

were successful in the latter. Intensity data were collected on a second similar crystal, mounted in the same way, after the unit cell data and orientation were obtained from 24 automatically aligned reflections. The data were corrected for Lorentz and polarization effects and scaled by using three reference reflections, whose intensities had been remeasured every 50 cycles.

The structure was solved by using conventional heavy-atom methods. Full-matrix isotropic refinement converged at  $R_1 = 0.084$  and  $R_2 = 0.125$ , after four cycles. At this point, a general absorption correction using the Gaussian summation method was applied and isotropic refinement was continued to a new convergence with  $R_1 = 0.072$  and  $R_2 = 0.119$ . Thereafter, all atoms were assigned anisotropic vibrational parameters and the refinement was continued. It converged at  $R_1 = 0.035$  and  $R_2 = 0.053$ , after five cycles using the block-diagonal approximation. A final four cycles of refinement, with hydrogen atoms placed in calculated positions with the mean isotropic thermal parameter of their carbon atom, yielded the final coordinates reported in Table IV. Tables of thermal parameters and observed and calculated structure

factors are included as supplementary material.

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**Registry No.** *cis-1a*, 119997-19-2; *trans-1a*, 120056-12-4; *cis-1b*, 119997-20-5; *trans-1b*, 120056-13-5; *cis-1c*, 108366-49-0; *trans-1c*, 120056-14-6; *cis-1d*, 108366-48-9; *trans-1d*, 110043-11-3; **2a**, 120022-20-0; **2b**, 119997-21-6; **2c**, 119997-22-7; CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)H, 33085-24-4; CS<sub>2</sub>, 75-15-0; 2-(isopropylthio)phthalimide, 17796-72-4; 2-(benzylthio)phthalimide, 14204-26-3; 2-(4-methylphenylthio)phthalimide, 15199-26-5; 2-(phenylthio)phthalimide, 14204-27-4.

**Supplementary Material Available:** A full-length table of crystallographic data (Table 6) and a table of anisotropic temperature factors (Table 7) (2 pages); a table of observed and calculated structure factors (Table 8) (15 pages). Ordering information is given on any current masthead page.

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## Nuclear Magnetic Resonance Studies of Dicopper(II) Complexes with Binucleating Ligands Containing Imidazoles

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<sup>1</sup>H NMR spectra of aqueous and nonaqueous solutions of [Cu<sub>2</sub>LX]Y<sub>2</sub> (L = 2,6-bis[[(4-imidazolylethyl)imino)methyl]-4-methylphenolate, 2,6-bis[[(4-imidazolylethyl)amino)methyl]-4-methylphenolate; X = OH<sup>-</sup>, Cl<sup>-</sup>; Y = ClO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>) have been observed, together with the measurement of their solution magnetic susceptibilities. The obtained signals are narrow enough to characterize the species in solution. It has been found that both observed chemical shifts and line widths at half-height decrease as the magnetic moments of the corresponding copper(II) complexes in solution decrease. The line widths of <sup>1</sup>H NMR signals are controlled by the population distribution in singlet and triplet states of the complexes. Methanol solutions of [Cu<sub>2</sub>L(OH)]<sup>2+</sup> showed equilibria that are associated with the apical coordination of water molecules: in addition to the water-free complex, two species, [Cu<sub>2</sub>L(OH)(H<sub>2</sub>O)]<sup>2+</sup> and [Cu<sub>2</sub>L(OH)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, are found by <sup>1</sup>H NMR spectra. One of these species was crystallized from methanol solution. The crystal and molecular structures of [Cu<sub>2</sub>L(OH)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> have been determined: space group P2<sub>1</sub>/c, *a* = 7.354 (4) Å, *b* = 21.781 (19) Å, *c* = 16.175 (8) Å, β = 90.70 (4)°, *Z* = 4, *R* = 0.111, *R*<sub>w</sub> = 0.095. The two Cu atoms in this copper(II) complex are bridged by the oxygen atoms of the phenolate and hydroxy groups. The axial position at one Cu atom is occupied by a water molecule, while another Cu has no apical ligand. The coordinate geometries around the two Cu atoms are distorted tetragonal-pyramidal and square-planar.

### Introduction

Interest<sup>2</sup> in copper proteins has centered on the design, preparation, and characterization of small-molecular binuclear copper(II) complexes, which offer insight into the coordination chemistry of copper(II) systems in laccase, oxyhemocyanin, and so on. Among a vast body of binuclear copper(II) complexes that have so far been synthesized,<sup>3,4</sup> the complexes containing imidazoles are of marked importance in relation to the copper center of native proteins because a histidyl imidazole is one of the most probable coordinated ligands.<sup>2</sup>

In addition to single-crystal X-ray structural information, the characterization of binuclear copper(II) complexes in solution is of significance. Although NMR spectroscopy has been successfully used to investigate the structural and bonding properties of metal complexes,<sup>5</sup> there are few NMR studies of paramagnetic copper(II) complexes because signals are usually broadened out.<sup>6</sup> On the other hand, antiferromagnetically coupled copper(II)

complexes are expected to give relatively narrow NMR signals.<sup>7-10</sup> However, there are still few reports that demonstrate the usefulness of NMR spectra of binuclear copper(II) complexes in solution.

The purpose of this work was to obtain NMR spectra of some binuclear copper(II) complexes having imidazoles. On the basis of these spectra, the structures in solution and equilibria are discussed, which are simultaneously compared with the X-ray crystallographic molecular structure determined in this paper. Finally, the relationship between the structure and NMR parameters is examined.

### Experimental Section

**Materials.** Copper(II) salts were commercially available and utilized after recrystallization. 2-Hydroxy-5-alkylisophthalaldehydes (alkyl = methyl, ethyl) were prepared by the method of Okawa.<sup>11</sup> Histamine free base was isolated from histamine dihydrochloride (Sigma Chemical Co.) by the usual procedure.<sup>12</sup>

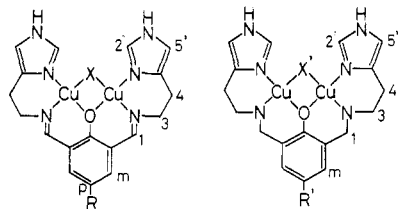
Deuterated solvents were purchased from Merck and Wako Pure Chemical Industry Ltd. In order to obtain rigorously dry methanol, CD<sub>3</sub>OD was refluxed over Mg and distilled before use. Acetone-*d*<sub>6</sub> was treated with molecular sieves. Both solvents were purified under pure

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argon. Deuterium-labeled histamines were synthesized in the following manner. The deuterium at the 2-position of an imidazole group was introduced by use of deuterium oxide. Histamine having deuterium at the  $\alpha$ -position of the aminoethyl group was obtained from the reduction of 4-(cyanomethyl)imidazole (Sigma Chemical Co.) with lithium aluminum deuteride.<sup>12</sup> Both products were checked by  $^1\text{H}$  and  $^2\text{H}$  NMR spectra, which show the good yield (99%) of the deuterated species.

**Copper Complexes.** 1-4 were synthesized according to the Urbach method.<sup>13</sup> The isolated copper(II) complexes were checked optically and by elementary analyses.



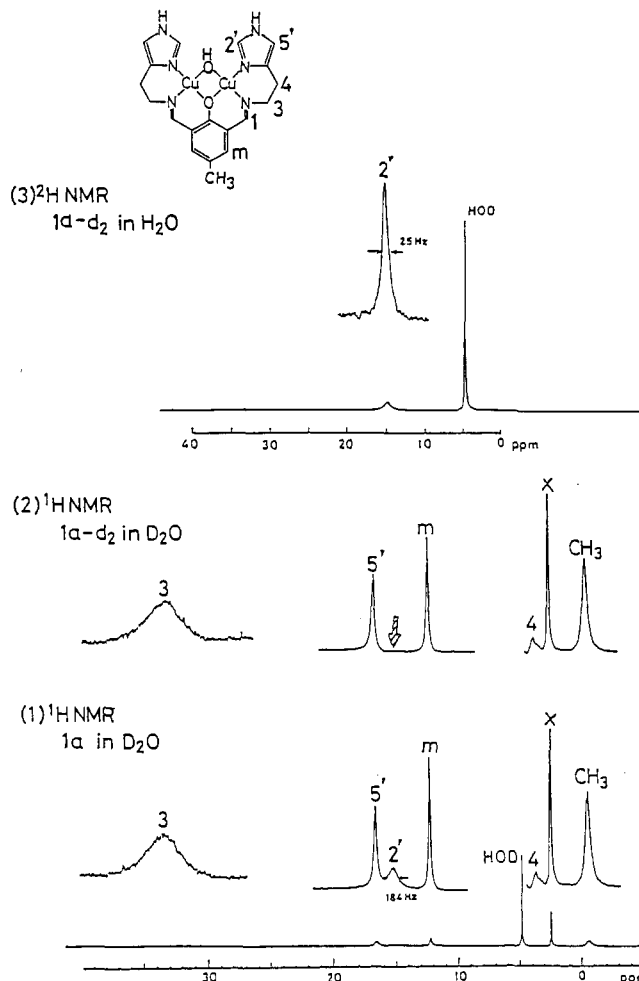
	R	X		R'	X'
1a	CH <sub>3</sub>	OH <sup>-</sup>	3	CH <sub>3</sub>	OH <sup>-</sup>
1b	CH <sub>3</sub>	Cl <sup>-</sup>	4	C <sub>2</sub> H <sub>5</sub>	OH <sup>-</sup>
2	C <sub>2</sub> H <sub>5</sub>	OH <sup>-</sup>			

**$^1\text{H}$  NMR Measurements.**  $^1\text{H}$  NMR spectra were measured on a JEOL FX 200 FT NMR spectrometer.  $(\text{CH}_3)_4\text{Si}$  was used as an internal standard for methanol and acetone solutions, while  $\text{C}_6\text{H}_{15}\text{SiSO}_3\text{Na}$  was used for aqueous solution. Between 1000 and 5000 transients were accumulated with the use of a 14- $\mu\text{s}$  pulse (90°): 8K data points were collected over a bandwidth of 10–40 kHz. A 5-mm-diameter sample tube was used. The probe temperature was varied from -90 to 80 °C. For the measurement of  $^1\text{H}$  NMR spectra in Figure 4, a JEOL GSX 270 FT NMR spectrometer was used: 1000–3000 transients, 4.0- $\mu\text{s}$  pulse (45°), and 15-kHz bandwidth with 16K data points.

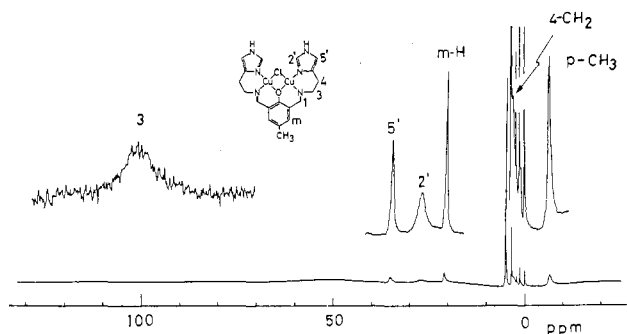
**Preparation of Crystals.** The perchlorate salt of 1a was dissolved in methanol at 80 °C in a 7-mm-diameter glass tube. This solution was gradually cooled to an ambient temperature, yielding dark green-blue plate crystals. One of these crystals were taken for X-ray diffraction study.

A crystal of dimensions 0.10 × 0.10 × 0.20 mm<sup>3</sup> was mounted on a Rigaku AFC-6B four-circle diffractometer equipped with graphite-monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The compound  $\text{Cu}_2\text{Cl}_2\text{C}_{19}\text{O}_{10}\text{N}_6\text{H}_{22}$  (fw 692.38) gave the following crystal data:<sup>14</sup> monoclinic space group  $P2_1/c$ ,  $a = 7.354(4) \text{ \AA}$ ,  $b = 21.781(19) \text{ \AA}$ ,  $c = 16.175(8) \text{ \AA}$ ,  $\beta = 90.70(4)^\circ$ ,  $V = 2590.7 \text{ \AA}^3$ ,  $d_{\text{calcd}} = 1.775 \text{ g/cm}^3$ ,  $Z = 4$ . A total of 2178 reflections were refined<sup>15</sup> to the current residual values of  $R = 0.111$  and  $R_w = 0.095$ .

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- (14) The intensity data were collected at 296 K in the  $\omega$ - $2\theta$  scan mode with a 3.1° scan width,  $2\theta_{\text{max}}$  of 120°,  $-8 < h < 8$ ,  $0 < k < 22$ ,  $0 < l < 17$ , and a scan rate of 8° min<sup>-1</sup>. Three standard reflections were monitored every 56 reflections. There was no significant variation of the intensities during data collection. The intensity data were converted to  $|F_o|$  data in the usual manner. An absorption correction was not applied ( $\mu = 45.20 \text{ cm}^{-1}$ ). Of the 4165 measured reflections, 2178 were observed ( $|F_o| > 3\sigma(|F_o|)$ ), where  $(\sigma(|F_o|))$  is the standard deviation estimated by counting statistics.
- (15) The structure was solved by a direct methods (MULTAN 78)<sup>16</sup> and refined by block-diagonal least-squares calculations with anisotropic thermal parameters, including isotropic H atoms located on a difference Fourier synthesis. In the least squares, the function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure factor amplitudes, respectively, and where  $w = 1/\sigma^2(|F_o|)$ . The final  $R$  and  $R_w$  values were 0.111 and 0.095, respectively. The atomic scattering factors and anomalous dispersion terms for all atoms were obtained from ref 17, Vol. IV. All computations were performed on a FACOM M-382 computer at the Data Processing Center of Kyoto University by using the program system KPPXRAY.<sup>18</sup>
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**Figure 1.**  $^1\text{H}$  NMR spectra at 23 °C of 1a (1) and its partially deuterated form 1a- $d_2$  (2) in  $\text{D}_2\text{O}$  (shaded arrow denotes the resonance position of the 2-H signal) and  $^2\text{H}$  NMR spectrum at 23 °C of 1a- $d_2$  (3) in  $\text{H}_2\text{O}$ .



**Figure 2.**  $^1\text{H}$  NMR spectrum at 23 °C of 1b in  $\text{CD}_3\text{OD}$ .

## Results

**$^1\text{H}$  NMR Spectra.** All the copper(II) complexes prepared here gave relatively narrow  $^1\text{H}$  NMR signals. Figure 1 shows typical  $^1\text{H}$  NMR spectra of 1a, together with its  $^2\text{H}$  NMR spectrum. Six  $^1\text{H}$  NMR signals in Figure 1(1) are sharp enough to obtain chemical shifts and line widths at half-height. This is in good contrast to the case of paramagnetic Cu(II) complexes. According to the structure of 1a, seven proton signals are expected. In order to assign these signals, the chelate ligand was selectively deuterated. We are especially interested in an imidazole group coordinated to a copper(II) ion in relation to the active site of copper proteins. First, the 2-position of histamine was deuterated, from which 1a was synthesized. This deuterated 1a showed a clearly characteristic spectrum: a signal at 15.2 ppm disappeared as in Figure 1(2), and the corresponding  $^2\text{H}$  NMR signal appeared as in Figure 1(3), whose chemical shift is in good agreement with

**Table I.** Observed  $^1\text{H}$  NMR Chemical Shifts and Line Widths at Half-Height of Binuclear Copper(II) Complexes

complex; $-2J$ , $\text{cm}^{-1}$ <sup>b</sup>	solvent	$\delta$ , ppm <sup>a</sup> ( $\nu_{1/2}$ , Hz)								
		1-CH(CH <sub>2</sub> )	3-CH <sub>2</sub>	4-CH <sub>2</sub>	<i>m</i> -CH	<i>p</i> -CH <sub>2</sub>	<i>p</i> -CH <sub>3</sub>	2'-CH	5'-CH	NH
[Cu <sub>2</sub> ((ha) <sub>2</sub> mipa)OH](ClO <sub>4</sub> ) <sub>2</sub> ( <b>1a</b> ); 529	D <sub>2</sub> O	<i>c</i>	33 (580)	3.5 (85)	12.2 (28)		-0.6 (128)	15.2 (184)	16.5 (57)	<i>j</i>
	CD <sub>3</sub> OD <sup>d</sup>	<i>c</i>	20.3 (585)	<i>f</i>	10.4 (86)		0.9 <sup>e</sup>	12.9 <sup>e</sup>	12.3 <sup>e</sup>	<i>j</i>
	(CD <sub>3</sub> ) <sub>2</sub> CO	<i>c</i>	23.3 <sup>h</sup> (442)	<i>f</i>	10.9 <sup>e</sup> (23)		<i>f</i> (51)	<i>f</i> (108)	14.4 <sup>e</sup> (43)	<i>j</i> (80)
[Cu <sub>2</sub> ((ha) <sub>2</sub> mipa)Cl]Cl <sub>2</sub> ( <b>1b</b> ); 156	D <sub>2</sub> O <sup>g</sup>	<i>c</i>	34 (485)	3.5 <sup>e</sup>	12.2 (35)		-0.6 (116)	15.2 (174)	16.6 (58)	<i>j</i>
	CD <sub>3</sub> OD	<i>c</i>	103 (1890)	2.9 <sup>f</sup>	21.0 (115)		-6.7 (172)	27.5 (460)	35.1 (149)	<i>j</i>
[Cu <sub>2</sub> ((ha) <sub>2</sub> eipa)OH](ClO <sub>4</sub> ) <sub>2</sub> ( <b>2</b> )	D <sub>2</sub> O	<i>c</i>	33 (656)	3.6 <sup>e</sup>	12.3 (29)	-0.7 <sup>f</sup>	3.6 <sup>e</sup>	15.3 (185)	16.6 (57)	<i>j</i>
	CD <sub>3</sub> OD <sup>d</sup>	<i>c</i>	20.1 (412)	<i>f</i>	10.3 (20)	1.1 <sup>f</sup>	2.7 (20)	13 <sup>e</sup>	12.4 (50)	<i>j</i>
	(CD <sub>3</sub> ) <sub>2</sub> CO	<i>c</i>	24.3 (349)	<i>f</i>	11.0 <sup>e</sup> (14)	<i>f</i>	<i>f</i> (42)	<i>e</i> (113)	14.4 (42)	<i>j</i> (59)
[Cu <sub>2</sub> ((h <sub>2</sub> ha) <sub>2</sub> mipa)OH](ClO <sub>4</sub> ) <sub>2</sub> ( <b>3</b> ); 545	D <sub>2</sub> O	23.8 <sup>e</sup>	23.8 <sup>e</sup>	-1.7 (113)	10.5 (28)		-2.3 (79)	15.3 (170)	16.2 (57)	<i>j</i>
	CD <sub>3</sub> OD <sup>d</sup>	<i>c</i>	<i>f</i>	3.2 (56)	9.4 (31)		-0.6 <sup>e</sup>	13.7 <sup>e</sup>	13.3 <sup>e</sup>	<i>j</i>
	(CD <sub>3</sub> ) <sub>2</sub> CO	18.6 <sup>e</sup>	17.4 <sup>e</sup>	<i>f</i> <i>e</i>	9.6 (29)		<i>f</i> (54)	<i>e</i> (114)	14.7 <sup>e</sup> (54)	<i>j</i> (83)
[Cu <sub>2</sub> ((h <sub>2</sub> ha) <sub>2</sub> eipa)OH](ClO <sub>4</sub> ) <sub>2</sub> ( <b>4</b> )	D <sub>2</sub> O	23.6 <sup>e</sup>	23.6 <sup>e</sup>	-1.7 (84)	10.5 (28)	3.3 <sup>i</sup>	-2.3 (56)	15.4 (113)	16.3 (59)	<i>j</i>
	CD <sub>3</sub> OD <sup>d</sup>	<i>c</i>	<i>c</i>	<i>f</i>	9.4 (34)	<i>f</i>	<i>f</i>	<i>f</i>	13.2 <sup>e</sup>	<i>j</i>
	(CD <sub>3</sub> ) <sub>2</sub> CO	18.7 <sup>e</sup>	17.5 <sup>e</sup>	<i>f</i> <i>f</i>	9.6 (20)	<i>f</i>	-0.87 <sup>i</sup> (43)	14.3 <sup>e</sup> (111)	14.9 <sup>e</sup> (43)	<i>j</i> (77)

<sup>a</sup>Observed  $^1\text{H}$  NMR chemical shifts at 23 °C from DSS (D<sub>2</sub>O) and TMS ((CD<sub>3</sub>)<sub>2</sub>CO and CD<sub>3</sub>OD). <sup>b</sup>Reference 13. <sup>c</sup>Not observed due to quite a broadened signal. <sup>d</sup>Two species were observed in wet CD<sub>3</sub>OD. The values in the upper line are ascribed to water-free species discussed in the text. The values in the lower line are dependent on water concentration. These values are obtained at  $[\text{H}_2\text{O}]/[\text{MeOH}] = 5 \times 10^{-3}$ . <sup>e</sup>Overlapping with each other. <sup>f</sup>Overlapping with another intense signal. <sup>g</sup>Signals in the range 1–10 ppm were observed, ascribed to the small amounts of decomposed material. <sup>h</sup>Not obtained due to a very broad signal, in order to avoid read error. <sup>i</sup>Tentatively assigned. <sup>j</sup>Not observed because of the formation of ND group in deuterated solvents.

that of the  $^1\text{H}$  NMR signal. The signal at 15.2 ppm is undoubtedly assigned to 2'-H of the imidazole group. Similarly, the 3-CH<sub>2</sub> proton signal is assigned to a broad signal at 33 ppm by use of a deuterated **1a**. The line widths at half-height,  $\Delta\nu_{1/2}$ , of both  $^2\text{H}$  NMR signals are 25 and 48 Hz for 2'- $^2\text{H}$  and 3-C<sup>2</sup>H<sub>2</sub>, respectively. The narrowing ratios,  $\nu_{1/2}(^2\text{H})/\nu_{1/2}(^1\text{H})$ , are 1/7 (2'-H) and 1/10 (3-CH<sub>2</sub>).  $^2\text{H}$  NMR spectroscopy is quite useful for binuclear copper(II) complexes as well as for copper(II) monomers.<sup>19,20</sup> The CH<sub>3</sub> protons of **1a** resonate at -0.61 ppm, which assignment is readily made by comparison of the spectra of **1a** and the corresponding derivatives **2**. On the basis of signal intensities, other proton signals are also assigned as shown in Table I. The aldimine proton (1-CH), however, could not be detected because of its significant line broadening. A spectrum of **1b** in Figure 2 shows a spectral pattern similar to that of **1a**, and hence, the assignments can be made in analogy with those of **1a**. It is to be emphasized that the observed chemical shift range differs from that of **1a**: the six signals of **1a** fall within the range of 40 ppm, while the corresponding signals of **1b** spread over the range of 120 ppm.

Analogous complexes **3** and **4**, in which the enamine position is hydrogenated, give spectra similar to that of **1a**. Two closely located signals of **3** in D<sub>2</sub>O appeared at -2.3 and -1.7 ppm, which are assigned to *p*-CH<sub>3</sub> and 4-CH<sub>2</sub>, respectively. A broad signal at 23.8 ppm splits into two signals when the temperature is raised. These are assigned to the 1- and 3-CH<sub>2</sub> groups because compound **3** containing deuteriums at the 1- and 3-positions gives  $^2\text{H}$  NMR signals at -24 ppm. The 1- and 3-CH<sub>2</sub> signals accidentally overlap

each other at ambient temperature. The substitution of *p*-C<sub>2</sub>H<sub>5</sub> for *p*-CH<sub>3</sub> gives rise to no significant effect on the  $^1\text{H}$  NMR spectrum, and this fact indicates that **1a** and **2** have quite similar antiferromagnetic interactions in solution.

### Discussion

The usual mononuclear copper(II) complexes provide quite broad  $^1\text{H}$  NMR signals.<sup>6</sup> On the other hand, when two copper(II) ions are close to each other so that the superexchange interaction occurs effectively, the narrowing of NMR signals as well as the decrease in isotropic shifts occurs.

An equation of the isotropic shift for the antiferromagnetic coupling systems ( $\mathcal{H} = -2JS_1S_2$ ;  $S = 1/2$ ) has been given<sup>8,21</sup> by the explicit use of the  $J$  value:

$$\Delta\delta_{\text{iso}} = -\frac{g\beta A}{(\gamma/2\pi)kT}[(\exp(-2J/kT)) + 3]^{-1} \quad (1)$$

where  $A$  is the hyperfine coupling constant of a nucleus with an electronic spin moment in the  $S = 1$  level in the magnetically coupled copper homodimer,  $\gamma$  is gyromagnetic ratio of an observed nucleus, and  $k$  is Boltzmann constant. This equation is available to interpret the observed chemical shifts for **1–4**. The isotropic shifts<sup>7–10</sup> are governed by population distributions in the  $S = 0$  and  $S = 1$  states of dimeric copper(II) complexes, thus being decreased by a factor of  $[(\exp(-2J/kT)) + 3]^{-1}$ . Prior to the discussion of the antiferromagnetic systems, a monomeric (imidazole)copper(II) complex,  $[\text{Cu}(\text{im})_4(\text{H}_2\text{O})_2]\text{F}_2$ , was synthesized,<sup>22</sup> and its NMR spectrum were recorded. However, the  $^1\text{H}$

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**Table II.** Magnetic Moments of Binuclear Copper(II) Complexes in Solution

complex; $-2J$ , $\text{cm}^{-1}$	solvent	$\mu_{\text{eff}}/\text{Cu}$ , $\mu_{\text{B}}$ soln <sup>a</sup>	solid <sup>b</sup>
[Cu <sub>2</sub> ((ha) <sub>2</sub> mpia)OH](ClO <sub>4</sub> ) <sub>2</sub> ; <sup>c</sup> 529	D <sub>2</sub> O	1.3	0.9
	CD <sub>3</sub> OD	0.7	
[Cu <sub>2</sub> ((ha) <sub>2</sub> mpia)Cl]Cl <sub>2</sub> ; <sup>c</sup> 156	D <sub>2</sub> O	1.5 <sup>d</sup>	1.7
	CD <sub>3</sub> OD	2.1	
[Cu <sub>2</sub> ((ha) <sub>2</sub> eipa)OH](ClO <sub>4</sub> ) <sub>2</sub> <sup>e</sup>	D <sub>2</sub> O	1.2	
	(CD <sub>3</sub> ) <sub>2</sub> CO	1.3	
	CD <sub>3</sub> OD	1.1	0.9
[Cu <sub>2</sub> ((h <sub>2</sub> ha) <sub>2</sub> mpia)OH](ClO <sub>4</sub> ) <sub>2</sub> ; <sup>e</sup> 545	(CD <sub>3</sub> ) <sub>2</sub> CO	1.0	
	CD <sub>3</sub> OD	1.2	
[Cu <sub>2</sub> ((h <sub>2</sub> ha) <sub>2</sub> eipa)OH](ClO <sub>4</sub> ) <sub>2</sub> <sup>e</sup>	CD <sub>3</sub> OD	1.2	
	(CD <sub>3</sub> ) <sub>2</sub> CO	0.9	

<sup>a</sup> Obtained at 23 °C from 3.0 mM solution sample by the Evans Method; error limit 0.2  $\mu_{\text{B}}$ . <sup>b</sup> Calculated from  $-2J$  value of crystalline sample in ref 13. <sup>c</sup> Unsuccessful due to the low solubility of the compound in (CD<sub>3</sub>)<sub>2</sub>CO. <sup>d</sup> Converted into a form having OH<sup>-</sup> bridging. <sup>e</sup> Unsuccessful due to the low solubility of the compound in D<sub>2</sub>O.

NMR signals of coordinated imidazoles were not detected. The broad <sup>2</sup>H NMR signal 2-<sup>2</sup>H was observed at 33 ppm ( $\nu_{1/2} = 270$  Hz) by use of deuterated imidazole. The line width,  $\Delta\nu_{1/2}(x)$ , is proportional to  $\gamma_x^{2.5}$ .<sup>5</sup> According to this relationship,  $\nu_{1/2}(^1\text{H})$  of 2'-H may be 11 kHz<sup>23</sup> when  $\nu_{1/2}(^2\text{H})$  is multiplied by a factor of  $(\gamma_{\text{H}}/\gamma_{^2\text{H}})^2$ . This tremendously large line width makes <sup>1</sup>H NMR experiments with mononuclear copper(II) compounds impossible. On the other hand, we have demonstrated that the 2'-H resonances of binuclear complexes 1-4 result in sharp <sup>1</sup>H NMR signals, of which line widths fall within 10<sup>2</sup> Hz. The antiferromagnetic interactions in 1-4 significantly influence both isotropic shifts and line widths with the propensity to reduce them.<sup>7-10</sup> Then, a question arises: Is there any relationship between  $J$  and/or  $\Delta\delta_{\text{iso}}$  and  $\Delta\nu_{1/2}$ ?

**Relationship between NMR Parameters and Magnetic Properties of Binuclear Copper(II) Complexes.** Some binuclear copper(II) complexes of interest have been magnetically<sup>13</sup> characterized in the solid state, and these have been concluded to be antiferromagnetic systems. The value of  $|2J|$  increases from 156 to 545  $\text{cm}^{-1}$  in the order **1b** < **1a** < **3**. In order to examine the relationship between their NMR parameters and magnetism, we need the magnetic moments of binuclear copper(II) complexes in solution. The magnetic moments obtained in the solid state do not necessarily agree with those in solution because the coordination of solvent molecules and/or the dissociation of coordinated ligands may occur. We can estimate the magnetism from a magnetic susceptibility study of the solution by NMR spectroscopy.<sup>24</sup> The magnetic susceptibilities  $\chi_{\text{M}}$  of 1-4 were measured in D<sub>2</sub>O, CD<sub>3</sub>OD, and (CD<sub>3</sub>)<sub>2</sub>CO. From these  $\chi_{\text{M}}$ , the effective magnetic moment ( $\mu_{\text{eff}}$ ) are readily obtained according to the standard equation,  $\mu_{\text{eff}} = 2.83(\chi_{\text{M}}T)^{1/2}$ ,<sup>25a</sup> and presented in Table II, together with the  $\mu_{\text{eff}}$ <sup>25b</sup> values calculated from  $2J$  values<sup>13</sup> in the solid state. Table II reveals that all the  $\mu_{\text{eff}}$ (solution) values are comparable<sup>26</sup> with those in the solid state. Ligand dissociation

(23) We can estimate the line width of the <sup>1</sup>H NMR signal by multiplying by a factor<sup>19,20</sup> of  $(26753/4107)^2 = 42$  and then obtain the value of 11 kHz, which could be nearly equal to the line width of the <sup>1</sup>H NMR signal.

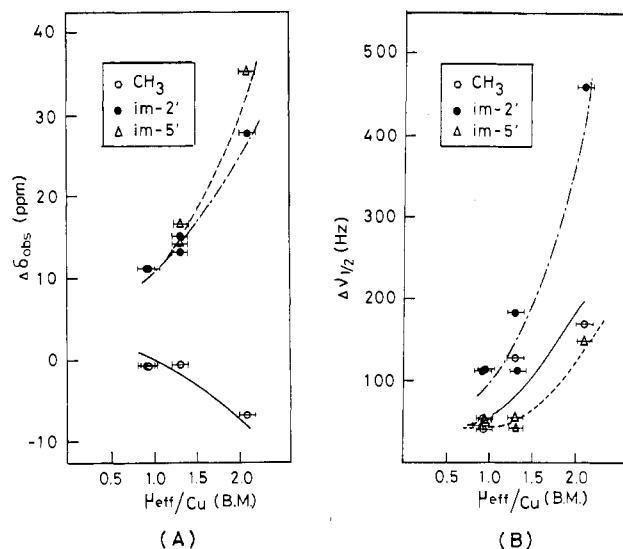
(24) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(25) (a) Reference 4, equation on p 140. (b) The magnetic susceptibility of a Cu(II) dimer is modeled by

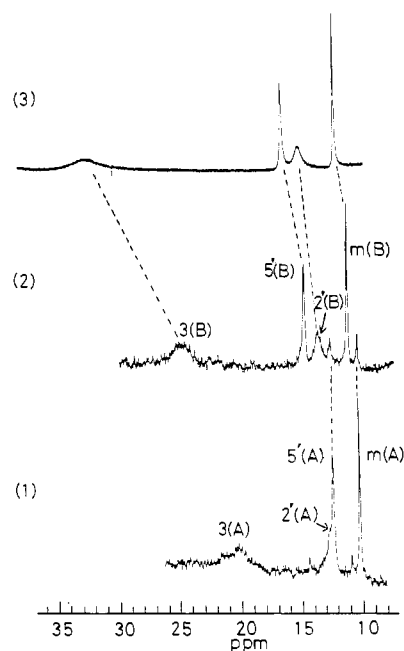
$$\chi_{\text{dimer}} = \frac{2Ng^2\beta^2}{3kT} \left[ 1 + \frac{1}{3} \exp(-2J/kT) \right]^{-1}$$

We used the magnetic susceptibility of half of  $\chi_{\text{dimer}}$  in order to obtain the magnetic susceptibility per copper,  $\chi_{\text{Cu}} = \chi_{\text{dimer}}/2$ . By using this, we can calculate the effective magnetic moment per copper.

(26) The  $2J$  values in the solid state have been determined much more accurately than those in solution because the measurement of magnetic susceptibility can be made over a wide temperature range in the solid state. The experimental temperature range in the case of the solution is quite restricted, giving rise to an ambiguity in the  $2J$  value. The values of  $\mu_{\text{eff}}$  are essentially the same in both states within experimental errors if they are measured for the same chemical species.



**Figure 3.** Plots of (a) observed <sup>1</sup>H NMR chemical shifts ( $\Delta\delta_{\text{obs}}$ ) vs magnetic moment ( $\mu_{\text{eff}}$ ) and (b) observed line widths at half-height vs  $\mu_{\text{eff}}$ .



**Figure 4.** <sup>1</sup>H NMR spectra of **1a** (1) in dry CD<sub>3</sub>OD at 24 °C and (2 and 3) in pure CD<sub>3</sub>OD titrated with 0.55 mmol and 10 mol of D<sub>2</sub>O, respectively.

is unlikely in these chelating systems because no evidence of the dissociation was obtained by NMR spectra. The structures of solution species are, thus, similar to those characterized in the solid state.

The order of magnitude of  $\mu_{\text{eff}}$ (solution) values among **1a**, **1b**, and **3** is in agreement with that of  $\mu_{\text{eff}}$ (solid) values. <sup>1</sup>H NMR spectra of **1a**, **1b**, and **3** show no decomposition in any solvents besides **1b** in D<sub>2</sub>O. In Table I, both the observed shifts and the magnetic moments increase in the order **3**, **1a** < **1b**. This relationship is well illustrated in Figure 3A. These results support the relationship between the isotropic shift and the magnetic moment as in eq 1.<sup>27</sup> The similar relation is also found in the line width at half-height, being presented in Figure 3B. Although the Solomon-Bloembergen equation<sup>28</sup> has been available for the line widths of paramagnetic systems, there are no relations for the line widths of copper(II) dimeric complexes, which give

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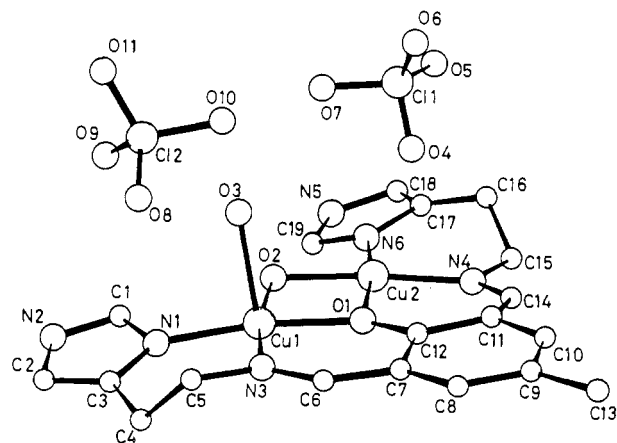
relatively narrow NMR signals as well as small isotropic shifts. Bertini<sup>29</sup> and Drago<sup>30</sup> discussed the dimeric metal complexes that have superexchange interactions ( $\mathcal{H} = -2JS_1S_2$ ) to the extent that  $|J| > h\tau_s^{-1}$  and  $|J| \approx kT$ . According to them, longitudinal ( $T_{1M}$ ) and transverse relaxation ( $T_{2M}$ ) times of copper homodimers are controlled by the population distribution in the  $S = 0$  and  $S = 1$  states rather than by a significant decrease in an electron relaxation time ( $\tau_s$ ). Figure 3B apparently shows the dependence of the line width on the magnetic moment of the systems, indicating that the population-controlled relaxation mechanism is dominant.

**Equilibria of Binuclear Copper(II) Complexes in Solution.** The  $D_2O$  solution of **1b** gives completely the same  $^1H$  NMR spectrum as that of **1a**. The replacement of  $OD^-$  for  $Cl^-$  occurs in  $D_2O$ , and **1a** forms to the extent of 100% conversion. This phenomenon has been found by optical spectroscopy.<sup>13</sup> The  $^1H$  NMR spectrum quantitatively support this replacement.

In the course of the  $^1H$  NMR measurements, the methanol solution of **1a** gave broad signals at 10–30 ppm, quite different from those of the aqueous solution. These broad signals were found to comprise at least two species; when the methanol solution was cooled at  $-70^\circ C$ , two types of signals appeared well-separated. These species are in equilibrium, where water molecules are involved. The dry methanol solution of **1a** gives a spectrum of pure species, whose signals are denoted by character A in Figure 4(1). Upon the addition of water to the methanol solution, signals A decrease and concurrently new signals B grow with downfield shifts. Other signals did not form during this titration. Figure 4(2) displays an intermediate profile of the  $^1H$  NMR spectrum containing both signals A and B. Figure 4(3) illustrates that considerably large amounts of water give a  $^1H$  NMR spectrum that is in good agreement with that of **1a** in  $D_2O$ . Signals A also appear when methanol is added to the pure aqueous solution of **1a**. The assignment of signals B is easily made in analogy with that in Figure 1, while signals A are assigned by use of deuterated compounds and by comparison with other derivatives. The species A is characterized by the behavior of the  $2'-H$  signal, which shifts downfield more than the other two  $5'-H$  and  $m-H$  signals in this region. The difference in chemical shifts between the corresponding two signals A and B indicates that these species are in different magnetic interactions. The details of species B will be discussed in the following section.

The binuclear copper(II) compound studied here can have ligands at the apical position. X-ray structure determination of the analogues have demonstrated the presence of an apical coordination of water.<sup>31,32</sup> In our study, possible ligands are water or methanol. In order to demonstrate water coordination, we have characterized the structure of a single crystal of **1a** obtained from methanol solution.

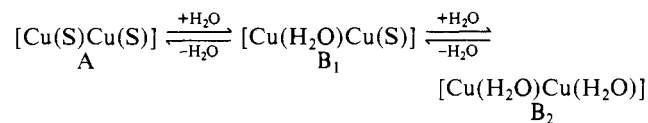
**Crystal Structure of 1a.** The obtained molecular structure of  $[Cu_2((ha)_2mipa)(OH)(H_2O)](ClO_4)_2$  is shown in Figure 5. Each Cu(II) ion is coordinated to two N atoms, and both Cu(II) ions are coordinated to the phenolic oxygen, O1, forming an O atom bridge, and are also bridged through another oxygen, O2, of the hydroxide ion. In addition, one of two Cu(II) ions is coordinated to the oxygen atom, O3, of the water molecule, the distance being  $Cu1-O3 = 2.185$  (18) Å. The geometry around Cu1 ion is distorted square-pyramidal. This  $Cu1-O3$  distance is the shortest of the analogous binuclear copper(II) compounds,<sup>31,32</sup> indicative of strong bonding. Another perchlorate ion may have hydrogen bonding with one of the hydrogens of this water molecule. The perchlorate anion sits above another Cu2 ion, the distance between Cu2 and O4 of the perchlorate being 2.990 (14) Å, indicative of no bonding and the geometry around Cu2 being nearly square-



**Figure 5.** Structure of  $[Cu_2((ha)_2mipa)(OH)(H_2O)](ClO_4)_2$  (**1a**), showing the atom-labeling scheme. Selected values of interatomic distances (Å) and angles (deg):  $Cu1-Cu2 = 3.011$  (4),  $Cu1-N1 = 1.936$  (12),  $Cu1-N3 = 1.943$  (14),  $Cu2-N4 = 1.931$  (14),  $Cu2-N6 = 1.961$  (14),  $Cu1-O1 = 1.933$  (13),  $Cu1-O2 = 1.952$  (15),  $Cu1-O3 = 2.185$  (18),  $Cu2-O1 = 1.943$  (11),  $Cu2-O2 = 1.897$  (15),  $Cu2-O4 = 2.990$  (14);  $Cu1-O1-Cu2 = 101.14$  (51),  $Cu1-O2-Cu2 = 102.94$  (65),  $N1-Cu1-N3 = 94.52$  (55),  $N1-Cu1-O2 = 96.18$  (54),  $O1-Cu1-N3 = 91.97$  (54),  $O2-Cu1-O1 = 77.69$  (53),  $O3-Cu1-N3 = 96.12$  (62),  $O3-Cu1-N1 = 95.84$  (48),  $O3-Cu1-O1 = 98.80$  (55),  $O3-Cu1-O2 = 82.84$  (63),  $N4-Cu2-N6 = 95.10$  (59),  $N4-Cu2-O1 = 93.75$  (54),  $O1-Cu2-O2 = 78.22$  (57),  $O2-Cu2-N6 = 92.83$  (61).

planar. This apical water ligand may come from waters that are contained in methanol solution.

**Comparison of the Structures in Solution and in the Solid State.** From the results of NMR spectroscopy (Figure 4) and X-ray diffraction (Figure 5), it is concluded that water preferably binds to copper much easier than do perchlorate anion and methanol. Among X-ray crystallographic structures of analogous binuclear copper(II) diperchlorates, the molecular structures, when obtained from nonaqueous solution,<sup>31,32</sup> have a perchlorate anion as an apical ligand, while, from water-containing solvent,<sup>33,34</sup> the structures show the presence of an apical water ligand. It is hard to get single crystals from aqueous solutions. In our systems, two species A and B are also associated with the coordination of water, as discussed in the previous section. The spectral pattern of B in Figure 4 is similar to that in the case of aqueous species, as shown in Figure 1(1). It is to be emphasized that the chemical shifts of the signals B are dependent on the water concentration: the more water is added, the more downfield the signals move. This fact indicates that there is an additional equilibrium between species associated with water coordination and that the chemical exchange process exists, which averages signals. Hence, signals B come from the two species. The possible structures involved in this process are  $[Cu(H_2O)Cu(S)]$  (species  $B_1$ ) and  $[Cu(H_2O)Cu(H_2O)]$  (species  $B_2$ ). On the other hand, species A is  $[Cu(S)Cu(S)]$ , where only apical ligands are written and S denotes  $ClO_4^-$  or solvent or no coordination. Due to a chemical exchange between  $B_1$  and  $B_2$  the two spectra are averaged to be a single one, while those of A and the others are not averaged but well distinguishable. Summarized equations are shown as follows:



S = vacant or  $ClO_4^-$  or solvent

These phenomena also happen in the case of **2-4** and have been similarly demonstrated by  $^1H$  NMR spectra. In the case of

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acetone,  $^1\text{H}$  NMR spectra reveal the averaged signals ascribed to  $\text{B}_1$  and  $\text{B}_2$  except in rigorously dry acetone solution.

**Effect of Water Coordination on Observed Chemical Shifts.** From the results discussed above, it is concluded<sup>35</sup> that a compound having apical water molecules has spectra with the isotropic shifts larger than those of compounds with no apical water molecules. The coordination of water reduces the antiferromagnetic interaction of the two copper ions and/or changes the spin densities transmitted via metal-ligand bonds.<sup>36</sup>

The coordinate geometries of the compounds studied here are approximately square-pyramidal when the apical ligand is bound to copper. In this structure, if a strong ligand such as water is coordinated to copper(II), the copper atom slightly deviates from the  $\text{N}_2\text{O}_2$  coordination plane. For instance, Cu1 atom sits 0.09 Å out of the mean plane described by N1, N3, O1, and O2 in Figure 5. An analogous compound having an apical water ligand also indicates a deviation, 0.15 Å,<sup>31</sup> from the square-planar mean plane. This structural variation may reduce the overlap of a  $d_{x^2-y^2}$  orbital with two oxygen (oxo and hydroxy) orbitals, leading to reduction<sup>37</sup> of the antiferromagnetic exchange interaction and/or

change on spin densities from the orbital. At the present stage it is hard to conclude which is most possible because the isotropic shifts are very sensitive to both cases. Even if the antiferromagnetic interaction is mainly changed by this structural variation, it may be quite small. It can be said that NMR spectroscopy is the most useful of the few methods used to detect such a subtle event.

The methanolic solution of **1b** gives a simple  $^1\text{H}$  NMR spectrum, in which only one species is observed. This compound undergoes no solvent effect because the apical chloride anion is tightly bound to copper ion.

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**Supplementary Material Available:** Full listings of atomic and thermal parameters for non-hydrogen atoms, fractional coordinates and isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond lengths and angles, and torsion angles, figures showing the plot of the chemical shifts of signals B in Figure 4 vs  $[\text{D}_2\text{O}]/[\text{CD}_3\text{OD}]$  in titration experiments and the  $^1\text{H}$  NMR spectra monitoring the titration with  $\text{D}_2\text{O}$ , and figure captions (7 pages); a table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

(35) Even for **2** and **3**, it is possible to conclude that more water molecules afford isotropic shifts greater than those for compounds having less water molecules.

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## Kinetic Proof That the Tetranuclear Oxocopper(II) Complex $(\text{py})_3\text{Cu}_4\text{Cl}_4\text{O}_2$ Initiates and Catalyzes the Oxidative Coupling of 2,6-Dimethylphenol by Dioxygen in Nitrobenzene

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Copper(I) chloride reacts with equimolar pyridine, py, in ambient-temperature nitrobenzene under dinitrogen to give solutions of the tetranuclear copper(I) complex  $(\text{py})_4\text{Cu}_4\text{Cl}_4$  (I). Stoichiometric, cryoscopic, and kinetic measurements indicate that I is oxidized to the tetranuclear oxocopper(II) complex  $(\text{py})_3\text{Cu}_4\text{Cl}_4\text{O}_2$  (IIa) by dioxygen in nitrobenzene in a second-order process whose rate is independent of the concentration of 2,6-dimethylphenol, [DMP]. Insertion of  $\text{O}_2$  into the tetranuclear halo core of I is the proposed rate-determining step. Slurry oxidation of  $\text{CuCl}$  with dioxygen at the molar ratio  $[\text{py}]/[\text{CuCl}] = 0.75$  in nitrobenzene gives the tetranuclear oxocopper(II) complex  $(\text{py})_3\text{Cu}_4\text{Cl}_4\text{O}_2$  (IIb). The rate of direct, first-order oxidation of excess DMP to stoichiometric yields of 3,3',5,5'-tetramethyl-1,4-diphenquinone (DPQ) and water by IIa or IIb ( $9.45 \times 10^{-5}$  M) in nitrobenzene is independent of which oxidant is used, of  $[\text{DMP}]_0 = (2.2-12.2) \times 10^{-3}$  M, and of  $[\text{O}_2]$ . The system becomes catalytic at higher  $[\text{DMP}]_0$  or lower  $[\text{II}]_0$  because destruction of II and inhibition of copper(I) reoxidation by coproduct water are prevented through interaction of the latter with excess phenol. Data at different [DMP] indicate that conversion of a strong complex of stoichiometry IIb-2DMP to products DPQ, water, and copper(I) is the rate-determining catalytic step. Properties of IIa and IIb likely to be responsible for this behavior are discussed.

### Introduction

Metal-catalyzed reactions of dioxygen are very important processes, and there is sustained interest in their products and mechanisms.<sup>1-11</sup>

Natural oxidation systems have evolved from the biosynthesis of oxidatively stable, polydentate ligands for metals that can confer reaction specificity as subtle as the difference between dioxygen transport and oxygenase or dehydrogenase activity. Part of this specificity has to do with the extent of dioxygen reduction.<sup>1-6</sup> Active-site models based on carefully chosen polydentate ligands have been especially helpful in clarifying cobalt,<sup>4</sup> iron,<sup>5</sup> and copper<sup>6</sup> dioxygen systems. Such metals are tightly held at each active site, and there are excellent prospects of determining catalytic

mechanisms from direct kinetic measurements, as emphasized in recent reviews.<sup>1-6</sup>

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