

# Thermal Stability and Absorption Spectroscopic Behavior of ( $\mu$ -Peroxo)dicopper Complexes Regulated with Intramolecular Hydrogen Bonding Interactions

Syuhei Yamaguchi,<sup>[a]</sup> Akira Wada,<sup>[a]</sup> Yasuhiro Funahashi,<sup>[a]</sup> Shigenori Nagatomo,<sup>[b]</sup>  
Teizo Kitagawa,<sup>[b]</sup> Koichiro Jitsukawa,<sup>\*[a]</sup> and Hideki Masuda<sup>\*[a]</sup>

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In order to clarify the effect of hydrogen bonding on the stabilities of ( $\mu$ -peroxo)dicopper complexes with a *trans*- $\mu$ -1,2-peroxo form, novel copper complexes with intramolecular hydrogen bonding interaction sites have been synthesized, and their spectroscopic properties and thermal stabilities studied. The selected tripodal tetradentate ligands were tris(2-pyridylmethyl)amine (TPA) derivatives bearing pivalamido and amino groups at the 6-position of the pyridine ring in TPA, {[6-(pivalamido)pyrid-2-yl]methyl}bis(pyrid-2-ylmethyl)amine (MPPA) and {[6-aminopyrid-2-yl]methyl}bis(pyrid-2-ylmethyl)amine (MAPA). The single-crystal X-ray structure of a monomeric Cu<sup>II</sup> complex with N<sub>3</sub><sup>−</sup> namely [Cu(mppa)N<sub>3</sub>]ClO<sub>4</sub> (**1a**), revealed an interligand hydrogen bonding interaction between the substituent NH group of MPPA and the azide nitrogen atom in the axial position. The Cu<sup>I</sup> complexes of MPPA and MAPA were immediately oxygenated with dioxygen in acetone solution at −78 °C to give the  $\mu$ -peroxo dinuclear copper(II) complexes {[Cu(mppa)]<sub>2</sub>(O<sub>2</sub>)]<sup>2+</sup> (**1b**) and {[Cu(mapa)]<sub>2</sub>(O<sub>2</sub>)]<sup>2+</sup> (**2b**). These

complexes exhibited two kinds of characteristic absorption bands ( $\pi^*_{\sigma} \rightarrow d_{\sigma}$ ,  $\pi^*_{\nu} \rightarrow d_{\sigma}$ ) originating from the ligand–metal charge transfer (LMCT) of O<sub>2</sub><sup>2−</sup> to Cu. Affected by the hydrogen bonding interaction, the  $\pi^*_{\sigma} \rightarrow d_{\sigma}$  CT band shifted significantly to a higher energy region and the  $\pi^*_{\nu} \rightarrow d_{\sigma}$  CT absorbance decreased due to stabilization of the  $\pi^*_{\sigma}$  orbital and restriction of the Cu–O bond rotation. The thermal stabilities of the ( $\mu$ -peroxo)dicopper(II) complexes were estimated from their decomposition rates which decreased in the order, **2b**  $\approx$  {[Cu(tpa)]<sub>2</sub>(O<sub>2</sub>)]<sup>2+</sup> (**3b**) > **1b** >> {[Cu(6-metpa)]<sub>2</sub>(O<sub>2</sub>)]<sup>2+</sup> (**4b**) [6-MeTPA = {[6-methylpyrid-2-yl]methyl}bis(pyrid-2-ylmethyl)amine]. The above findings indicate that the interligand hydrogen bonding interaction, although overcome to some extent by the adverse effect of the steric bulk of the NH group, is inclined to stabilize ( $\mu$ -peroxo)dicopper(II) complexes.

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## Introduction

In biological systems, O<sub>2</sub> binding and its activation by metalloenzymes are important processes for respiratory and metabolic systems.<sup>[1]</sup> Detailed examinations using biomimetic model systems are required for understanding the natural processes, such as dioxygen transport, oxidation, oxygenation, and dehydrogenation.<sup>[1–3]</sup> These processes are catalyzed by heme iron,<sup>[4,5]</sup> non-heme iron<sup>[6,7]</sup> and copper centers<sup>[8–13]</sup> at the active sites of the metalloenzymes. In order to clarify the catalytic reaction mechanism of the dicopper-containing enzymes, dicopper–dioxygen adduct complexes have been investigated as biomimetic

models.<sup>[14–35]</sup> The binding of dioxygen to dinuclear copper complexes has been previously found to result in (*trans*- $\mu$ -1,2-peroxo)dicopper(II),<sup>[14–25]</sup> [ $\mu$ -( $\eta^2$ : $\eta^2$ )-peroxo]dicopper(II),<sup>[14,26–31]</sup> and [bis( $\mu$ -oxo)]dicopper(III) forms.<sup>[14,32–35]</sup> These coordination modes in dicopper sites are known to depend on the stereochemistry of the coordination environment. The geometries of dicopper–dioxygen complexes are likely to be regulated by the number of coordinating ligands;<sup>[14–35]</sup> (*trans*- $\mu$ -1,2-peroxo)dicopper(II) complexes<sup>[14–25]</sup> have been generally formed using tetradentate ligands and the structural and spectroscopic properties of (*trans*- $\mu$ -1,2-peroxo)dicopper(II) complexes were first systematically investigated by Karlin and co-workers.<sup>[16–23]</sup>

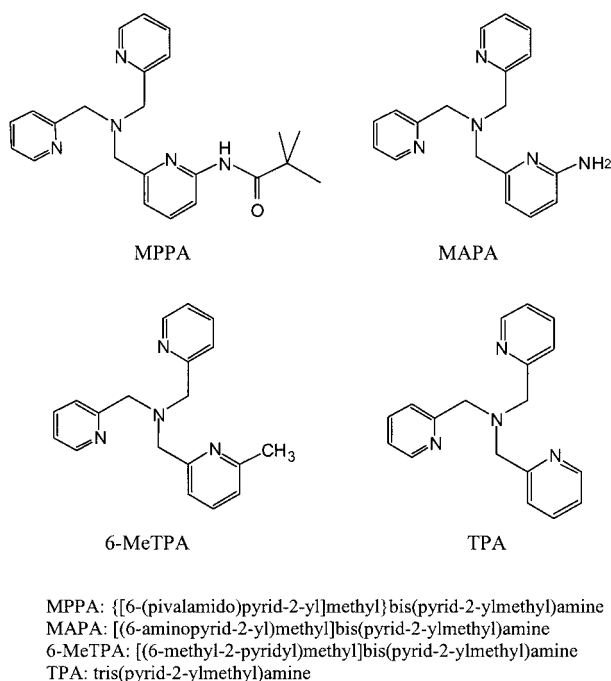
In biological catalysts, environmental factors such as the proximal effect of amino acid residues are frequently required for regulating reaction intermediates and activating substrates. We have demonstrated that the hydrogen bonding interaction can control the reactivity of metal–dioxygen species, and have succeeded in the preparation of the stable monomeric (hydroperoxo)copper(II) complex [Cu<sup>II</sup>(bppa)-(OOH)]<sup>+</sup> [BPPA = bis{[6-(pivalamido)pyrid-2-yl]methyl}-(pyrid-2-ylmethyl)amine].<sup>[36]</sup> The crystal structure of this

<sup>[a]</sup> Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan  
Fax: (internat.) + 81-52-7355228  
E-mail: masuda@ach.nitech.ac.jp

<sup>[b]</sup> Center of Integrative Bioscience, Okazaki National Research Institutes, Myodaiji, Okazaki 444-8585, Japan

complex revealed a hydrogen bonding interaction between the pivalamido NH group of BPPA and the ligating hydroperoxo oxygen atom.<sup>[36]</sup> The remarkable stability of  $[\text{Cu}^{\text{II}}(\text{bppa})(\text{OOH})]^+$  was acquired by the intramolecular hydrogen bonding interaction. From this point of view, it has been previously discussed that the interligand hydrogen bonding interaction can stabilize (superoxo)-, (alkylperoxo)-, and (hydroxo)metal complexes with tripodal tetradentate ligands.<sup>[37–43]</sup>

As an expansion of our previous research, tripodal ligands having the hydrogen bonding feature, such as {[6-(pivalamido)pyrid-2-yl]methyl}bis(pyrid-2-ylmethyl)amine (MPPA) and [(6-amino-2-pyridyl)methyl]bis(pyrid-2-ylmethyl)amine (MAPA) (Scheme 1), have been newly prepared for complexation with copper ions. It was expected that these tetradentate ligands would form (*trans*- $\mu$ -1,2-peroxo)-dicopper(II) complexes that would be dominated by their coordination numbers. In this paper, we describe details of the following: (i) the coordination structures and hydrogen bonding modes of copper complexes with MPPA and MAPA and (ii) formation of the corresponding  $\mu$ -peroxo dinuclear copper complexes and their characteristic absorption spectroscopic behavior and thermal stabilities. We also discuss the intrinsic effect of the proximal hydrogen bonding interaction in  $\mu$ -peroxo dinuclear copper complexes in detail and compare these with the cases of copper complex systems of TPA and Cu-6-MeTPA {6-MeTPA = [(6-methyl-2-pyridyl)methyl]bis(pyrid-2-ylmethyl)amine} without a hydrogen bonding site (Scheme 1).<sup>[44,45]</sup>



Scheme 1. Tripodal pyridylamine ligands

## Results and Discussion

### Formation of $\text{Cu}^{\text{II}}\text{--L--N}_3$ Complexes ( $\text{L} = \text{mppa}$ , $\text{mapa}$ , $\text{tpa}$ , $\text{6-metpa}$ ) and Their Spectroscopic Properties

$[\text{Cu}^{\text{II}}(\text{mppa})(\text{ClO}_4)_2]$  (**1**) [ $\text{mppa} = \text{bis}(\text{pyrid-2-ylmethyl})\{[6\text{-(pivalamido)pyrid-2-yl}]\text{methyl}\}\text{amine}$ ] was synthesized by mixing equimolar amounts of  $\text{Cu}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and MPPA in methanol. Addition of  $\text{NaN}_3$  to **1** in  $\text{CH}_3\text{CN}$  results in a color change of the solution from blue to green, indicating formation of  $[\text{Cu}^{\text{II}}(\text{mppa})(\text{N}_3)]^+$  (**1a**).  $[\text{Cu}^{\text{II}}(\text{L})(\text{N}_3)]^+$  complexes [ $\text{L} = \text{mapa}$  (**2a**),  $\text{tpa}$  (**3a**),<sup>[46]</sup> and  $\text{6-metpa}$  (**4a**)] were also prepared in  $\text{CH}_3\text{CN}$  solution by a similar procedure and the azide complexes all showed almost the same spectroscopic properties corresponding to the analogous coordination geometries. Electronic absorption and ESR spectroscopic data for  $[\text{Cu}^{\text{II}}(\text{L})(\text{N}_3)]^+$ , **1a**, **2a**, **3a** and **4a**, are listed in Tables 1 and 2, respectively. The electronic absorption spectrum of **1a** exhibited d-d transition bands centered at 647 nm ( $300 \text{ M}^{-1}\text{cm}^{-1}$ ) and 833 nm ( $220 \text{ M}^{-1}\text{cm}^{-1}$ ), and an intense absorption band at 395 nm ( $2700 \text{ M}^{-1}\text{cm}^{-1}$ ). The latter intense absorption band in the UV region can be assigned to LMCT since the other azide complexes,  $[\text{Cu}(\text{mapa})(\text{N}_3)]^+$  (**2a**) and  $[\text{Cu}(\text{tpa})(\text{N}_3)]^+$  (**3a**), exhibited intense LMCT bands between the bound  $\text{N}_3^-$  anion and the copper ion in the same region [at 403 nm ( $2940 \text{ M}^{-1}\text{cm}^{-1}$ )<sup>[46]</sup> and 413 nm ( $2130 \text{ M}^{-1}\text{cm}^{-1}$ ), respectively] (Table 1).

$[\text{Cu}^{\text{II}}(\text{6-metpa})(\text{N}_3)]^+$  (**4a**) also showed the same characteristic LMCT band at 414 nm ( $2600 \text{ M}^{-1}\text{cm}^{-1}$ ), indicating that the azide ion is bound to the  $\text{Cu}^{\text{II}}$  center. The frozen solution ESR spectrum of the azide complex **1a** at 77 K gave signals typical for a  $\text{Cu}^{\text{II}}$  complex with a  $d_{z^2}$  ground state ( $g_{\parallel} = 2.03 < g_{\perp} = 2.20$ ,  $|A_{\parallel}| = 71 \text{ G}$ , and  $|A_{\perp}| = 130 \text{ G}$ ). Including other azide complexes, the ESR spectroscopic patterns of **1a**, **2a**, and **3a** are characteristic of a trigonal-bipyramidal geometry ( $g_{\parallel} < g_{\perp}$ ) which agrees well with those speculated from their absorption spectroscopic features showing lower d-d transition energies (Table 2).

### Crystal Structures of $[\text{Cu}(\text{mppa})(\text{ClO}_4)_2]$ (**1**) and $[\text{Cu}(\text{mppa})(\text{N}_3)]\text{ClO}_4$ (**1a**)

$[\text{Cu}(\text{mppa})(\text{ClO}_4)_2]$  (**1**) and  $[\text{Cu}(\text{mppa})(\text{N}_3)]\text{ClO}_4$  (**1a**) were obtained as blue and green crystals, respectively, which were suitable for X-ray structural analysis. The molecular structures of the cationic parts of **1** and **1a** are shown in Figures 1 and 2, respectively. Selected bond lengths and angles around the copper cores are listed together in Table 3. The  $\text{Cu}^{\text{II}}$  ion in **1** is coordinated by three pyridine nitrogen atoms of MPPA [ $\text{Cu--N}(2) = 1.970(6) \text{ \AA}$ ,  $\text{Cu--N}(3) = 2.062(6) \text{ \AA}$ ,  $\text{Cu--N}(4) = 2.079(6) \text{ \AA}$ ] in the trigonal plane and by one tertiary amine nitrogen and one pivalamido oxygen atom of MPPA [ $\text{Cu--N}(1) = 2.006(7) \text{ \AA}$  and  $\text{Cu--O}(1) = 1.940(6) \text{ \AA}$ ] in the axial positions. The  $\text{Cu}^{\text{II}}$  ion in the azide complex **1a** has almost the same coordination mode as in **1** except for substitution of an azide ion for the pivalamido oxygen atom of MPPA. The copper

Table 1. UV/Vis spectroscopic data for  $[\text{Cu}(\text{L})(\text{N}_3)]^+$  in MeCN

| Complex                                                   | LMCT ( $\text{N}_3^- \rightarrow \text{Cu}^{\text{II}}$ )<br>$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) | d-d bands<br>$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) |
|-----------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| $[\text{Cu}(\text{mppa})(\text{N}_3)]^+$ ( <b>1a</b> )    | 395 (2700)                                                                                                                               | 647 (300), 833 (220)                                                                     |
| $[\text{Cu}(\text{mapa})(\text{N}_3)]^+$ ( <b>2a</b> )    | 403 (2940)                                                                                                                               | 670 (300), 878 (250)                                                                     |
| $[\text{Cu}(\text{tpa})(\text{N}_3)]^+$ ( <b>3a</b> )     | 413 (2130) <sup>[a]</sup>                                                                                                                | 674 (277), 882 (275) <sup>[a]</sup>                                                      |
| $[\text{Cu}(\text{6-metpa})(\text{N}_3)]^+$ ( <b>4a</b> ) | 414 (2600)                                                                                                                               | 670 (300), 845 (210)                                                                     |

[a] Ref.<sup>[46]</sup>Table 2. ESR spectroscopic data for  $[\text{Cu}(\text{L})(\text{N}_3)]^+$  in MeCN

| Complex                                                   | $g_{\parallel}$  | $ A_{\parallel} /\text{Gauss}$ | $G_{\perp}$      | $ A_{\perp} /\text{Gauss}$ |
|-----------------------------------------------------------|------------------|--------------------------------|------------------|----------------------------|
| $[\text{Cu}(\text{mppa})(\text{N}_3)]^+$ ( <b>1a</b> )    | 2.03             | 71                             | 2.20             | 130                        |
| $[\text{Cu}(\text{mapa})(\text{N}_3)]^+$ ( <b>2a</b> )    | 2.00             | 76                             | 2.21             | 100                        |
| $[\text{Cu}(\text{tpa})(\text{N}_3)]^+$ ( <b>3a</b> )     | 2.00             | 82                             | 2.19             | 92                         |
| $[\text{Cu}(\text{6-metpa})(\text{N}_3)]^+$ ( <b>4a</b> ) | — <sup>[a]</sup> | — <sup>[a]</sup>               | — <sup>[a]</sup> | — <sup>[a]</sup>           |

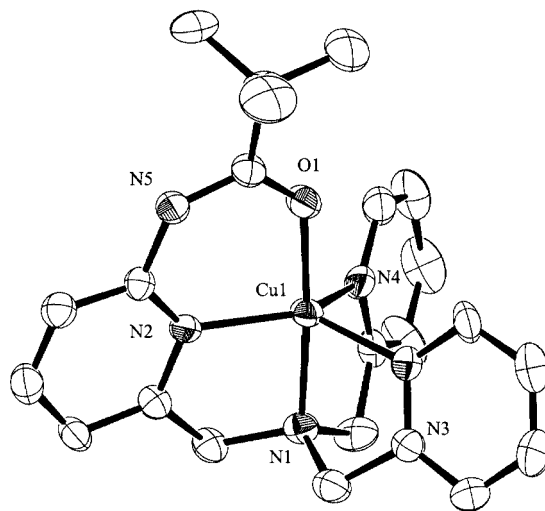
[a] Broadened signal.

Table 3. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^{\circ}$ ] for  $[\text{Cu}(\text{mppa})](\text{ClO}_4)_2$  (**1**) and  $[\text{Cu}(\text{mppa})(\text{N}_3)]\text{ClO}_4$  (**1a**)

| $[\text{Cu}(\text{mppa})](\text{ClO}_4)_2$ ( <b>1</b> )          |          |                 |          |  |
|------------------------------------------------------------------|----------|-----------------|----------|--|
| Bond length [ $\text{\AA}$ ]                                     |          |                 |          |  |
| Cu(1)—O(1)                                                       | 1.940(6) | Cu(1)—N(3)      | 2.062(6) |  |
| Cu(1)—N(1)                                                       | 2.006(7) | Cu(1)—N(4)      | 2.079(6) |  |
| Cu(1)—N(2)                                                       | 1.970(6) |                 |          |  |
| Bond angle [ $^{\circ}$ ]                                        |          |                 |          |  |
| O(1)—Cu(1)—N(1)                                                  | 176.0(2) | N(1)—Cu(1)—N(2) | 85.3(3)  |  |
| O(1)—Cu(1)—N(2)                                                  | 90.8(2)  | N(1)—Cu(1)—N(3) | 83.8(3)  |  |
| O(1)—Cu(1)—N(3)                                                  | 98.6(3)  | N(1)—Cu(1)—N(4) | 82.6(3)  |  |
| O(1)—Cu(1)—N(4)                                                  | 99.8(3)  | N(2)—Cu(1)—N(3) | 127.3(3) |  |
|                                                                  |          | N(2)—Cu(1)—N(4) | 125.3(3) |  |
|                                                                  |          | N(3)—Cu(1)—N(4) | 104.0(2) |  |
| $[\text{Cu}(\text{mppa})(\text{N}_3)]\text{ClO}_4$ ( <b>1a</b> ) |          |                 |          |  |
| Bond length [ $\text{\AA}$ ]                                     |          |                 |          |  |
| Cu(1)—N(6)                                                       | 1.936(5) | Cu(1)—N(3)      | 2.050(6) |  |
| Cu(1)—N(1)                                                       | 2.010(5) | Cu(1)—N(4)      | 2.070(5) |  |
| Cu(1)—N(2)                                                       | 2.180(5) | N(5)···N(6)     | 2.893(6) |  |
| Bond angle [ $^{\circ}$ ]                                        |          |                 |          |  |
| N(6)—Cu(1)—N(1)                                                  | 175.3(2) | N(1)—Cu(1)—N(2) | 80.0(2)  |  |
| N(6)—Cu(1)—N(2)                                                  | 96.5(2)  | N(1)—Cu(1)—N(3) | 81.0(2)  |  |
| N(6)—Cu(1)—N(3)                                                  | 98.0(2)  | N(1)—Cu(1)—N(4) | 81.2(2)  |  |
| N(6)—Cu(1)—N(4)                                                  | 103.2(2) | N(2)—Cu(1)—N(3) | 116.7(2) |  |
|                                                                  |          | N(2)—Cu(1)—N(4) | 116.5(2) |  |
|                                                                  |          | N(3)—Cu(1)—N(4) | 119.2(2) |  |

center is surrounded by three pyridine nitrogen atoms from MPPA [ $\text{Cu}-\text{N}(2) = 2.180(5) \text{ \AA}$ ,  $\text{Cu}-\text{N}(3) = 2.050(5) \text{ \AA}$ ,  $\text{Cu}-\text{N}(4) = 2.070(5) \text{ \AA}$ ] in the trigonal plane and one tertiary amine nitrogen atom [ $\text{Cu}-\text{N}(1) = 2.010(5) \text{ \AA}$ ] from MPPA and one azide nitrogen atom [ $\text{Cu}-\text{N}(6) = 1.936(5) \text{ \AA}$ ] in the axial positions. Judging from the coordination geometric parameter  $\tau$  around the  $\text{Cu}^{\text{II}}$  ion [ $\tau = (\beta - \alpha)/$

$60$ , where  $\alpha$  and  $\beta$  represent two basal angles ( $\beta \geq \alpha$ )],<sup>[47]</sup> the coordination structures for **1** (0.81) and **1a** (0.94) are both almost trigonal-bipyramidal as listed in Table 3. As shown by the above spectroscopic and structural results, it is clear that the  $\text{Cu}^{\text{II}}$  complexes with an azide group exhibit a trigonal-bipyramidal structure both in solution and in the solid state. In the molecular structure of **1a**, a hydrogen bond was observed between the pivalamido NH group of MPPA and the coordinated azide ion. The distance between N(5) and N(6) [ $2.893(6) \text{ \AA}$ ] corresponds well to a hydrogen bonding interaction (Figure 2), which apparently contributes to the fixation of the azide ion, as found in the previously reported Cu-TPPA and Cu-BPPA complexes with the pivalamido group [TPPA: tris{[6-(pivalamido)pyrid-2-yl]methyl}amine; BPPA: bis{[6-(pivalamido)pyrid-2-yl]methyl}(pyrid-2-ylmethyl)amine].<sup>[36–41]</sup>

Figure 1. ORTEP plots of  $[\text{Cu}(\text{mppa})]^{2+}$  (**1**) with the atomic labeling scheme; hydrogen atoms have been omitted for clarity

### Electrochemical Properties

In order to understand the electrochemical properties of the  $\text{Cu}^{\text{II}}$  complexes with tripodal tetradentate ligands, the cyclic voltammograms of the azide complexes were measured in MeCN under argon relative to the SCE. The cyclic voltammograms of **1a**, **2a**, **3a**, and **4a** showed a reversible one-electron redox potential wave. The redox potential values were converted into the NHE scale by adding  $244.4 \text{ mV}$ ,<sup>[48]</sup> and the electrochemical data are listed in Table 4. The  $E_{1/2}$  values of the azide complexes are significantly dif-

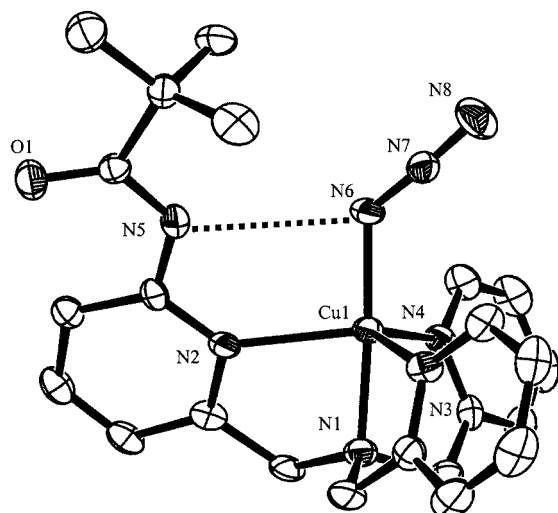


Figure 2. ORTEP plots of  $[\text{Cu}(\text{mppa})(\text{N}_3)]^+$  (**1a**) with the atomic labeling scheme; hydrogen atoms have been omitted for clarity

ferent from each other: those of **1a** and **4a** are in the range of  $-40$  mV whilst those of **2a** and **3a** are  $-138$  and  $-89$  mV, respectively (vs. NHE).

Table 4. Electrochemical parameters for  $[\text{Cu}(\text{L})(\text{N}_3)]^+$  in MeCN (reduction and oxidation potentials are given relative to the NHE)

| Complex                                                   | $E_{\text{pa}}/\text{mV}$ | $E_{\text{pc}}/\text{mV}$ | $\Delta E/\text{mV}$ | $E_{1/2}/\text{mV}$ |
|-----------------------------------------------------------|---------------------------|---------------------------|----------------------|---------------------|
| $[\text{Cu}(\text{mppa})(\text{N}_3)]^+$ ( <b>1a</b> )    | $-4$                      | $-84$                     | $80$                 | $-44$               |
| $[\text{Cu}(\text{mapa})(\text{N}_3)]^+$ ( <b>2a</b> )    | $-98$                     | $-178$                    | $80$                 | $-138$              |
| $[\text{Cu}(\text{tpa})(\text{N}_3)]^+$ ( <b>3a</b> )     | $-37$                     | $-140$                    | $103$                | $-89$               |
| $[\text{Cu}(\text{6-metpa})(\text{N}_3)]^+$ ( <b>4a</b> ) | $+16$                     | $-85$                     | $101$                | $-34$               |

### Reaction of Copper(I) Complexes with Dioxygen and Characterization of the Oxygenated Complexes

The reactions of the  $\text{Cu}^{\text{I}}$ -MPPA or -MAPA complexes with dioxygen were performed in acetone and EtCN solutions, which were monitored by spectroscopic methods such as electronic absorption, resonance Raman and ESR spectroscopy. Bubbling dioxygen into the solution of each  $\text{Cu}^{\text{I}}$  complex at  $-78$  °C resulted in an intense color change from light yellow to violet. The absorption spectra of these violet species in acetone solution showed intense bands at  $517$  nm ( $\epsilon = 5600 \text{ M}^{-1}\text{cm}^{-1}$ ) and  $503$  nm ( $\epsilon = 7500 \text{ M}^{-1}\text{cm}^{-1}$ ) for the Cu-MPPA and Cu-MAPA systems, respectively. These bands exhibited shoulder bands around  $600$  nm ( $\epsilon = 1500 \text{ M}^{-1}\text{cm}^{-1}$ ). The intense absorption bands in the visible region have been tentatively assigned as resulting from charge transfer (CT) transitions from the *trans*- $\mu$ -1,2-peroxo groups to the copper(II) centers.<sup>[14–25]</sup> A detailed interpretation of the spectroscopic features of these CT bands for the Cu-MPPA and Cu-MAPA systems will be discussed in the following section together with those of the Cu-TPA system.<sup>[16–23]</sup> The resonance Raman spectra of EtCN or acetone solutions containing these copper–dioxygen adduct complexes measured at  $-78$  °C ( $514$  nm laser excitation) showed a strong resonance enhanced Raman peak

at  $837 \text{ cm}^{-1}$  for the Cu-MPPA system, which shifted to  $792 \text{ cm}^{-1}$  ( $\Delta\nu = 45 \text{ cm}^{-1}$ ) when  $^{18}\text{O}$ -labeled dioxygen was used and a corresponding peak for the Cu-MAPA complex was observed at  $847 \text{ cm}^{-1}$ , which shifted to  $800 \text{ cm}^{-1}$  ( $\Delta\nu = 45 \text{ cm}^{-1}$ ) when  $^{18}\text{O}_2$  was used. The frequencies and  $^{18}\text{O}$ -isotope shifts of these bands are characteristic of (*trans*- $\mu$ -1,2-peroxo)dicopper(II) complexes.<sup>[14–25]</sup> The ESR spectra of these oxygenated complexes in solution were silent which also suggests that two copper(II) ions are bridged by a dioxygen molecule and are antiferromagnetically coupled.

On the basis of these spectroscopic observations, we conclude that the (*trans*- $\mu$ -1,2-peroxo)dicopper(II) complexes  $[\{\text{Cu}(\text{mppa})\}_2(\text{O}_2)]^{2+}$  (**1b**) and  $[\{\text{Cu}(\text{mapa})\}_2(\text{O}_2)]^{2+}$  (**2b**) have formed in solution.

### Spectral Changes in the LMCT Bands of $\text{O}_2$ Adduct Complexes Affected by a Hydrogen Bonding Interaction

Bubbling dioxygen into an acetone solution containing  $[\text{Cu}(\text{L})]\text{PF}_6$  complexes with  $\text{L} = \text{MPPA}$  or  $\text{MAPA}$  afforded  $[\{\text{Cu}(\text{mppa})\}_2(\text{O}_2)]^{2+}$  (**1b**) or  $[\{\text{Cu}(\text{mapa})\}_2(\text{O}_2)]^{2+}$  (**2b**), respectively, as described above. The intense charge-transfer bands (LMCT) observed at  $517$  nm for the Cu-MPPA system and at  $503$  nm for the Cu-MAPA system can be attributed to the formation of a (*trans*- $\mu$ -peroxo)dicopper(II) core in each case. The absorption spectra of four kinds of  $\mu$ -peroxide complexes namely **1b**, **2b**,  $[\{\text{Cu}(\text{tpa})\}_2(\text{O}_2)]^{2+}$  (**3b**),<sup>[16–23]</sup> and  $[\{\text{Cu}(\text{6-metpa})\}_2(\text{O}_2)]^{2+}$  (**4b**),<sup>[44]</sup> are shown in Figure 3 and Table 5. Interesting spectroscopic behavior was observed as follows: the LMCT bands of the complexes exhibited blue shifts in the order **4b** < **3b** < **1b** < **2b**. The intensities of the shoulder peaks of the LMCT bands observed in the former two complexes **1b** and **2b** at about  $600$  nm were quite weak compared with those in the latter two complexes **3b** and **4b**. In the following section we discuss this by use of Solomon's theoretical consideration.

Solomon et al. first explained the LMCT bands of copper(II) peroxide complexes using a mononuclear copper(II) model with a peroxide ion in the end-on mode (Figure 4).<sup>[49]</sup> The highest occupied molecular orbitals of the peroxide have two degenerate  $\pi^*$  sets which split into two energy levels upon binding to the copper(II) ion. One  $\pi^*$  orbital ( $\pi^*_\sigma$ ) along the Cu–O bond has a larger overlap with the  $d_\sigma$  orbital of the copper ion and is critically stabilized by this interaction. The other  $\pi^*$  orbital ( $\pi^*_\perp$ ) perpendicular to the  $d_\sigma$  orbital undergoes a weaker d- $\pi$  interaction. On the basis of this consideration, there are two types of CT transitions from the peroxide to the copper(II) ion, that is, the band in the shorter wavelength region ( $500$ – $540$  nm) corresponds to a  $\pi^*_\sigma \rightarrow d_\sigma$  transition and the shoulder band at longer wavelength ( $\approx 600$  nm) can be ascribed to a  $\pi^*_\perp \rightarrow d_\sigma$  transition.

Firstly, considering the  $\pi^*_\sigma \rightarrow d_\sigma$  transition wavelength region ( $500$ – $540$  nm), the LMCT band for **4b** was observed at  $537$  nm, indicating that the energy gap between the  $\pi^*_\sigma$  and the  $d_\sigma$  orbitals is relatively small in comparison with that of **3b** at  $523$  nm, as shown in Table 5. This low energy shift of the  $\pi^*_\sigma \rightarrow d_\sigma$  transition band can be explained by a decrease in the energy splitting of the d orbitals because the

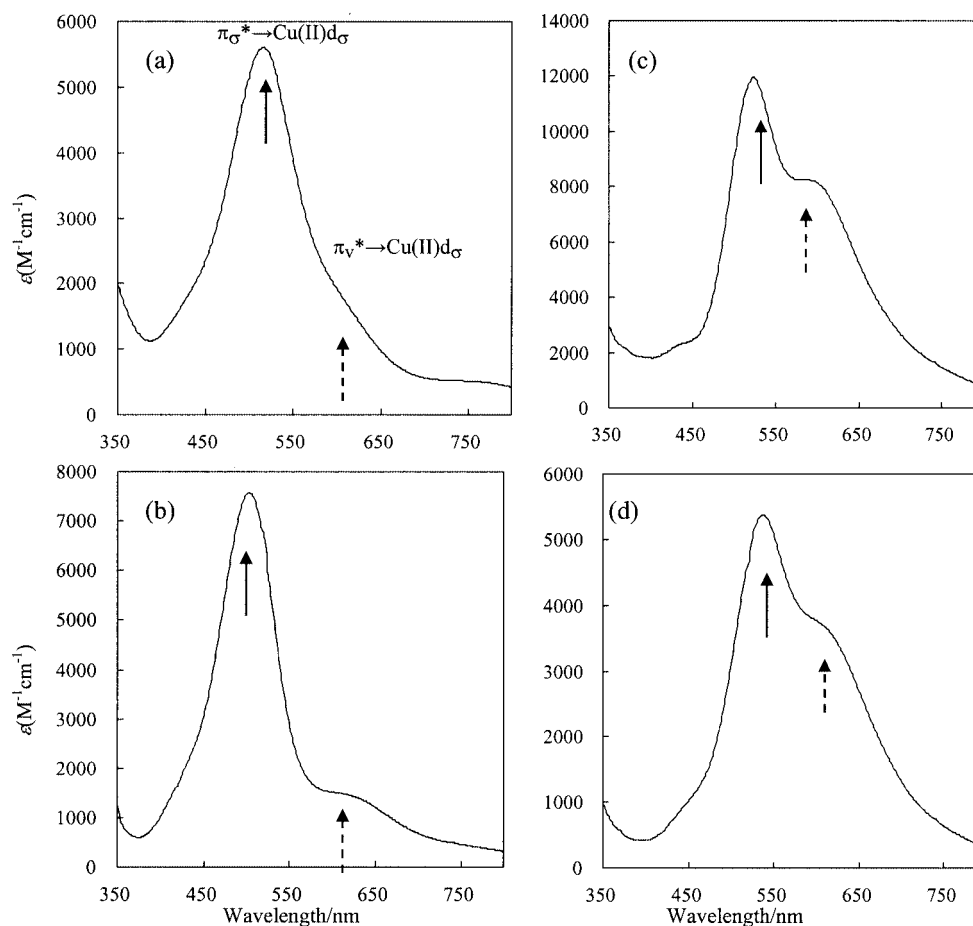


Figure 3. Absorption spectra of  $[(\text{CuL})_2(\text{O}_2)]^{2+}$  complexes in acetone at  $-78^\circ\text{C}$  [ $\text{L} = \text{MPPA}$  (a),  $\text{MAPA}$  (b),  $\text{TPA}$  (c),  $6\text{-MeTPA}$  (d)]

Table 5. Absorption spectroscopic data for  $[(\text{CuL})_2(\text{O}_2)]^{2+}$  complexes

| L (Ligand)            | $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) | Ref.      |
|-----------------------|-----------------------------------------------------------------------------|-----------|
| MPPA ( <b>1b</b> )    | 517 (5600), 600 (1500)                                                      | this work |
| MAPA ( <b>2b</b> )    | 503 (7500), 600 (1500)                                                      | this work |
| TPA ( <b>3b</b> )     | 524 (12000), 600 (8000)                                                     | [16–23]   |
| 6-MeTPA ( <b>4b</b> ) | 537 (5500), 600 (4000)                                                      | [44]      |

ligation of the pyridine nitrogen atoms to the copper(II) ion is weakened by the steric hindrance of the methyl group substituents at the 6-position of the pyridine ring.<sup>[44,45]</sup> On the other hand, the  $\pi_{\sigma}^* \rightarrow d_{\sigma}$  CT bands of **1b** (517 nm) and **2b** (503 nm) were observed in a higher energy region than that of **3b** (523 nm) in spite of the larger steric hindrance of the 6-(pivalamido)- and 6-amino substituted derivatives. In these cases, the pivalamido and amino groups in the 6-positions of the pyridine ring in MPPA and MAPA can be considered to form intramolecular hydrogen bonding interactions with the ligating peroxide ion in the same mode as in the previously reported monomeric (hydroperoxo)-copper(II) complex  $[\text{Cu}^{\text{II}}(\text{bppa})(\text{OOH})]^+$  [BPPA = bis{[6-(pivalamido)pyrid-2-yl]methyl}(2-pyridylmethyl)amine].<sup>[36]</sup> The electronic absorption spectra of the azide complexes,

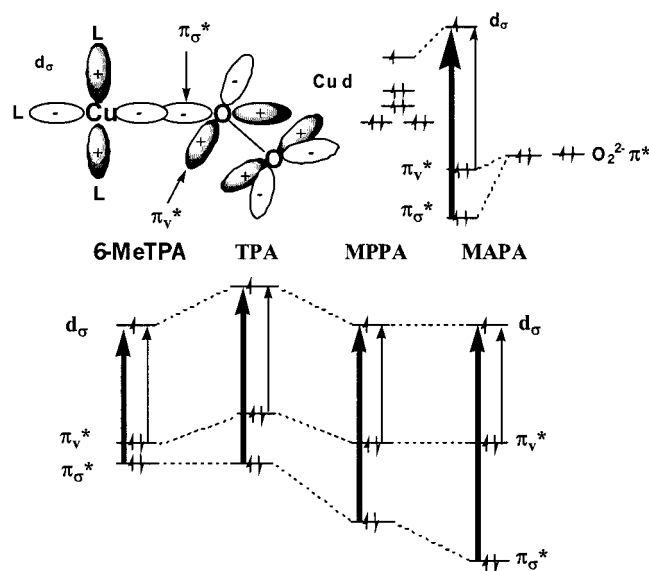


Figure 4. Schematic diagram of the energy levels of the molecular orbitals participating in the copper–peroxo bond

**1a**, **2a**, **3a** and **4a**, also exhibited a similar tendency: the LMCT energies of the azide complexes with MPPA and MAPA detected at 395 and 403 nm are relatively larger than

those of the azide complexes with TPA and 6-MeTPA observed at 413 and 414 nm. Indeed, in the crystal structures of the azide complexes with MPPA and MAPA, **1a** and **2a**, the intramolecular hydrogen bonding interactions were clearly formed between the 6-amido/amino NH hydrogen and the axially bound azide nitrogen atoms. These findings suggest that similar hydrogen bonds can also be formed in the corresponding (peroxo)dicopper(II) complexes, **1b** and **2b**. Taking this into account, it can be understood that the higher energy shifts of the  $\pi^*_{\sigma} \rightarrow d_{\sigma}$  CT bands in the (peroxo)dicopper(II) species, **1b** and **2b**, were caused by a stabilizing  $\pi^*_{\sigma}$  orbital energy level giving the larger  $\pi^*_{\sigma} - d_{\sigma}$  CT energy gap.

In the  $\pi^*_{\nu} \rightarrow d_{\sigma}$  transition wavelength region ( $\approx 600$  nm), the shoulder LMCT bands of **1b** and **2b** are broadened as shown in Figure 4. The shoulder LMCT absorbances of **1b** and **2b** at 600 and 600 nm ( $\epsilon = 1500$  and  $1500 \text{ M}^{-1}\text{cm}^{-1}$ ) are smaller than those of **3b** and **4b** at 600 and 600 nm ( $\epsilon = 8000$  and  $4000 \text{ M}^{-1}\text{cm}^{-1}$ ), respectively. The decrease in the  $\pi^*_{\nu} \rightarrow d_{\sigma}$  CT absorbance would also be affected by the intramolecular hydrogen bonding interaction. In the case of **3b** and **4b** without a hydrogen bonding moiety, the  $\pi^*_{\nu}$  orbital of the peroxide can overlap well with the  $d_{\sigma}$  orbital of copper because of the free rotation of the Cu–O bond in these (peroxo)dicopper(II) complexes. In **1b** and **2b**, however, such a rotation around the Cu–O bond is apparently inhibited by the hydrogen bond formed between the groups in the 6-position of the pyridine ring and the ligating peroxide ion with the result that overlap of the  $\pi^*_{\nu}$  and the  $d_{\sigma}$  orbitals would become small enough so as to decrease the CT transition probability.

In summary, the absorption spectroscopic behavior of the (peroxo)dicopper(II) complexes in question can be interpreted in terms of the contribution of the hydrogen bonding ability of the NH group of the pivalamido or amino groups introduced into pyridine 6-position of the ligands.

### Thermal Stability of the ( $\mu$ -Peroxo)dicopper Complexes with Hydrogen Bonding Interaction Sites

In our previous report, we found that the copper(II) complex with pivalamido at the 6-position of pyridine ring in the ligand forms the stable (hydroperoxo)copper(II) complex,  $[\text{Cu}^{\text{II}}(\text{bppa})(\text{OOH})]^+$  [BPPA = bis{[6-(pivalamido)pyrid-2-yl]methyl}(2-pyridylmethyl)amine]<sup>[36]</sup> which remains stable in solution at room temperature for more than one month. The first crystal structure of a monomeric (hydroperoxo)copper(II) complex  $[\text{Cu}^{\text{II}}(\text{bppa})(\text{OOH})]^+$  revealed that the pivalamido NH group of BPPA interacts with the ligated hydroperoxide oxygen atom by hydrogen bonding, thus promoting its thermal stability.<sup>[36]</sup> Based on this study, we expected that the hydrogen bond interaction might stabilize ( $\mu$ -peroxo)dicopper(II) species generated from the Cu-MPPA and -MAPA systems. The thermal stability of these peroxo species at 183 or 213 K was established by monitoring the decrease in their LMCT absorbances. The reduction of the LMCT bands occurred with first-order kinetics, demonstrating the decomposition of the ( $\mu$ -peroxo)dicopper(II) species. The decomposition rate constants are listed in

Table 6. The effects on the thermal stabilities of the ( $\mu$ -peroxo)dicopper(II) species as a result of substitution at the 6-position of pyridine ring are described in detail in the following discussion.

Table 6. Decomposition rate constants of  $[(\text{CuL})_2(\text{O}_2)]^{2+}$  complexes

| L (Ligand)            | $\lambda_{\text{max}}/\text{nm}$ | $k_{\text{obsd.}}/\text{min}^{-1}$ [a] | $T/\text{K}$ |
|-----------------------|----------------------------------|----------------------------------------|--------------|
| MPPA ( <b>1b</b> )    | 517                              | $0.2 \times 10^{-3}$                   | 183          |
| 6-MeTPA ( <b>4b</b> ) | 537                              | $39.4 \times 10^{-3}$                  | 183          |
| MPPA ( <b>1b</b> )    | 517                              | $13.3 \times 10^{-3}$                  | 213          |
| MAPA ( <b>2b</b> )    | 503                              | $2.5 \times 10^{-3}$                   | 213          |
| TPA ( <b>3b</b> )     | 523                              | $2.9 \times 10^{-3}$                   | 213          |

[a] The  $k_{\text{obsd.}}$  values are estimated by following the decrease of absorption band ( $\lambda_{\text{max}}$ ).

The ( $\mu$ -peroxo)dicopper(II) complex **4b** is remarkably unstable and its decomposition rate is the fastest of all the complexes listed in Table 6 ( $k_{\text{obsd.}} = 39.4 \times 10^{-3} \text{ min}^{-1}$  at 183 K). Unlike the other systems, the decomposition of **4b** at 213 K was too fast to allow estimation of the rate constant. This clearly indicates that the thermal stability of the ( $\mu$ -peroxo)dicopper(II) complex is extensively decreased by the sterically hindered 6-methyl substituent around the metal center.<sup>[44,45]</sup> Substitution of the 6-pivalamido group in place of the 6-methyl substituent dramatically improves the thermal stability and stabilized the ( $\mu$ -peroxo)dicopper(II) complex, **1b** ( $k_{\text{obsd.}} = 0.2 \times 10^{-3} \text{ min}^{-1}$  at 183 K). Furthermore, the analogous 6-amino-substituted ( $\mu$ -peroxo)dicopper(II) complex **2b** ( $k_{\text{obsd.}} = 2.5 \times 10^{-3} \text{ min}^{-1}$ ) is more stable than **1b** ( $k_{\text{obsd.}} = 13.3 \times 10^{-3} \text{ min}^{-1}$  at 213 K) and its thermal stability was improved to the same extent as that of **3b** ( $k_{\text{obsd.}} = 2.9 \times 10^{-3} \text{ min}^{-1}$ ), although the amino group in the 6-position of pyridine ring is as bulky as the methyl group in **4b**.

The order of the thermal stability of these peroxo complexes can therefore be determined as follows: **2b**  $\approx$  **3b**  $>$  **1b**  $\gg$  **4b**. The ( $\mu$ -peroxo)dicopper complexes are partially stabilized by the hydrogen bonding interaction, although the stability was reduced by the adverse effect of the steric bulk around the metal ion.

### Conclusion

In order to examine the mode of the hydrogen bonding interaction and its effect on the ( $\mu$ -peroxo)dicopper(II) species, we have prepared copper complexes with the tripodal tetradentate ligands MPPA and MAPA which bear a hydrogen bonding site. The crystal structures of the azide complexes **1a** and **2a** revealed that pivalamido and amino NH groups in 6-position of the pyridine ring can interact with the axially coordinated azide ion via the hydrogen bond. The tripodal ligands with a hydrogen bonding ability exerted significant influence on two LMCT bands of the ( $\mu$ -peroxo)dicopper(II) species. The energy of the  $\pi^*_{\sigma} \rightarrow d_{\sigma}$  CT transition was raised and the absorbance of the  $\pi^*_{\nu} \rightarrow d_{\sigma}$  CT band was decreased. Such characteristic spectroscopic

behavior was interpreted in terms of stabilization of the  $\pi^*$  orbital and restriction of rotation of the Cu–O bond by the hydrogen bond between the NH group and the axially coordinated peroxide groups of the copper complexes. Finally, the hydrogen bonding interaction was found to overcome the adverse effect of steric bulk and thus stabilize the ( $\mu$ -peroxo)dycopper(II) complexes.

## Experimental Section

**Materials and Measurements:** Reagents and solvents employed were of the highest grade available. All solvents for spectroscopy were further purified by distillation before use. Other chemicals were used without further purification. Tris(pyrid-2-ylmethyl)amine (TPA) and [(6-methylpyrid-2-yl)methyl]bis(pyrid-2-ylmethyl)amine (6-MeTPA) were prepared using literature methods.<sup>[16,44]</sup> Electronic absorption spectra were recorded at low temperature with a JASCO Ubest-35 spectrophotometer equipped with an Oxford Variable Temperature Liquid Nitrogen Cryostat Optistat. X-Band ESR spectra of frozen solutions were recorded at 77 K by using a JEOL RE-1X ESR spectrometer. <sup>1</sup>H NMR spectra were measured with a Bruker Avance-600 spectrometer with chemical shift values referenced relative to TMS as an internal standard. Cyclic voltammetric measurements were performed using a Bioanalytical Systems (BAS) CV-1B electrochemical analyzer. A three-electrode system was used with a 3-mm diameter glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a Pt-wire electrode as the counter electrode in a glass cell having a working compartment of approximately 3 mL in volume. All measurements were made in solution at 25 °C under argon with tetra(*n*-butyl)ammonium tetrafluoroborate (0.1 M) as a supporting electrolyte at a scan rate of 100 mVs<sup>−1</sup>. The potential of the regular ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple in acetonitrile was −0.33 V under our experimental conditions. In order to discuss the electrochemical values in comparison with other data, all the electrochemical potentials were converted into values with the normal hydrogen electrode (NHE) as a standard by adding 244.4 mV. Resonance Raman spectra were recorded with a liquid-nitrogen-cooled CCD detector (Model LN/CCD-1300-PB, Princeton Instrument) attached to a 100-cm single polychromator (Model MC-100DG, Ritsu Oyo Kogaku). The excitation was provided by the 476.5-nm line of an Ar laser (Model GLG3200, NEC). <sup>16</sup>O<sub>2</sub> samples were prepared by bubbling dry dioxygen into acetone or EtCN solutions of the copper(I) complexes with tetradentate ligands at −78 °C. Isotopic substitution of the peroxo oxygen atoms bridged to the dicopper ions was accomplished by oxygenation of the copper(I) complexes with <sup>18</sup>O<sub>2</sub>. All measurements were carried out with a spinning cell maintained at −78 °C by a stream of liquid N<sub>2</sub> vapor.

### Synthesis of Ligands

**{[6-(Pivalamido)-2-pyridyl]methyl}bis(pyrid-2-ylmethyl)amine (MPPA):** Reaction of the primary amine, 2-(aminomethyl)-6-(pivalamido)pyridine,<sup>[37,38]</sup> (2.80 g, 13.5 mmol) with 2 equiv. of 2-(chloromethyl)pyridine (5.25 g, 32.0 mmol) was carried out in a dioxane/H<sub>2</sub>O (4:1) solution (300 mL) containing KOH (2.92 g, 52.0 mmol). The solution was stirred at 50 °C for 3 d followed by removal of the solvent by evaporation in vacuo. Dissolving the resultant crude brownish oil in diethyl ether and allowing it to stand at room temperature gave colorless needle-like crystals of MPPA (2.32 g, 45.9% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.33 (s, 9 H), 3.78 (s, 2 H), 3.89 (s,

2 H), 7.15 (m, 2 H), 7.28 (d, 2 H), 7.56 (d, 2 H), 7.66 (t, 3 H), 7.95 (b, 1 H), 8.06 (b, 1 H), 8.10 (d, 1 H), 8.53 (d, 2 H) ppm.

**[(6-Aminopyrid-2-yl)methyl]bis(pyrid-2-ylmethyl)amine (MAPA):** To an ethanol solution (500 mL) of MPPA (3.89 g, 10.0 mmol) was added KOH (28.1 g, 0.50 mol). The solution was stirred at 50 °C for 1 week. After removal of the solvent from the reaction mixture by evaporation in vacuo, the resultant crude brownish oil was dissolved in dichloromethane (100 mL) which was washed with water and dried with MgSO<sub>4</sub>. The resultant solution was concentrated in vacuo to give the crude product as an oil. Pure MAPA was obtained as colorless needle-like crystals by recrystallization from diethyl ether (2.13 g, 70.0% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.54 (s, 2 H), 3.76 (s, 4 H), 5.79 (s, 2 H), 6.30 (d, 1 H), 6.73 (d, 1 H), 7.24 (t, 2 H), 7.35 (t, 1 H), 7.62 (d, 2 H), 7.77 (t, 1 H), 8.48 (d, 2 H) ppm.

### Synthesis of Cu Complexes

**Preparation of [Cu(mppa)](ClO<sub>4</sub>)<sub>2</sub>:** To a stirred MeOH solution (10 mL) of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (74.1 mg, 0.2 mmol) was added MPPA (77.8 mg, 0.2 mmol). After the resultant mixture was allowed to stand at room temperature for a few days, blue crystals of [Cu(mppa)](ClO<sub>4</sub>)<sub>2</sub>, suitable for X-ray structural analysis, were obtained. Yield: 109 mg (85%). C<sub>23</sub>H<sub>27</sub>Cl<sub>2</sub>CuN<sub>5</sub>O<sub>9</sub> (651.94): calcd. C 42.37, H 4.17, N 10.73; found C 42.57, H 4.16, N 11.05.

**Preparation of [Cu(mppa)(N<sub>3</sub>)]ClO<sub>4</sub>:** To a stirred MeCN solution (10 mL) of [Cu(mppa)](ClO<sub>4</sub>)<sub>2</sub> (151.9 mg, 0.2 mmol) was added NaN<sub>3</sub> (13.0 mg, 0.2 mmol). A green precipitate formed immediately. After filtration, recrystallization of the precipitate from MeCN gave plate-like green single crystals, suitable for X-ray structural analysis. Yield: 85 mg (71%). C<sub>23</sub>H<sub>27</sub>ClCuN<sub>8</sub>O<sub>5</sub> (594.51): calcd. C 46.46, H 4.47, N 18.84; found C 46.38, H 4.47, N 19.15.

**X-ray Structural Analysis of [Cu(mppa)](ClO<sub>4</sub>)<sub>2</sub> and [Cu(mppa)(N<sub>3</sub>)]ClO<sub>4</sub>:** Crystals suitable for X-ray diffraction measurements were mounted on glass fibers. The diffraction data were collected with a Rigaku Mercury diffractometer using graphite-monochromated Mo-*K*<sub>α</sub> radiation at −100 °C with the oscillation technique. Crystal data and experimental details are listed in Table 7. All structures were solved by a combination of direct methods and Fourier techniques. Non-hydrogen atoms were anisotropically refined by full-matrix least-squares calculations. Hydrogen atoms were included but not refined. Refinements were continued until all shifts were smaller than one-third of the standard deviations of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography.<sup>[50]</sup> All calculations were carried out with a Japan SGI workstation computer using the teXsan crystallographic software package.<sup>[51]</sup> CCDC-211622 and -211623 contain the crystallographic data for this paper. This data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/](http://www.ccdc.cam.ac.uk/conts/) or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ [Fax: (internat.) + 44-1223-336-033; E-mail: [depost@ccdc.cam.ac.uk](mailto:depost@ccdc.cam.ac.uk)].

**Reaction of [Cu(L)]PF<sub>6</sub> (L = MPPA, MAPA, TPA, 6-MeTPA) with Dioxygen:** Sample solutions of [Cu(L)]PF<sub>6</sub> (L = MPPA, MAPA, TPA, 6-MeTPA) were prepared by mixing [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (0.7 mg, 2.0 mmol) and each ligand (2.1 mmol) in acetone (4 mL) at room temperature under nitrogen. The resultant solutions containing [Cu(L)]PF<sub>6</sub> were oxygenated by bubbling dioxygen through them at −78 °C. The formation and decomposition of the peroxo intermediates were monitored by following the increase or decrease in their characteristic ligand–metal charge transfer (LMCT) absorption bands at  $\lambda_{\text{max}}$  = 517, 503, 524, and 537 nm, for [ $\{\text{Cu(L)}\}_2(\text{O}_2)\}^{2+}$ ] [L = MPPA (**1b**), MAPA (**2b**), TPA (**3b**), 6-

Table 7. Crystallographic data for [Cu(mppa)](ClO<sub>4</sub>)<sub>2</sub> (**1**) and [Cu(mppa)(N<sub>3</sub>)]ClO<sub>4</sub> (**1a**)

|                                                                                | [Cu(mppa)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>1</b> )                         | [Cu(mppa)(N <sub>3</sub> )]ClO <sub>4</sub> ( <b>1a</b> )         |
|--------------------------------------------------------------------------------|---------------------------------------------------------------------------------|-------------------------------------------------------------------|
| Empirical formula                                                              | C <sub>21</sub> H <sub>26</sub> Cl <sub>2</sub> CuN <sub>5</sub> O <sub>9</sub> | C <sub>23</sub> H <sub>27</sub> ClCuN <sub>8</sub> O <sub>5</sub> |
| Formula mass                                                                   | 743.64                                                                          | 594.52                                                            |
| Crystal system                                                                 | triclinic                                                                       | monoclinic                                                        |
| Space group                                                                    | $P\bar{1}$ (No. 2)                                                              | $P2_1/a$ (No. 14)                                                 |
| <i>a</i> [Å]                                                                   | 11.721(4)                                                                       | 14.156(2)                                                         |
| <i>b</i> [Å]                                                                   | 14.191(2)                                                                       | 10.032(1)                                                         |
| <i>c</i> [Å]                                                                   | 9.897(1)                                                                        | 18.645(2)                                                         |
| $\alpha$ [°]                                                                   | 103.058(10)                                                                     | 90                                                                |
| $\beta$ [°]                                                                    | 90.34(2)                                                                        | 102.262(7)                                                        |
| $\gamma$ [°]                                                                   | 73.26(2)                                                                        | 90                                                                |
| <i>V</i> [Å <sup>3</sup> ]                                                     | 1535.6200                                                                       | 2587.5(6)                                                         |
| <i>Z</i>                                                                       | 2                                                                               | 4                                                                 |
| <i>D</i> <sub>calcd.</sub> [g cm <sup>-3</sup> ]                               | 1.608                                                                           | 1.526                                                             |
| <i>F</i> (000)                                                                 | 752.00                                                                          | 1228.00                                                           |
| $\mu$ [cm <sup>-1</sup> ]                                                      | 14.39                                                                           | 9.98                                                              |
| $\lambda$ [Å]                                                                  | 0.71070                                                                         | 0.71070                                                           |
| <i>T</i> [K]                                                                   | 298                                                                             | 173                                                               |
| No. of refls. measured                                                         | 4361                                                                            | 5832                                                              |
| No. of refls. used [ <i>I</i> > 2 $\sigma$ ( <i>I</i> <sub>0</sub> )]          | 2616                                                                            | 4452                                                              |
| <i>R</i> <sub>1</sub> [ <sup>a</sup> ]/ <i>R</i> <sub>w</sub> [ <sup>b</sup> ] | 0.081/0.111                                                                     | 0.094/0.235                                                       |
| GOF                                                                            | 1.02                                                                            | 1.61                                                              |

[<sup>a</sup>]  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . [<sup>b</sup>]  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ;  $w = 4F_o^2 / \sigma^2(F_o)^2$ .

MeTPA (**4b**)], respectively. The thermal stability of the peroxo species was examined under constant temperature (183 or 213 K) by following the absorption intensity at 5-min intervals for 12 or 24 h. The decomposition process of the respective complex was analyzed using first order kinetics in which  $\ln([A]/[A_0])$  values were plotted according to the time course (where [*A*<sub>0</sub>] and [*A*] are absorption intensities of the LMCT bands observed initially and at a given time). It was observed that decreasing of the LMCT bands exhibited good first-order kinetics for each peroxo complex.

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