product of an intramolecular oxygenation reaction bearing bridging phenoxide and hydroxy units (Figure 6). Each $Cu^{II}$ ion adopts a slightly distorted square pyramidal coordination environment. The nitrogen atom N1 (N6), N2 (N5) and the two oxygen atoms O1, O2 form the basal equatorial plane (the sum of the angles is 358°). In contrast to **5a**, the two axial imine donors (N3, N4) are deposited *cis* with respect to the $Cu_2O_2$ plane, which leads to the observed unusual "U"-form of the macrocyclic ligand system. However, this coordination is less pronounced than in literature reports of five-coordinated species (2.409−2.437 Å relative to 2.0 −2.3 Å, Table 4).[20,22,46] The effect is probably due to repulsive steric interactions of the bulky *tert*-butyl substituents of **5b**.

### Magnetic Measurements

The magnetic susceptibilities of complexes **5a** and **5b** from 2 to 400 K (or 300 K) were determined by variable temperature magnetic susceptibility measurements. The curve of complex **5a** shows a pronounced antiferromagnetic behavior over the whole temperature range, due to the coupling of the two copper(II) ions in the same molecule, where the superexchange is mediated by the bridging me-

Table 3. Crystallographic data overview for **5a** and **5b**

| | **5a** | **5b** |
|---|---|---|
| Empirical formula | $C_{26}H_{36}Cl_2Cu_2N_6O_{10}$ | $C_{32}H_{46}Cl_2Cu_2N_6O_{10}$ |
| Formula mass [g/mol] | 790.61 | 872.73 |
| Crystal size [mm] | 0.40 × 0.30 × 0.10 | 0.35. × 0.31× 0.04 |
| Crystal color | green | green |
| Crystal system | monoclinc | monoclinc |
| Space group | *A2/a* | $P2_1/a$ |
| *a* [Å] | 15.261(2) | 11.816(2) |
| *b* [Å] | 10.105(2) | 13.583(2) |
| *c* [Å] | 22.544(3) | 24.471(5) |
| β [°] | 112.000(16) | 99.02(2) |
| *V* [Å$^3$] | 3223.6(10) | 3879.0(12) |
| *Z* | 4 | 4 |
| $D_{calcd.}$ [g/cm$^3$] | 1.621 | 1.494 |
| μ [mm$^{-1}$] | 1.55 | 1.30 |
| Temperature [K] | 293(2) | 223(2) |
| θ range [°] | 2.24−25.94 | 2.26−25.92 |
| Refl. collected | 12348 | 29855 |
| $R_{int}$ | 0.048 | 0.085 |
| Refl. unique | 3005 | 7464 |
| Refl. observed[$I > 2\sigma(I)$] | 2285 | 5167 |
| *R*1, *wR*2 [$I > 2\sigma(I)$] | 0.046/0.122 | 0.0468/0.1120 |
| *R*1, *wR*2 (all data) | 0.061/0.128 | 0.073/0.121 |
| Goodness-of-fit on $F^2$ | 0.99 | 0.95 |
| Largest diff. peak and hole [e Å$^{-3}$] | 0.62 and −0.64 | 075 and −0.39 |

Table 4. Selected lengths [Å] and angles [°] of some dinuclear $Cu^{I}$, $Cu^{II}$ complexes

| | Lengths [Å] | | | | | Angles [°] | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | Cu···Cu | O···O | Cu−O | Cu−$N_{eq}$ | Cu−$N_{ax}$ | Cu−O−Cu | O−Cu−O | |
| **4a** | 4.28 | – | – | 2.003(2), 2.092(2), 2.034(2), 2.043(2) | 2.200(2), 2.192(2) | – | – | this work |
| **4d** | 6.86 | – | – | 2.0212(8), 2.0221(9), 2.0106(8), 2.0791(9) | 2.1743(9), 2.1374(10) | – | – | this work |
| **5a** | 3.0278(9) | 2.410 | 1.948(2), 1.9215(19) | 2.027(3), 2.029(3) | 2.624 | 101.99, 103.95 | 77.01(11) | this work |
| **5b** | 3.0206(7) | 2.470 | 1.905(3), 1.988(3), 1.978(3), 1.925(3) | 1.931(3), 2.043(3), 2.028(3), 1.948(3) | 2.437(3), 2.409(3) | 99.23(10), 104.11(14) | 78.17(11), 77.94(11) | this work |
| **6**[a] | 7.04 | – | – | 2.022(5), 2.045(4) | 2.185(4) | – | – | [35] |
| **7**[b] | 3.560(3) | 1.412(12) | 1.903(11) | 2.000(8), 1.993(14) | 2.258(8) | 136.7(5) | 43.3(4) | [13] |
| **8**[c] | 2.794(2) | 2.287(2) | 1.808(5), 1.803(5) | 1.986(6), 1.987(6) | 2.298(6) | 101.4(2) | 78.6(2) | [23] |
| **9**[d] | 2.9769(9) | 2.454(2) | 1.940(4), 1.921(5), 1.924(5), 1.949(4) | 2.087(5), 2.054(4), 2.085(5), 2.029(5) | 2.289(5), 2.266(5) | 100.8(2), 100.5(2) | 78.6(2) | [23] |
| **10**[e] | 2.990(2) | – | 1.968(4), 1.909(4), 1.967(4), 1.911(4) | 1.933(6), 1.996(5), 1.939(5), 1.991(5) | – | – | 78.3(2), 78.3(2) | [46] |

[a] **6**: $[L^{p\text{-}H,H}Cu_2(MeCN)_2](ClO_4)_2$. [b] **7**: $[(HB(3,5\text{-}iPr_2pz)_3]Cu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)$. [c] **8**: $[(Bz_3TACD)Cu]_2(\mu\text{-}O)_2(SbF_6)_2$. [d] **9**: $[(Bz_3TACN)(HBz_2TACN)Cu]_2(\mu\text{-}OH)_2(CF_3SO_3)_2$; [e] **10**: $[(m\text{-}XYLO)Cu_2(\mu\text{-}OH)](BF_4)_2$.

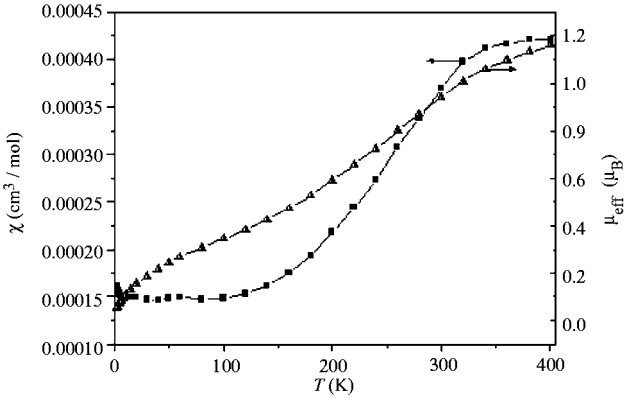



Figure 7. Temperature dependence of the corrected molar susceptibility of $[L^{H,H}Cu_2(\mu\text{-}OMe)_2](ClO_4)_2$ (**5a**)

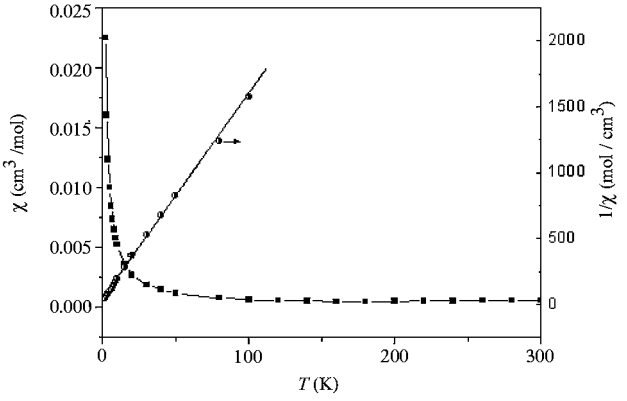



Figure 8. Temperature dependence of the corrected molar susceptibility of $[(L^{tBu,H}O)Cu_2(\mu\text{-}OH)](ClO_4)_2$ (**5b**)

thoxy groups (Figure 7). The effective magnetic moment per copper ($\mu_{eff}$/Cu) is about 1.2 $\mu_B$ in solid state. A value of $-2J = 587\ cm^{-1}$ is obtained at room temperature, indicating a strong coupling between the two copper ions even at room temperature. This is however in accordance with the result of the $^1H$ NMR spectra.

The magnetic behavior of the phenoxo- hydroxo-bridged dicopper complex **5b** is significantly different from **5a**, despite the relatively similar Cu···Cu distance. The data obtained for **5b** suggest that the copper ions are essentially independent centers or, at best, very weakly coupled (Figure 8). In the low temperature range, the molar susceptibility of **5b** is in a good agreement with the Curie−Weiss law[48,49] as indicated by the linear relation of $1/\chi$ over $T$ below 100 K.

## Conclusion

Our results show that macrocycles containing suitable sites for transition metal coordination can be designed to hold two metal centers at a well-defined distance and orientation relative to each other. In agreement with natural oxidation catalysts, such as monooxygenase tyrosinase, this seems to be a major requirement to fine-tune the reactivity of artificial cyclic di- or multinuclear structures. In our case, *meta*-substituted dialdehyde building blocks resulted in macrocyclic complexes with Cu···Cu distances that allowed the activation and transfer of molecular dioxygen. It has been shown that subsequent oxygen transfer reactions can follow multiple pathways from which one intra- and one intermolecular reaction product could be isolated and characterized. Interestingly, the unwanted intramolecular reaction could be blocked effectively by introduction of methyl substituents in the 2-position of the bridging aromatic spacer, favoring other oxygen-transfer routes. This gives good hope that macrocyclic complexes can be designed to bind oxygen and allow selective transfer to substrates of technical importance.

## Experimental Section

**General Remarks:** All operations concerning air- or moisture sensitive substances were performed under argon with standard Schlenk

techniques. Reagents and solvents were purchased from commercial sources and were used as received unless stated otherwise. Acetonitrile and methanol were purchased as dry solvents (water <0.005%) and were subsequently kept together with activated 3 Å or 4 Å molecular sieves. Dichloromethane and diethyl ether were refluxed with $CaH_2$ and $LiAlH_4$, respectively, and stored over activated molecular 4 Å sieves. All dry solvents were degassed prior to use. 2-Methylisophthalaldehyde[50], 5-*tert*-butylisophthalaldehyde[51] as well as **3a**[33] and **3d**[35] were prepared according to literature methods[32]. $^1$H NMR and $^{13}$C NMR spectra were recorded with a Bruker AMX400. Infrared measurements were obtained on KBr pellets using a Bruker IFS 113V and IFS 66V instrument. UV/Vis scan spectra were recorded with a J&M detector connected to a TIDAS spectrometer at room temperature. MS measurements were carried out using a Finnigan SSQ 7000 spectrometer with the methods of CI, FAB and MALDI. Magnetic measurement was carried out with a SQUID Magnetometer with constant field of 10000 Gauss. Elemental analyses were determined in the Microanalytical Laboratory of the University of Ulm.

***Caution!*** *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and handled with great care.*

**General Synthesis of Macrocyclic Imine Ligands:** In a typical reaction the aldehyde (1 mmol) in 20 mL of acetonitrile was added dropwise to a stirred solution of the amine (1 mmol) in about 30 mL of acetonitrile. The addition was done over 1−2 h at room temperature. After stirring the reaction mixture for 24 h the crystalline precipitates were filtered and washed with acetonitrile in small portions. If necessary the products can be recrystallized from chloroform/acetonitrile. The compounds were characterized by $^1$H NMR, $^{13}$C NMR, IR spectroscopy, and by MS and elemental analysis.

**$L^{tBu,H}$ (3b):** Yield 78%. FT IR (KBr): ν(C=N) = 1650 (s) cm$^{-1}$. $C_{32}H_{46}N_6$ (514.76): calcd. C 74.67, H 9.01, N 16.33; found C 74.51, H 8.98, N 16.25. $^1$H NMR ($CDCl_3$): δ = 8.1 (d, 2 H), 7.83 (m, 2 H), 7.44 (m, 2 H), 7.35 (m, 2 H), 3.13−4.0 (m, 14 H), 2.25−2.39 (m, 4 H), 1.85 (s, 2 H), 1.21 (m, 18 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = 160.8, 150.3, 140.1, 135.9, 128.2, 126.0, 120.6, 83.4, 58.4, 51.4, 51.1, 43.9, 33.6, 30.3 ppm. CI-MS, FAB-MS, MH$^+$: 515 (2+2 macrocycle), MALDI-Tof (dithranol): *m*/*z* = 514.38.

**$L^{H,Me}$ (3c):** Yield 79%. FT IR (KBr): ν(C=N) = 1629 (s) cm$^{-1}$. $C_{26}H_{34}N_6$ (430.34): calcd. C 72.50, H 7.90, N 19.52, found C 72.09, H 7.74, N 19.48. CI-MS, FAB-MS, MH$^+$: 431 (2+2 macrocycle), minor amount 646 (3+3 macrocycle), MALDI-Tof (dithranol): *m*/*z* = 514.38. The $^1$H and $^{13}$C NMR spectra in $CDCl_3$ are complex, suggesting the presence of isomers of the macrocycle.

**General Preparation Method for $Cu^I$ Complexes:** $Cu^I$ precursors were synthesized from $Cu^{II}$ salts according to literature procedures in a mixture of oxygen-free methanol/acetonitrile (1:1). This solution was filtered directly into a degassed solution of the ligand in dichloromethane. After stirring for several hours at room temperature, the complexes can be either isolated by evaporating the solvent to dryness or by precipitating the product with degassed diethyl ether after concentration of the solution. The yellow to orange products were characterized by a combination of $^1$H NMR and IR spectroscopy and elemental analysis.

**$[L^{H,H}Cu_2(MeCN)_2](ClO_4)_2$ (4a):** Yield 95%. FT IR (KBr): ν(C=N) = 1640 (s) cm$^{-1}$; ν($ClO_4^-$) = 1111 (s), 1091 (s), 624 (s) cm$^{-1}$. $C_{28}H_{36}N_8Cu_2Cl_2O_8$ (810.26): calcd. C 41.46, H 4.44, N 13.82, found C 41.38, H 4.46 N 13.79. $^1$H NMR ($CD_3CN$): δ = 9.3−8.3 (m, 6 H), 7.65 (s, 4 H), 7.1 (s, 2 H), 3.5 (s, 8 H), 3.25 (s, 2 H), 2.85 (m, 8 H) ppm. $^{13}$C NMR ($CD_3CN$): δ = 164.2, 152.2, 135.9, 132.0, 129.6, 60.3, 48.5 ppm.

**$[L^{tBu,H}Cu_2(MeCN)_2](ClO_4)_2$ (4b):** Yield 93%. FT IR (KBr): ν(C=N) = 1621(s) cm$^{-1}$; ν($ClO_4^-$) = 1111 (s), 1091 (s), 624 (s) cm$^{-1}$. $C_{36}H_{52}Cu_2Cl_2N_8O_8$ (922.08): calcd. C 46.85, H 5.64, N 12.15, found C 46.49, H 5.68, N 12.27. $^1$H NMR ($CD_3CN$): δ = 9.24 (s, 2 H), 8.25 (s, 4 H), 7.62 (s, 4 H), 3.45 (m, 8 H), 3.2 (s, 2 H), 2.9 (m, 8 H), 1.3 (m, 18 H) ppm.

**$[L^{H,Me}Cu_2(MeCN)_2](ClO_4)_2$ (4c):** Yield 90%. FT IR (KBr, cm$^{-1}$): ν(C=N) = 1619 (s), ν($ClO_4^-$) = 1111 (s), 1091 (s), 624 (s). $C_{30}H_{40}Cu_2Cl_2N_8O_8$ (838.4): calcd. C 42.94, H 4.77, N 13.36, found C 41.66, H 4.85, N 13.51. $^1$H NMR spectra could not be obtained, due to the very low solubility of the complex.

**$[L^{p\text{-}H,H}Cu_2(MeCN)_2](CF_3SO_3)_2$ (4d):** Yield 95%. FT IR (KBr, cm$^{-1}$): ν(C=N) = 1626 (s). $C_{30}H_{36}Cu_2F_6N_8O_6S_2$ (909.14): calcd. C 39.59, H 3.96, N 12.32, found C 39.84, H 4.18, N 12.12. $^1$H NMR ($CD_3CN$): δ = 8.5 (s, 4 H), 8.0 (s, 8 H), 3.6 (m, 8 H), 3.3 (s, 2 H), 2.9 (m, 8 H) ppm.

**Isolation of $[L^{H,H}Cu_2(\mu\text{-}OMe)_2](ClO_4)_2$ (5a):** Blue crystals of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.370 g, 1 mmol) were added to a suspension of excess Cu powder in acetonitrile (25 mL) and methanol (25 mL). The reaction mixture was stirred for 3 h. After filtration, the obtained clear colourless solution was added dropwise to a solution of macrocyclic ligand **3a** (0.402 g, 1 mmol) in dichloromethane (30 mL). An orange solution was obtained at once and was stirred overnight. Dioxygen was then bubbled gently via a gas releasing apparatus into the above solution at room temperature for 2 days. The solution became green within the first 10 minutes. After removal of the solvents, 50 mL of acetonitrile was injected to dissolve the dark green powder. Trace amounts of impurities were removed by filtration. The clear solution was concentrated to about 15 mL (warming the solution during this process slightly), and kept at room temperature for one day. Green prismatic crystals were separated from the solution (50 mg), and characterized as **5a**. MS (*m*/*z*, FAB): 627 (52) [M + H − $ClO_4^-$ − $Cu^{2+}$], 565 (22) [M + H − $ClO_4^-$ − 2 $MeO^-$] 527 (30) [M − 2 $ClO_4^-$ − $Cu^{2+}$], 500 (19) [M − $HClO_4$ − 2 $Cu^{2+}$ − 2 $MeO^-$], 465 (100) [M − 2 $ClO_4^-$ − $Cu^{2+}$ − 2 $MeO^-$]. IR (KBr): $\tilde{\nu}$ = 3436 br, 3270 m, 3077 w, 2930 m, 2819 m, 1642 s, 1604 sh, 1580 sh, 1456 m, 1434 sh, 1336 m, 1294 w, 1258 w, 1232 m, 1011 s, 1081 s, 1054 s, 967 m, 891 m, 794 m, 685 m, 622 s, 538 m, 450 m cm$^{-1}$. $C_{26}H_{36}Cl_2Cu_2N_6O_{10}$: calcd. C 39.50, H 4.58, N 10.63; found C 39.69, H 4.44, N 10.89. $^1$H NMR ($CD_3CN$): δ = 10.6 (br, 4 H), 8.2 (s, 2 H, Ar-*H*), 7.85 (m, 2 H, Ar-*H*), 7.4 (d, 4 H, Ar-*H*), 4.8−6.2 (br, 6 H, C*H*$_3$O), 3.2 (d, 8 H), 2.1 (s, 2 H, N-*H*), 1.8 (m, 8 H) ppm.

**Isolation of $[(L^{tBu,H}O)Cu_2(\mu\text{-}OH)](ClO_4)_2$ (5b):** Dioxygen was bubbled gently through a violently stirred solution of **4b** (500 mg, 0.54 mmol) in dichloromethane (150 mL) at room temperature. The solution turned green immediately and some green precipitate appeared. After 24 h, the reaction mixture was concentrated to dryness to afford a green powder. Acetonitrile (15 mL) was added to dissolve it and a trace amount of impurities was removed by filtration. The filtrate was then concentrated to about 3−4 mL (warming the solution during this process slightly), and kept at room temperature. Green planar crystals were obtained in a yield of 45% (190 mg), which were characterized as complex **5b**. MS (FAB): *m*/*z* = 655 (100) [M − 2 $ClO_4^-$ − OH], 672 (31) [M − 2 $ClO_4^-$]. IR (KBr): $\tilde{\nu}$ = 3566 s, 3267 s, 2960 s, 2871 m, 1647 s, 1597 w, 1559 m, 1455 m, 1395 w, 1366 w, 1399 m, 1287 w, 1238 m, 1098 s, 1010 m, 968 m, 889 w, 766 w, 706 w, 621 s, 575 w, 481 w, 445 m cm$^{-1}$.

$C_{32}H_{46}Cl_2Cu_2N_6O_{10}$: calcd. C 44.04, H 5.31, N 9.63; found C 44.62, H 5.30, N 9.71.

**Magnetic Susceptibility Measurements:** Solid-state magnetic susceptibility measurements of copper complexes **5a** and **5b** were obtained at a constant field of 10KOe on a SHE SQUID magnetometer operating between 2 and 400 K. Determinations were made on crystalline samples loaded into gelatine capsules. Diamagnetic corrections for the capsules were made by direct measurements, while corrections for the ligands were calculated by use of Pascal's constants.[49] A fixed TIP correction of $60 \times 10^{-6}$ cm$^3$/mol was adopted.[48]

**X-ray Photoelectron Spectroscopy:** Measurements for **5a** were carried out under the conditions of 5.85 eV, 250.0 W at 45.0° over 83.33 min for the Cu2p energy region. The same curve was also obtained by combining the energy bands reported for $CuCl_2$ and CuO.

**X-ray Crystallographic Study:** The crystal data of copper(I) complexes **4a** and **4d** and copper(II) complexes **5a** and **5b** were collected on a Rigaku AFC7S four-circle diffractometer or a STOE IPDS unit (Imaging Plate Diffraction System) using graphite monochromatized Mo-$K_\alpha$ radiation, $\lambda = 0.71073$ Å, ω-scans. Intensities were corrected for Lorentz and polarization effect.[52] A psi-scans absorption correction was applied for **4d**.[53] The structures of **4a** and **5b** were solved by the Patterson method (SHELXS-86 program), while the structures of **4d** and **5a** were solved primarily by direct methods. A refinement of full-matrix least-squares on $F^2$ was performed for all reflections with the SHELXL-97 program. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the final refinement cycle in a riding mode except for those of the methoxy bridges in **5a** and the *tert*-butyl groups of **5b**. In the case of **4d**, one triflate anion is disordered with site occupation factors of 0.25 and 0.75. DFIX was needed to refine both ordered and disordered triflate anions, which stabilize the structure by H bonds through oxygen atom with the macrocycle or its symmetry equivalent.[54,55] The perchlorate anions in **5a** are also disordered. Four oxygen atoms were represented by eight half-populated oxygen atoms. Crystal data of **4a**, **4d**, **5a** and **5b**, details about data collection, analysis and refinement were listed in Tables 1 and 3. CCDC-182382, -182229, -182383 and -182384 for **4a**, **4d**, **5a,** and **5b** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].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