

### Interaction of Pyridine with Copper(II) $\beta$ -Diketonates; a $^1\text{H}$ Nuclear Magnetic Resonance Study\*

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Previously, the axial coordination of optically active amines to various kinds of copper(II)  $\beta$ -diketonates was discussed in terms of induced circular dichroism [1]. From this investigation, the coordination of the optically active amine to the axial position of the copper(II) complexes, which are achiral, was expected to play an important role in the position fixing or in the bridging between  $\beta$ -diketonate moieties and the added amine. In this paper, we have studied the ligation mode of the added pyridine to the copper(II)  $\beta$ -diketonates in terms of the paramagnetic effects of the copper(II) ion on the  $^1\text{H}$  nuclear magnetic resonance (NMR) spectra of the added pyridines and the ligating acetylacetonate moieties.

Copper(II)  $\beta$ -diketonates can form 1:1 or 1:2 adducts with pyridine and other organic bases [2]. Such an adduct formation through the axial ligation of the bases has been analyzed by circular dichroism [1], electronic spectrum [2], electron spin resonance spectrum [3] and NMR [4]. In the NMR approach, much attention has been paid to the paramagnetic shift effect on the observed NMR spectra of the ligating bases in the analysis of the ligation modes. In this work the paramagnetic effect of the copper(II) ion on the NMR spectra of the ligating bases was analyzed successfully using their longitudinal and transverse relaxation times.

The paramagnetic shift is divided into the Fermi-contact and pseudo-contact contributions as follows [5]. The Fermi-contact shift,  $\Delta\nu_c$ , is given by eqn. (1) [6]

$$\Delta\nu_c = -A(\gamma_e/\gamma_N)\{[S(S+1)]/3kT\}\bar{g}\beta\nu P \quad (1)$$

where  $A$  is the Fermi-contact constant,  $\gamma_e$  and  $\gamma_N$  the gyromagnetic ratios for electron and the given nuclear spin,  $S$  the spin quantum number for the paramagnetic complex,  $\bar{g}$  the rotationally averaged value of the  $g$  tensors,  $\beta$  the value of Bohr magneton,  $\nu$  the nuclear Larmor-frequency, and  $P$  the fraction of the ligand molecules coordinating to the paramagnetic metal ion, respectively.

On the other hand, the pseudo-contact shift is given by eqn. (2) [7]

$$\Delta\nu_d = [\nu\beta^2 S(S+1)/9kT]\bar{g}(g_{\parallel} - g_{\perp}) \times \{(1-3\cos^2\theta)/R^3\}P \quad (2)$$

where  $R$  is the length of a vector from the paramagnetic metal ion center to the observing nucleus, and  $\theta$  is the polar angle at which the observing nucleus is facing to the paramagnetic metal ion situated at the coordinate origin.

In the presence of the paramagnetic metal ion, the observed transverse relaxation time,  $T_{2\text{obs}}$ , is given by eqn. (3) [8]

$$1/T_{2\text{obs}} = 1/T_{2\text{L}} + 1/T_{2\text{P}} = 1/T_{2\text{L}} + P/(T_{2\text{B}} + \tau_{\text{B}}) \quad (3)$$

where  $T_{2\text{L}}$  is the transverse relaxation time in the absence of the paramagnetic metal ion,  $T_{2\text{P}}$  is the contribution of the paramagnetic metal ion to transverse relaxation time,  $T_{2\text{B}}$  is the transverse relaxation time of the ligand bound to the paramagnetic metal ion, and  $\tau_{\text{B}}$  is the life-time of the bound state. In the fast exchange limit,  $\tau_{\text{B}} \ll T_{2\text{B}}$ , eqn. (3) reduces to eqn. (4)

$$1/T_{2\text{P}} = 1/T_{2\text{obs}} - 1/T_{2\text{L}} = P/T_{2\text{B}} \quad (4)$$

The transverse relaxation time,  $T_2$ , is conveniently related to the observed line width at the half-height,  $\omega_{1/2}$ , through the following eqn. (5)

$$\omega_{1/2} = 1/2\pi T_2 \quad (5)$$

The longitudinal and transverse relaxation times of the ligand bound to the paramagnetic metal ion,  $T_{1\text{B}}$  and  $T_{2\text{B}}$ , can be expressed by the Solomon-Bloembergen equation [9, 10]. Assuming  $\omega_{\text{H}}\tau_{\text{C}} \ll 1$ ,  $\omega_{\text{S}}\tau_{\text{e}} \cong 1$ , and  $\omega_{\text{S}}\tau_{\text{e}} \gg 1$ , these are represented by eqns. (6) and (7) [11], where  $\omega_{\text{H}}$  and  $\omega_{\text{S}}$  are the proton nuclear and electronic Larmor frequencies, and  $\tau_{\text{C}}$  and  $\tau_{\text{e}}$  are the correlation times modulating the dipolar and Scalar interactions, respectively.

$$1/T_{1\text{B}} = (13/15)S(S+1)[g^2\beta^2\gamma_{\text{N}}^2/(\hbar^2 R^6)]\tau_{\text{C}} \quad (6)$$

$$1/T_{2\text{B}} = (9/10)S(S+1)[g^2\beta^2\gamma_{\text{N}}^2/(\hbar^2 R^6)]\tau_{\text{C}} + (1/3)S(S+1)(A^2/\hbar^2)\tau_{\text{e}} \quad (7)$$

$$\cong 1/T_{1\text{B}} + (1/3)S(S+1)(A^2/\hbar^2)\tau_{\text{e}} \quad (8)$$

\*Abbreviations used are: NMR, nuclear magnetic resonance; Cu(aa)<sub>2</sub>, bis(acetylacetonato)copper(II), bis(2,4-pentanediono)copper(II); Cu(taa)<sub>2</sub>, bis(trifluoroacetylacetonato)copper(II), bis(1,1,1-trifluoro-2,4-pentanediono)copper(II); Py, pyridine;  $\gamma$ -MePy,  $\gamma$ -picoline, 4-picoline, 4-methylpyridine;  $\alpha$ -H, the chemical shifts of the hydrogen atoms attached to the  $\alpha$ -carbons on pyridine molecule added to the copper(II) complex;  $\beta$ -H, the chemical shifts of the hydrogen atoms attached to the  $\beta$ -carbons on pyridine molecule added to the copper(II) complex;  $\gamma$ -H, the chemical shift of the hydrogen atom attached to the  $\gamma$ -carbon on pyridine molecule added to the copper(II) complex;  $\gamma$ -CH<sub>3</sub>, the chemical shifts of the hydrogen atoms of the methyl group at the  $\gamma$ -position of 4-methylpyridine added to the copper(II) complex.

## Experimental

The  $\beta$ -diketonate complexes of copper(II),  $\text{Cu}(\text{aa})_2$  and  $\text{Cu}(\text{taa})_2$ , were purchased from Nakarai Kagaku Co. Ltd. and Tokyo Kasei Co. Ltd., respectively, and purified by successive crystallizations. Pyridine (Py) and 4-methylpyridine ( $\gamma$ -MePy) were of the highest guaranteed grade and purified furthermore by fractional distillation immediately before NMR experiments. Chloroform of spectroscopic grade was purified through alumina column chromatography and was dried over a molecular sieve. Absorption spectra were recorded on a Jasco Uvidec 510 spectrophotometer.  $^1\text{H}$  NMR spectra were measured with a Bruker CXP-300 spectrometer and a JEOL FX-90 spectrometer. Chemical shifts were referred to the signal of an internal standard tetramethylsilane (TMS). The line widths were obtained as the full line widths at the half-height, and the paramagnetic chemical shifts were defined as the differences between the observed chemical shifts in the presence of the copper(II) complexes and the corresponding ones in the absence of the complexes. Up-field shifts were defined as positive and down-field shifts as negative.

Longitudinal relaxation time,  $T_1$ , was measured by the  $180^\circ-\tau-90^\circ$  pulse sequence. Transverse relaxation time,  $T_2$ , was measured by the  $90^\circ-\tau-180^\circ$  pulse sequence conventionally. All NMR and absorption spectra were measured for the chloroform solutions of the given systems.

## Results and Discussion

### Paramagnetic Shifts of Py and $\gamma$ -MePy Coordinated to $\text{Cu}(\text{aa})_2$ and $\text{Cu}(\text{taa})_2$

It is known that copper(II)  $\beta$ -diketonates form adducts with some organic bases in organic solutions [1, 12]. Visible absorption spectra of  $\text{Cu}(\text{aa})_2$  and  $\text{Cu}(\text{taa})_2$  in chloroform solutions containing various amounts of Py or  $\gamma$ -MePy were observed.  $\text{Cu}(\text{aa})_2$  forms only a 1:1 adduct with Py or  $\gamma$ -MePy over a wide range of the molar ratio of  $\text{Cu}(\text{aa})_2$  to the bases, while  $\text{Cu}(\text{taa})_2$  forms mainly a 1:1 adduct with Py or  $\gamma$ -MePy until the bases to  $\text{Cu}(\text{taa})_2$  ratio exceeds 200:1 or 140:1, respectively. The formation constants of the 1:1 adducts were obtained spectrophotometrically using the method of Rose-Drago [13] and are listed in Table I. These values are consistent with those reported elsewhere [14].

NMR shifts of Py and  $\gamma$ -MePy coordinated to  $\text{Cu}(\text{aa})_2$  and  $\text{Cu}(\text{taa})_2$  were measured in  $\text{CHCl}_3$ -d solution. NMR data are shown in Tables II and III. Observed paramagnetic shifts were defined as the differences between the observed chemical shifts in the presence of the copper(II) complexes and the chemical shifts in the absence of copper(II) complex.

TABLE I. The Formation Constants of 1:1 Base Adduct in Chloroform

Adduct		Formation constants ( $\text{M}^{-1}$ )
Base	Complex	
Py	$\text{Cu}(\text{aa})_2^{\text{a}}$	4.5
$\gamma$ -MePy	$\text{Cu}(\text{aa})_2^{\text{a}}$	4.8
Py	$\text{Cu}(\text{taa})_2^{\text{b}}$	342
$\gamma$ -MePy	$\text{Cu}(\text{taa})_2^{\text{c}}$	345

<sup>a</sup>This forms only a 1:1 adduct in all ratios. <sup>b</sup>This forms mainly a 1:1 adduct until the base to the complex ratio exceeds 200:1. <sup>c</sup>This forms mainly a 1:1 adduct until the base to the complex ratio exceeds 140:1.

The fractions of the ligands (Py or  $\gamma$ -MePy) coordinated to the copper(II) complexes,  $P$ , were estimated from the observed formation constants. Because the exact geometry of these adducts is not known, the magnitudes of the pseudo-contact shifts cannot be calculated exactly. Therefore, the following assumption was used for the estimation of pseudo-contact shifts. The values of geometric factors,  $(1-3 \cos^2 \theta)/R^3$ , for each proton on the ligating molecule, were calculated assuming the Cu-N bond distance to be 2.2 Å [15] and using the bond lengths and the bond angles of the pyridine molecule [16]. The  $g$  values are assumed to be almost constant for these adducts and are calculated assuming  $g_{\parallel}$  and  $g_{\perp}$  to be 2.30 and 2.07, respectively [17]. The calculated pseudo-contact values are shown in Table IV. The magnitudes of the contact shifts were attenuated as the distances between the given protons and the metal ion increased. In the Py and  $\gamma$ -MePy adduct systems, the magnitudes of the contact shifts increased in the order of  $\text{Cu}(\text{aa})_2 < \text{Cu}(\text{taa})_2$ , which is the same order as that of formation constants. NMR signals of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -protons on the pyridine molecule in the presence of the copper(II) complexes shifted to the down-field side, while  $\gamma$ -methyl signals shifted to the up-field side. The down- or up-field shift is caused by the spin density in positive or negative sign at the positions.

### Temperature Dependence of the Paramagnetic Shifts and the Line Widths

The temperature variations of the paramagnetic shifts of  $^1\text{H}$  NMR for the protons of  $\gamma$ -MePy in the presence of copper(II) complexes,  $\text{Cu}(\text{aa})_2$  and  $\text{Cu}(\text{taa})_2$ , are summarized in Fig. 1. For each case the linearity between the paramagnetic shifts and the reciprocal of the temperatures was held approximately, and this linearity was quite good for the methyl protons of the  $\beta$ -diketonate ligands in the complexes, as shown in Fig. 2. The temperature dependence of the paramagnetic shifts is appreciably

TABLE II. Paramagnetic Shifts of Bases Coordinated to Cu(aa)<sub>2</sub> in Chloroform-d at 22 °C

10 <sup>9</sup> [Cu(aa) <sub>2</sub> ]/[base]	Proton position	$\Delta\nu_{\text{obs}}^{\text{a}}$ (Hz)	$p^{\text{b}}$	Pseudo-contact <sup>c</sup> shift (Hz)	$\Delta\nu_{\text{c}}^{\text{d}}$ (Hz)	$\Delta\nu_{\text{c}} (P=1)^{\text{e}}$ (Hz)	$\Delta\nu_{\text{cm}}^{\text{f}}$ (Hz)
Base: Py							
48.7	$\alpha$ -H	-38	0.021	-14	-24	-1100	
	$\beta$ -H	-13		-6	-7	-300	
	$\gamma$ -H	-14		-5	-9	-400	
97.8	$\alpha$ -H	-67	0.035	-23	-44	-1300	
	$\beta$ -H	-22		-10	-12	-300	
	$\gamma$ -H	-25		-8	-17	-500	
146.2	$\alpha$ -H	-91	0.049	-32	-59	-1200	-1200
	$\beta$ -H	-30		-14	-16	-300	-300
	$\gamma$ -H	-33		-12	-21	-400	-400
Base: $\gamma$ -MePy							
49.6	$\alpha$ -H	-51	0.020	-13	-40	-2000	
	$\beta$ -H	-17		-6	-11	-600	
	$\gamma$ -Me	-2		-3	+1	+50	
99.2	$\alpha$ -H	-95	0.035	-23	-72	-2100	
	$\beta$ -H	-30		-10	-20	-600	
	$\gamma$ -Me	-4		-5	+1	+30	
149.1	$\alpha$ -H	-121	0.051	-33	-88	-1700	-1900
	$\beta$ -H	-39		-15	-24	-500	-600
	$\gamma$ -Me	-5		-8	+3	+60	+50

<sup>a</sup>Observed paramagnetic shift. <sup>b</sup>Fraction of the ligand coordinated to the complex. <sup>c</sup>Calculated pseudo-contact shift. <sup>d</sup>Paramagnetic shift corrected for the pseudo-contact shift. <sup>e</sup>Estimated contact shift, assuming to be  $P = 1$ . <sup>f</sup>Mean value of  $\Delta\nu_{\text{c}} (P = 1)$ .

TABLE III. Paramagnetic Shifts of Bases Coordinated to Cu(taa)<sub>2</sub> in Chloroform-d at 22 °C

10 <sup>3</sup> [Cu(taa) <sub>2</sub> ]/[base]	Proton position	$\Delta\nu_{\text{obs}}^{\text{a}}$ (Hz)	$p^{\text{b}}$	Pseudo-contact <sup>c</sup> shift (Hz)	$\Delta\nu_{\text{c}}^{\text{d}}$ (Hz)	$\Delta\nu_{\text{c}} (P=1)^{\text{e}}$ (Hz)	$\Delta\nu_{\text{cm}}^{\text{f}}$ (Hz)
Base: Py							
6.0	$\alpha$ -H	-22	0.006	-1.0	-21	-3500	
	$\beta$ -H	-9		-0.5	-8.5	-1400	
	$\gamma$ -H	-3		-0.4	-2.6	-400	
12.0	$\alpha$ -H	-48	0.012	-2.0	-46	-3800	
	$\beta$ -H	-16		-1.0	-15	-1200	
	$\gamma$ -H	-6		-0.8	-5.2	-400	
18.0	$\alpha$ -H	-79	0.018	-3.0	-76	-4200	-3800
	$\beta$ -H	-26		-2.0	-24	-1300	-1300
	$\gamma$ -H	-16		-1.0	-15	-800	-500
Base: $\gamma$ -MePy							
35.5	$\alpha$ -H	-631	0.034	-22	-609	-18000	
	$\beta$ -H	-183		-10	-173	-5100	
	$\gamma$ -Me	+45		-5.0	+50	+1500	
53.0	$\alpha$ -H	-887	0.053	-34	-853	-16000	
	$\beta$ -H	-262		-15	-247	-4700	
	$\gamma$ -Me	+64		-8.0	+72	+1400	

(continued)

TABLE III. (continued)

$10^3[\text{Cu}(\text{taa})_2]/[\text{base}]$	Proton position	$\Delta\nu_{\text{obs}}^{\text{a}}$ (Hz)	$p^{\text{b}}$ shift (Hz)	Pseudo-contact <sup>c</sup> shift (Hz)	$\Delta\nu_{\text{c}}^{\text{d}}$ (Hz)	$\Delta\nu_{\text{c}} (P = 1)^{\text{e}}$ (Hz)	$\Delta\nu_{\text{cm}}^{\text{f}}$ (Hz)
70.9	$\alpha$ -H	-1266	0.070	-45	-1181	-17000	-17000
	$\beta$ -H	-350		-20	-330	-4700	-4800
	$\gamma$ -Me	+86		-11	+97	+1400	+1400

<sup>a</sup>Observed paramagnetic shift. <sup>b</sup>Fraction of the ligand coordinated to the complex. <sup>c</sup>Calculated pseudo-contact shift. <sup>d</sup>Paramagnetic shift corrected for the pseudo-contact shift. <sup>e</sup>Estimated contact shift, assuming to be  $P = 1$ . <sup>f</sup>Mean value of  $\Delta\nu_{\text{c}} (P = 1)$ .

TABLE IV. Estimated Pseudo-contact Shift of Pyridine and  $\gamma$ -Methylpyridine Coordinated to the Copper(II) Complexes

Proton position	$\nu_{\text{pc}}$ (Hz)
$\alpha$ -H	-643
$\beta$ -H	-292
$\gamma$ -H	-241
$\gamma$ -Me	-157

large for the adduct with  $\text{Cu}(\text{taa})_2$  and for the complex itself, while it is rather small for the adduct with  $\text{Cu}(\text{aa})_2$  and for the  $\text{Cu}(\text{aa})_2$  ligand itself. The trifluoromethyl group lowers the ligand field of the acetylacetonato ligand to the copper(II) ion, and thus enables the axial ligation of the added pyridine to be more accessible than in the case of  $\text{Cu}(\text{aa})_2$ . This assumption is confirmed by the experimental results shown in Figs. 1 and 2. Since the pseudo-contact contribution to the observed para-

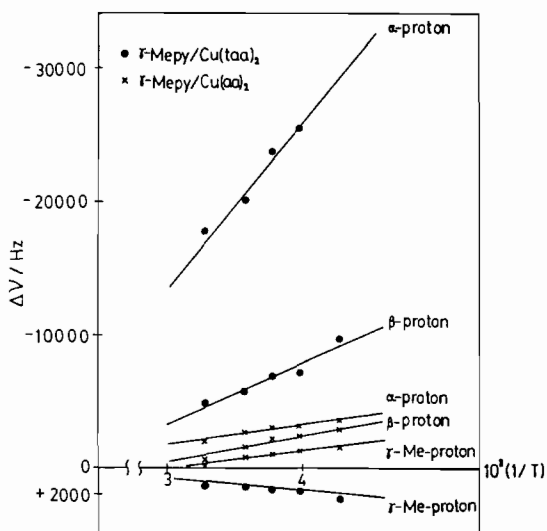


Fig. 1. Temperature dependence on paramagnetic shifts of  $\gamma$ -MePy/copper(II)  $\beta$ -diketonates in  $\text{CHCl}_3\text{-d}$ . These solutions consisted of  $\gamma$ -MePy (0.4 M) and  $\text{Cu}(\text{taa})_2$  (14.2 mM) ( $\bullet$ ), or  $\gamma$ -MePy (0.8 M) and  $\text{Cu}(\text{aa})_2$  (7.9 mM) ( $\times$ ). The magnitude of paramagnetic shift was normalized in  $P = 1$ .

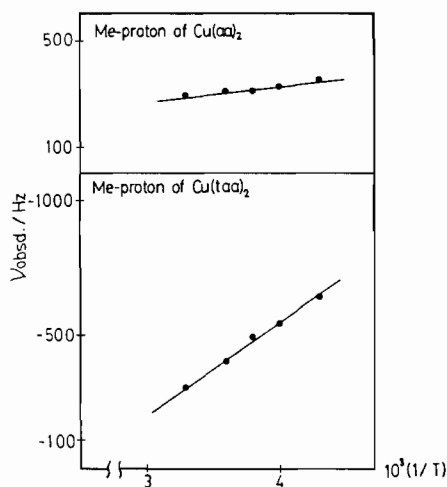


Fig. 2. Temperature dependence on paramagnetic shifts of copper(II)  $\beta$ -diketonates in  $\text{CHCl}_3\text{-d}$ . These solutions consisted of  $\text{Cu}(\text{aa})_2$  (5.0 mM) or  $\text{Cu}(\text{taa})_2$  (5.4 mM). The paramagnetic shift in this Figure was referred to the signal of an internal standard, TMS.

magnetic shifts for  $\text{Cu}(\text{taa})_2$ -pyridine system can be ignored, as can be seen in Table II, the ratios of the slopes in the linear plots of the paramagnetic shifts versus  $1/T$  are assumed to correspond to the ratios of the hyperfine coupling constants,  $A$ , in eqn. (1).

The temperature dependence of the line widths is also summarized in Fig. 3. In the solution which contains the paramagnetic species, when the relaxation time of the ligand molecules bound to the paramagnetic species,  $T_{2B}$ , is longer than the lifetime of the bound state,  $\tau_B$ , the line broadening may result from  $T_{2B}$  [18]. This condition is called the fast exchange, and is expressed as eqn. (4). In Fig. 3, the line width broadenings of  $\alpha$ -protons of  $\gamma$ -MePy in the  $\gamma$ -MePy copper(II)  $\beta$ -diketonates became greater on lowering the temperature. This indicates that the fast exchange limit is retained for these systems. In the systems with no chemical exchange, the temperature dependence on the line broadening of the methyl proton resonances should be the same as those of the  $\alpha$ -protons of  $\gamma$ -MePy and of the  $\beta$ -diketonates.

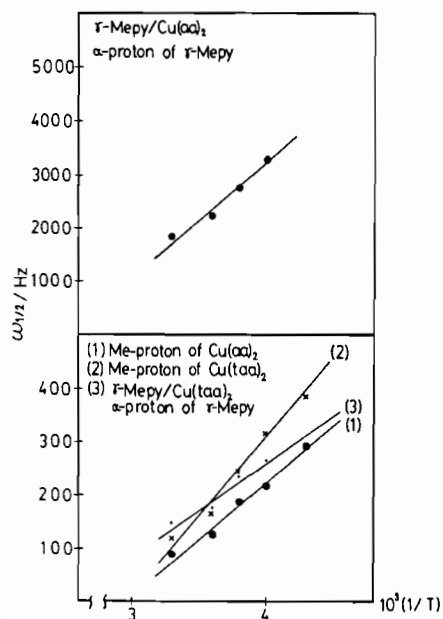


Fig. 3. Temperature dependence on line width of base adducts and copper(II)  $\beta$ -diketones in  $\text{CHCl}_3\text{-d}$ . These solutions consisted of  $\text{Cu}(\text{aa})_2$  (5.0 mM),  $\text{Cu}(\text{taa})_2$  (5.4 mM),  $\gamma\text{-MePy}$  (0.8 M) and  $\text{Cu}(\text{aa})_2$  (7.9 mM), or  $\gamma\text{-MePy}$  (0.4 M) and  $\text{Cu}(\text{taa})_2$  (14.2 mM). The magnitude of line width of base adduct was normalized in  $P = 1$ .

#### Relaxation Times; $T_1$ and $T_2$

The longitudinal and transverse relaxation times for the copper(II)  $\beta$ -diketonates and their pyridine adducts are listed in Table V. It can be seen that

the ratios of  $T_1/T_2$  or  $T_{1B}/T_{2B}$  were nearly equal to unity for  $^1\text{H}$  NMR of  $\gamma\text{-MePy}$  bound to  $\text{Cu}(\text{aa})_2$  and for the acetylacetonate ligands of  $\text{Cu}(\text{aa})_2$  and  $\text{Cu}(\text{taa})_2$  themselves, while the ratios were appreciably larger than unity for  $^1\text{H}$  NMR of  $\gamma\text{-MePy}$  bound to  $\text{Cu}(\text{taa})_2$ .

In the fast exchange limit, a combination of eqn. (6) with eqn. (7) yields the relation of  $T_{1B}/T_{2B} = 1$  under relaxation through the dipolar interaction mechanism only [19]. Values of the ratios greater than unity result from the other mechanism where the fast exchange limit is not attained and/or the scalar term of eqn. (7) is not negligible. Therefore, it can be assumed that there may be small contributions of contact term for  $\gamma\text{-MePy}$  adducts of  $\text{Cu}(\text{aa})_2$ , while there may be larger contributions of contact term for  $\gamma\text{-MePy}$  adduct of  $\text{Cu}(\text{taa})_2$ . Using eqn. (8), the magnitudes of contact terms estimated from the differences between  $1/T_{2B}$  and  $1/T_{1B}$  lie in the following order;  $\alpha\text{-H} > \beta\text{-H} > \gamma\text{-H} > \gamma\text{-Me}$  for  $^1\text{H}$  NMR signals of  $\gamma\text{-MePy}$  bound to  $\text{Cu}(\text{aa})_2$  or  $\text{Cu}(\text{taa})_2$ . The magnitudes of  $T_{1B}$  for the  $\gamma\text{-MePy}$  adduct of  $\text{Cu}(\text{aa})_2$  are nearly equal to those of the corresponding  $\text{Cu}(\text{taa})_2$ . This experimental result leads to the assumption that the extent of dipolar interaction is equal for both  $\gamma\text{-MePy}$  adducts of  $\text{Cu}(\text{aa})_2$  and  $\text{Cu}(\text{taa})_2$ .

#### Conclusions

(1) Paramagnetic shifts obtained here indicate that Fermi-contact shift is equivalent to pseudo-

TABLE V. Longitudinal and Transverse Relaxation Times for the Copper(II)  $\beta$ -Diketones and their Adducts with  $\gamma$ -Methylpyridine

Proton position	$P^a$	$T_{1P}^b$ (s)	$T_{2P}^b$ (s)	$T_{1B}^{-1c}$ ( $s^{-1}$ )	$T_{2B}^{-1c}$ ( $s^{-1}$ )	$T_{1P}/T_{2P}$	$T_{2B}^{-1} - T_{1B}^{-1}$ ( $s^{-1}$ )
<b>MePy-Cu(aa)<sub>2</sub></b>							
$\alpha\text{-H}$	0.065	0.006	0.004	2600	3800	1.5	1200
$\beta\text{-H}$		0.06	0.04	260	380	1.5	120
$\gamma\text{-Me}$		0.12	0.10	130	150	1.2	20
<b>MePy-Cu(taa)<sub>2</sub></b>							
$\alpha\text{-H}$	0.013	0.03	0.002	2600	38000	15	35400
$\beta\text{-H}$		0.33	0.03	230	2600	11	2370
$\gamma\text{-Me}$		0.71	0.15	110	510	5.0	400
<b>Cu(aa)<sub>2</sub></b>							
Me		0.004	0.004	250	250	1.0	0
<b>Cu(taa)<sub>2</sub></b>							
Me		0.005	0.003	200	330	1.7	130

<sup>a</sup>Fraction of ligand coordinated to the complex. of the bound ligand to the complex.

<sup>b</sup>Observed relaxation times in the paramagnetic systems.

<sup>c</sup>Relaxation rates

contact shift for the pyridine adducts of  $\text{Cu}(\text{aa})_2$ , while for those of  $\text{Cu}(\text{taa})_2$  Fermi-contact interaction is predominant.

(2) The temperature effects on the paramagnetic shift for the adducts of  $\text{Cu}(\text{taa})_2$  are larger than those for the adducts of  $\text{Cu}(\text{aa})_2$ .

(3) The temperature dependence on the line widths shows that fast exchange occurs.

(4) The measurements of paramagnetic relaxation times indicate that Fermi-contact interaction operates for the  $\gamma$ -MePy adduct of  $\text{Cu}(\text{taa})_2$ , but not for the  $\gamma$ -MePy adduct of  $\text{Cu}(\text{aa})_2$ .

(5) In the relaxations of the methyl groups in  $\text{Cu}(\text{aa})_2$  and  $\text{Cu}(\text{taa})_2$ , dipolar interaction is predominant.

(6) The results on the relaxation time measurements suggest that pseudo-contact terms on reciprocals of relaxation times in the systems of  $\gamma$ -MePy- $\text{Cu}(\text{aa})_2$  and  $\gamma$ -MePy- $\text{Cu}(\text{taa})_2$  are equivalent each other, but contact terms in the system of  $\gamma$ -MePy- $\text{Cu}(\text{taa})_2$  are larger than those in the system of  $\gamma$ -MePy- $\text{Cu}(\text{aa})_2$ .

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