The ^{13}C Magnetic Resonance Study on the Effects of Divalent Paramagnetic Metal Acetylacetonates on Pyridine, Quinoline, and Isoquinoline. Specific Interactions with Mn(AA)$_2$

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^{13}C nuclear magnetic resonance studies of pyridine solutions containing paramagnetic Ni(II), Co(II), Cu(II), or Mn(II) acetylacetonate are made by observing the induced chemical shift, the line width, and the spin-lattice relaxation time due to the paramagnetism of these metals. The origin of the paramagnetic effects on the ^{13}C spectra induced by Ni, Co, or Cu acetylacetonate is mainly the contact interaction, while the ^{13}C spectra of the pyridine-Mn(AA)$_2$ system can not be interpreted by the same interaction. The ^{13}C spectra of quinoline and isoquinoline containing Mn(AA)$_2$ are also studied; the results indicate that the predominant mechanism is the dipole-dipole interaction.

Up to now, the influences of paramagnetic metals on the ^{13}C nuclear magnetic resonance (NMR) spectra have been studied mainly from two different viewpoints. The ^{13}C spectra of *N*-heterocyclic compounds with addition of Ni(II) acetylacetonate, Ni(AA)$_2$, were investigated in order to observe the ^{13}C contact shift, where the molecule under study interacts with the paramagnetic Ni(AA)$_2$ at the position of the nitrogen atom.[1–4] In magnetic resonances of nuclei other than ^{13}C, especially in the ^{1}H NMR, the contact shifts induced by paramagnetic metals have been studied for many molecules and metals, and the nature of the interaction between them have been elucidated.[5] From the studies of the induced ^{13}C shift, much information has been obtained about the electronic structure of the carbon skelton of the molecules.[1–4]

Another study is the observation of the quenching of the nuclear Overhauser effect (NOE), which is characteristic of the ^{13}C resonance.[6–11] In this case, the molecule under study does not have any special interacting site with the paramagnetic metals in solution. The roles of the paramagnetic metals are to accelerate the slow ^{13}C relaxation and to reduce the NOE enhancement. An attempt has been made to use various paramagnetic metals as "paramagnetic relaxation agents" for this purpose, but clearly the utility of the paramagnetic metals is limited since many molecules are known to associate with metals.

Morishima and his co-workers[1–4] have studied the ^{13}C contact shifts induced by Ni(AA)$_2$ and indicated that the induced ^{13}C contact shifts show an alternation in sign and an attenuation in magnitude, depending on the distance from the nitrogen atom of the interacting site. They interpreted this phenomenon in terms of the electron spin densities on the carbon s atomic orbitals. The line broadening of the ^{13}C spectra of *N*-heterocyclic compounds due to Ni(AA)$_2$ is in the order of the β, α, and γ-carbons to the nitrogen atom attached by Ni(AA)$_2$; this order is the same as that of the absolute magnitude of the ^{13}C contact shift induced by Ni(AA)$_2$.

On the other hand, Kotowycz and Hayamizu first observed that when the paramagnetic Mn^{2+} ion was added to the aqueous adenosine monophosphate (AMP) solution, the ^{13}C line broadening was observed from the nearest position of the metal-binding site.[12] This trend has been shown to be the same for pyrimidine nucleoside and nucleotide in the presence of the Mn^{2+} ion,[13] while a different trend was observed upon the addition of the Cu^{2+} ion in similar aqueous solutions.[14] Clearly these results suggest that different paramagnetic metals affect the ^{13}C spectra in different manners.

Although many studies have been made to observe the ^{13}C contact shifts induced by Ni(AA)$_2$ for various *N*-heterocyclic compounds or to quench the NOE enhancement using various paramagnetic metals, only a few observations have been reported for the effects due to various paramagnetic metals on the ^{13}C parameters of *N*-heterocyclic compounds. In this paper we wish to report on the influences of four kinds of divalent paramagnetic metals, *i.e.*, Ni, Co, Cu, and Mn on the ^{13}C spectra of pyridine by observing the ^{13}C chemical shift, the line width, and the spin-lattice relaxation time, T$_1$. The behavior of these parameters upon the addition of Ni(AA)$_2$, Co(AA)$_2$, and Cu(AA)$_2$ is approximately similar, but Mn(AA)$_2$ gives quite different effects on the induced ^{13}C shifts and the line broadening. To confirm whether or not this is a general trend, the ^{13}C spectra of quinoline and isoquinoline were also studied upon the addition of Mn(AA)$_2$.

Experimental

The ^{1}H-decoupled ^{13}C spectra were obtained by an NV-14 spectrometer, NEVA Ltd., Tokyo, operating at 15.1 MHz with a Fourier transform mode. The deuterium signal from the solvent, CDCl$_3$, was used for the heteronuclear lock. The FID signals were accumulated in 8192 data points of a Varian 620 1 computer, and the spectral width was 800 Hz. To obtain reliable values, 16 to 1000 accumulations were made, depending on the line width, the tip angle being about 30°. The sample temperature was maintained at about 28°C by blowing in compressed air. As the chemical shift reference, internal benzene was used for pyridine and quinoline, while external benzene was used for isoquinoline in order to prevent overlapping of the signals. The chemical shift accuracy was within ±0.2 Hz. T_1 was measured by the usual 180°—90° pulse method. The rms errors of the semi-logarithmic plot of $(M_0-M(\tau))/M_0$ *vs.* τ were within 5%.

All the substances were obtained from commercial sources. The materials were used without further purification except for pyridine, which was distilled. The concentrations

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of the $CDCl_3$ solutions were 62, 41, and 41 mole % for pyridine, quinoline, and isoquinoline, respectively. The stock solution of various metal acetylacetonates, $M(AA)_2$, in $CDCl_3$ or in pyridine was added successively by means of a microsyringe to obtain 5 to 7 different concentration of $M(AA)_2$.

Results and Discussion

Effects of Paramagnetic Metals on the ^{13}C Chemical Shift, the Line Width, and the Spin-Lattice Relaxation Time. The chemical shift induced by paramagnetic species in solution, $\Delta\delta_M$, consists of two terms, *i.e.*, the pseudocontact and contact terms.[15]

$$\Delta\delta_M = -\left[f(g)\frac{\beta^2}{kT}\frac{3\cos^2\theta-1}{r^3}+A\frac{\gamma_e}{\gamma_N}\frac{g\beta}{3kT}\right]S(S+1) \qquad (1)$$

where $f(g)$ is the function of g component of the electron spin and other notations have the usual meanings. It has been reported that the pseudocontact term may be negligible for the ^{13}C shift induced by $Ni(AA)_2$ and that the contact term plays the main role.[1-4]

In a solution containing the paramagnetic species, the nuclear spin-lattice relaxation time, T_{1M}, and the nuclear spin-spin relaxation time, T_{2M}, due to the metal are written by [15]

$$\frac{1}{T_{1M}} = \frac{Nn_h}{N_p}S(S+1)\left[\frac{2}{15}\frac{g^2\beta^2\gamma_I^2}{r^6}\left(3\tau_c+\frac{7\tau_c}{1+\omega_s^2\tau_c^2}\right)+\frac{2}{3}\frac{A^2}{\hbar^2}\left(1+\frac{\tau_e}{1+\omega_s^2\tau_e^2}\right)\right] \qquad (2)$$

$$\frac{1}{T_{2M}} = \frac{Nn_h}{N_p}S(S+1)\left[\frac{1}{15}\frac{g^2\beta^2\gamma_I^2}{r^6}\left(7\tau_c+\frac{13\tau_c}{1+\omega_s^2\tau_c^2}\right)+\frac{1}{3}\frac{A^2}{\hbar^2}\left(\tau_e+\frac{\tau_e}{1+\omega_s^2\tau_e^2}\right)\right] \qquad (3)$$

where

$$\frac{1}{\tau_c} = \frac{1}{\tau_r}+\frac{1}{\tau_s}$$

and

$$\frac{1}{\tau_e} = \frac{1}{\tau_h}+\frac{1}{\tau_s}$$

τ_s is the electron spin relaxation time, τ_r is the characteristic time for the tumbling motion of the paramagnetic complex, and τ_h is the chemical exchange time for the ligand molecule between the coordination sphere and the bulk medium. n_h is the number of the ligand molecule in the solvation sphere, N_p is the molar concentration of the ligand molecule, and N is the molar concentration of paramagnetic metals.

The line broadening, $\Delta\nu_M$, induced by the paramagnetic metals is obtained from the difference between the full line width, $\Delta\nu_{obs}$, with the metal and $\Delta\nu_0$ without the metal:

$$\Delta\nu_M = \Delta\nu_{obs} - \Delta\nu_0$$

In a rough approximation, T_{2M} may be obtained from $\Delta\nu_M$ by the following relation:

$$1/T_{2M} = \pi\Delta\nu_M \qquad (4)$$

Equations (2) and (3) show that T_{1M} and T_{2M} are functions of the contact correlation time, τ_e, and the dipolar correlation time, τ_c, and at the same time, they depend upon the magnitude of the isotropic coupling constant, A, and the distance between the metal and the nuclei.

TABLE 1. THE EFFECTS OF VARIOUS METAL ACETYLACETONATES ON THE ^{13}C RESONANCE OF PYRIDINE[a)]

	S		α	β	γ
$Cu(AA_2)$	1/2	$1/T_{1M}(s^{-1})$	0.32	0.13	0.11
		$\Delta\nu_M$(Hz)	0.61	8.0	0.85
		$\Delta\delta_M$(Hz)	0.8	−1.8	0.3_5
$Ni(AA)_2$	1	$1/T_{1M}(s^{-1})$	0.20	0.17	0.04
		$\Delta\nu_M$(Hz)	0.30	1.75	0.08
		$\Delta\delta_M$(Hz)	1.4	−3.9	0.7
$Co(AA)_2$	2/3	$1/T_{1M}(s^{-1})$	0.018	0.012	0.008
		$\Delta\nu_M$(Hz)	0.032	0.032	0.013
		$\Delta\delta_M$(Hz)	1.6	−1.8	0.5
$Mn(AA)_2$	5/2	$1/T_{1M}(s^{-1})$	0.06	0.02	0.006
		$\Delta\nu_M$(Hz)	0.25	0.18	0.03
		$\Delta\delta_M$(Hz)	−1.1	−1.1	-0.3_5

a) These values are obtained from the linear plots of the parameters *vs.* the metal concentration at 5×10^{-3} M and normalized by $S(S+1)$.

In this paper, $\Delta\delta_M$, T_{1M}, and $\Delta\nu_M$ of the ^{13}C NMR spectra are measured in order to observe the influences of the four paramagnetic metals and to discuss the different effects according to Eqs. (1) to (4).

Interactions between Pyridine and $Ni(AA)_2$, $Co(AA)_2$, $Cu(AA)_2$, and $Mn(AA)_2$. To observe the paramagnetic effects due to $M(AA)_2$ (M=Ni, Co, Cu, and Mn) on the ^{13}C spectra, a pyridine solution was used with $M(AA)_2$ added successively. In Table 1 the values observed for $\Delta\delta_M$, $\Delta\nu_M$, and T_{1M} of each carbon of pyridine due to the four kinds of $M(AA)_2$ are summarized. These values are obtained from the plots of these parameters *vs.* the concentrations of $M(AA)_2$ at the point of 5×10^{-3} M, the mole ratio of pyridine to $M(AA)_2$ being approximately 1500 : 1. All the parameters, P_M, are calculated by means of

$$P_M = (P_{M\text{obs}}-P_0)\frac{1}{S(S+1)}$$

where $P_{M\text{obs}}$ and P_0 are the values with and without paramagnetic metals, and S is the electron-spin quantum number for each metal. In order to discuss the nature of the metal–pyridine interaction, all the parameters due to the presence of the metal must be normalized by $S(S+1)$, as is indicated by Eqs. (1) to (3).

Figure 1 shows the effects of various amounts of $M(AA)_2$ on the induced ^{13}C shifts of pyridine in $CDCl_3$, where the $\Delta\delta_M$'s are not normalized by $S(S+1)$. When the metals are Ni and Co, the $\Delta\delta_M$ values show a similar trend, *i.e.*, an increased concentration of the metals brings a larger shift. The singals of α and γ-carbons move to the higher field and that of β-carbons moves to the lower field, and the absolute magnitudes of $\Delta\delta_M$ are ordered as: $|\Delta\delta_M(\beta)|>|\Delta\delta_M(\alpha)|>|\Delta\delta_M(\gamma)|$. This trend was interpreted for the $Ni(AA)_2$–pyridine system in terms of the electron-spin densities on the carbon orbitals by Morishima and his co-workers.[1]

When $Cu(AA)_2$ was added to the pyridine solution (Figure 1(C)), each carbon signal behaves in a different manner from those of the $Ni(AA)_2$ and $Co(AA)_2$ systems, and the magnitudes of $\Delta\delta_M$ are rather small and not

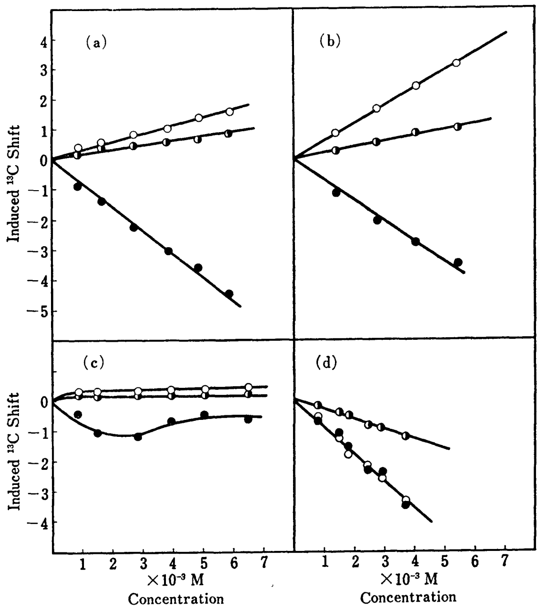


Fig. 1. The linear plots of the induced ^{13}C shifts for α(○), β(●), and γ(◑)-carbons of pyridine *vs.* the concentration of (a) $Ni(AA)_2$, (b) $Co(AA)_2$, (c) $Cu(AA)_2$, and (d) $Mn(AA)_2$.

linear to the concentration of $Cu(AA)_2$. However, the direction of the induced ^{13}C shifts for each carbon upon the addition of $Cu(AA)_2$ shows a trend similar to that in the addition of $Ni(AA)_2$ or $Co(AA)_2$.

The line broadening due to $Ni(AA)_2$, $Co(AA)_2$, and $Cu(AA)_2$ for each carbon resonance of pyridine arises in the same order as the magnitude of $\Delta\delta_M$, *i.e.*, $\Delta\nu_M(\beta) > \Delta\nu_M(\alpha) > \Delta\nu_M(\gamma)$. However, when $Cu(AA)_2$ was added, the line width of the β-carbon of pyridine was broadened to a large extent. It is known that $Cu(AA)_2$ takes a dimer structure in a pyridine solution; the non-linearity of $\Delta\delta_M$ *vs.* the concentration of $Cu(AA)_2$ and the particularly large line broadening of the β-carbon resonance line may be related to this fact.

Surprisingly, upon the addition of $Mn(AA)_2$ the carbon signals behave in a very different way, as is shown in Fig. 1(d); all the carbon signals move to a lower field, and the magnitudes of $\Delta\delta_M$ are ordered as: $|\Delta\delta_M(\alpha)| > |\Delta\delta_M(\beta)| > |\Delta\delta_M(\gamma)|$. The line broadening, $\Delta\nu_M$, due to $Mn(AA)_2$ occurs in the same way as the magnitude of $\Delta\delta_M$. This remarkable differences in the $\Delta\delta_M$ and $\Delta\nu_M$ may imply different mechanisms of the interactions between the metal and pyridine in the case of $Mn(AA)_2$.

To make clearer the pyridine–metal interaction mechanism, the T_{1M} values were measured; the results are shown in Table 1. The magnitude of $1/T_{1M}$ decreases in the order of the α, β, and γ-carbons of pyridine for all the $M(AA)_2$ systems, which suggests that $1/T_{1M}$ is mainly governed by the distance between the metal and each carbon of pyridine. Equation (2) shows that both the dipolar and scalar terms contribute to $1/T_{1M}$, but in this case the dipolar contribution is considered to be predominant, since this term is a function of $1/r^6$.

It is clear from Eq. (2) that, if $\omega_s\tau_e \gg 1$, the scalar term can be neglected. At the field of 15 MHz of the carbon resonance, the electron-spin resonance frequency, $\omega_s \approx 2.4\times10^{10}\,s^{-1}$,[16] and τ_s is known to be 3×10^{-9} and $4\sim7\times10^{-10}$ s for Mn^{2+} and Cu^{2+} respectively;[17] therefore, $\omega_s\tau_e \gg 1$ is valid for these two $M(AA)_2$ systems, and the scalar contribution to $1/T_{1M}$ can be neglected.

The τ_s of Co^{2+} is known to be rather short,[17] so that τ_e and τ_c are considered to be short also. The small values of $1/T_{1M}$ and $\Delta\nu_M$ upon the addition of $Co(AA)_2$ (see Table 1) may be due to the short correlation times. Here, the main mechanism for the spin-lattic relaxation is thought to be also a dipolar interaction.

For the system containing $Ni(AA)_2$, it is not obvious that the contribution of the scalar term to $1/T_{1M}$ of each carbon is negligible, although the $1/T_{1M}$ of the α-carbon is larger than that of the β-carbons. The ratio of the $1/T_{1M}$ of the α to the β-carbons in the $Ni(AA)_2$ system is a little smaller (1.2 : 1) than the other $M(AA)_2$ systems (about 3 : 1). However, the discussion of the $\Delta\delta_M$ values has indicated $|A_{\alpha\text{-carbon}}| < |A_{\beta\text{-carbon}}|$, and a remarkable line broadening is observed at the β-carbon resonance, but not at the α-carbon resonance. Therefore, as far as $1/T_{1M}(\alpha)$ is concerned, the contribution of the contact term may also be small and negligible in this system.

As has been discussed above, the values of the $1/T_{1M}$ of the α-carbons of pyridine containing these $M(AA)_2$ may be determined by the dipolar term. Actually assuming the distance between the metal and nitrogen atom of pyridine to be 3 Å, and using the observed values of $1/T_{1M}$ and Eq. (2), the τ_c values are calculated to be 4, 2.5, 0.76, and 0.23×10^{-11} s for the Cu-, Ni-, Mn-, and $Co(AA)_2$-pyridine complexes respectively. From these values, $\omega_s\tau_c \ll 1$ is shown to hold; therefore,

$$\frac{1}{T_{1M}} = \frac{Nn_h}{N_p} S(S+1) \frac{4}{5} \frac{g^2\beta^2\gamma_I{}^2}{r^6} \tau_c \tag{5}$$

The stability constants of metal-pyridine systems have been obtained by various methods.[18] Although the stability constants for the $M(AA)_2$–pyridine systems in $CDCl_3$ solution are not known, the order of the stability of the complexes of $M(AA)_2$ may be estimated to be Cu>Ni>Mn>Co from similar systems. This order agrees with that of the $1/T_{1M}$ values of the α-carbons in Table 1, and at the same time with the τ_c value of each $M(AA)_2$–pyridine complex. Since the τ_c is a measure of the duration time for the dipolar coupling between the ligand and the paramagnetic metal, it is reasonable that the stability constants of the complexes are proportional to τ_c. Therefore, T_1 measurement is shown to give useful information about the stability constants of paramagnetic metal–ligand complexes.

Unlike the mechanism of the spin-lattice relaxation due to the paramagnetic metals, both the scalar and the dipolar relaxation mechanisms are effective in the spin-spin relaxation, as is shown in Eq. (3), even if the two assumptions $\omega_s\tau_c \ll 1$ and $\omega_s\tau_e \gg 1$ (in the case of Cu and Mn), or $\omega_s\tau_e \ll 1$ (in the case of Co), are used. From equation (4), $\Delta\nu_M$ may be used as a measure of $1/T_{2M}$. In the system containing $Cu(AA)_2$ and $Ni(AA)_2$, the values of $1/T_{2M}$ as well as $\Delta\delta_M$ of the β-carbons are the largest, indicating that the scalar coupling is one of the most important mechanisms of the spin-spin relaxation. However, in the $Mn(AA)_2$–pyridine system, the $\Delta\nu_M$ values of the β-carbons are not the largest and takes place in the order of α, β, and γ-carbons, the same as the absolute magnitude of $\Delta\delta_M$. The different trends in both the $\Delta\delta_M$ and $\Delta\nu_M$ values of pyridine containing $Mn(AA)_2$ from the other $M(AA)_2$ suggest that the interaction between pyridine and $Mn(AA)_2$ seems to be quite different from the other metal systems.

Since pyridine is soluble in water, the ^{13}C spectra were observed for aqueous pyridine solutions containing the divalent metal ions. To D_2O solution of pyridine, Ni^{2+}, Co^{2+}, Cu^{2+}, or Mn^{2+} was added. The $\Delta\delta_M$ and $\Delta\nu_M$ due to these ions showed trends similar to those in the systems of pyridine–$CDCl_3$ solutions containing the corresponding $M(AA)_2$. In the D_2O system also, Mn^{2+} brings all the ^{13}C signals to a lower field, and the absolute magnitudes of $\Delta\delta_M$ are in the order of $|\Delta\delta_M(\alpha)|>|\Delta\delta_M(\beta)|>|\Delta\delta_M(\gamma)|$ and $\Delta\nu_M$ arises in the same way, *i.e.*, $|\Delta\nu_M(\alpha)|>|\Delta\nu_M(\beta)|>|\Delta\nu_M(\gamma)|$, while the paramagnetic effects due to the other ions are the largest in the β-carbon resonance line in both the induced shift and the line broadening.

Since the same trends are observed in $CDCl_3$ and the aqueous solutions containing Mn, the origin of the characteristic effects on the ^{13}C resonance due to Mn may come from the nature of the Mn–nitrogen bond. Thus, we extended our work to the systems of quinoline and isoquinoline interacting with $Mn(AA)_2$ in $CDCl_3$, in order to observe the paramagnetic effects on the ^{13}C resonance lines of nine carbons of these compounds.

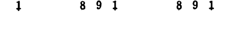
The Interactions of Quinoline and Isoquinoline with Mn-$(AA)_2$. When $Mn(AA)_2$ is added to quinoline or isoquinoline in $CDCl_3$ solutions, the $\Delta\delta_M$, $\Delta\nu_M$, and $1/T_{1M}$ of each carbon resonance increase linearly as the concentration of the metal increases, just as in the pyridine–$CDCl_3$ solution. Table 2 shows the effects of $Mn(AA)_2$ on the ^{13}C resonance parameters of pyridine, quinoline, and isoquinoline. These values were obtained from the slopes of the linear plots of the observed parameters *vs.* the concentration of $Mn(AA)_2$, and were calculated as the values relative to the corresponding parameters of a particular carbon of the γ-position to the nitrogen atom, *i.e.*, C-4 of pyridine and quinoline and C-10 of isoquinoline, which are set at unity. In the systems of quinoline and isoquinoline, the effect of $Mn(AA)_2$ on T_{1M} decreases in magnitude according to α, β, γ, $\cdots$ carbons, which is the same trend as that observed in the system of pyridine containing $Mn(AA)_2$ discussed above. All the $\Delta\delta_M$ values of quinoline and isoquinoline as well as those of pyridine due to $Mn(AA)_2$ shift to a lower field, and their magnitudes decrease in the order of the α, β, γ, $\cdots$ carbons. The $\Delta\nu_M$ value also shows the same trend, quite unlike the systems containing other $M(AA)_2$.

The facts described above suggest that the magnitudes of the paramagnetic effects on the ^{13}C resonance induced by $Mn(AA)_2$ mainly depend upon the distance between Mn and the carbon atoms. Equation (5) indicates that $1/T_{1M}$ is proportional to $1/r^6$; if the scalar interaction were neglected, $\Delta\delta_M$ and $1/T_{2M}$ would also become only a function of the geometric factor, as shown in Eqs. (1) and (3). Actually, the values of $1/T_{1M}$ and $\Delta\nu_M$ are plotted against $1/r^6$, together with the plot of $\Delta\delta_M$ against $(1-3\cos^2\theta)/r^3$, in Fig. 2. The molecular structures of quinoline and isoquinoline were assumed from those of pyridine and benzene. The metal–nitrogen distances in the crystal structures of the pyridine complexes have been reported to range from 2.0 to 2.3 Å,[19] but in solutions it is considered to become larger. Furthermore, the distance in a solution is assumed to be the averaged distance when the ligand molecule exchanges in the coordination sphere and in the bulk medium. The best fit of $1/T_{1M}$ as a function of $1/r^6$ was obtained for the metal–N distances at 3.3, 3.4, and 2.8 Å in pyridine, quinoline, and isoquinoline respectively. However, when the experimental errors are considered, it may be adequate to estimate 3 Å as

Table 2. The effects of $Mn(AA)_2$ on the ^{13}C spectra of pyridine, quinoline, and isoquinoline[a)]

Pyridine	α(2,6)-positions		β(3,5)-positions		γ(4)-position				
$1/T_{1M}$	10.0		2.3		1.0				
$\Delta\delta_M$[b)]	3.7		3.7		1.0				
$\Delta\nu_M$	7.9		5.9		1.0				
Quinoline	α-positions		β-positions			γ-positions			δ-position
	2	9	8	3	10	4	5	7	6
$1/T_{1M}$	9.4	7.7	5.5	2.0	1.9	1.0	0.9	1.2	1.2
$\Delta\delta_M$[b)]	1.9	1.8	1.4	1.3	1.1	1.0	1.1	0.6	0.0
$\Delta\nu_M$	11.3	12.7	6.7	3.3	2.7	1.0	0.0	0.6	0.0
Isoquinoline	α-positions		β-positions		γ-positions		δ-positions		ε-position
	1	3	4	9	10	8	7	5	6
$1/T_{1M}$	11.8	13.1	2.0	2.4	1.0	0.5	0.5	0.4	0.4
$\Delta\delta_M$[b)]	2.9	2.2	2.0	2.0	1.0	1.0	0.5	0.0	0.8
$\Delta\nu_M$	18.1	11.9	6.4	5.9	1.0	0.9	0.0	0.0	0.0

a) These values are obtained from the slopes of the linear plots of the parameters *vs.* $Mn(AA)_2$ concentration and normalized to those of C_4-carbon of pyridine and quinoline, and C_{10}-carbon of isoquinoline, which are set to unity. b) All the induced ^{13}C chemical shifts move to the lower field.



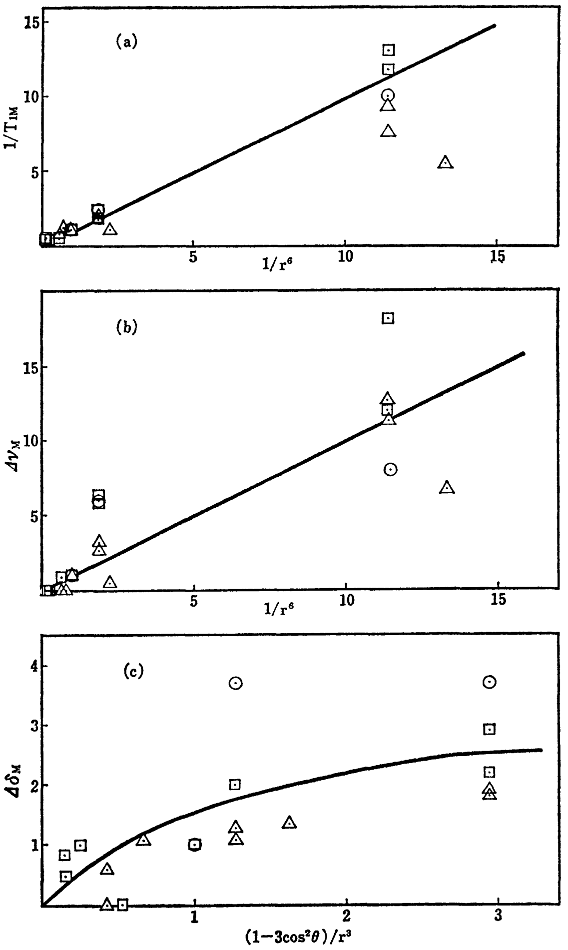


Fig. 2. The plots of (a) $1/T_{1M}$ and (b) $\Delta\nu_M$ against $1/r^6$, and (c) $\Delta\delta_M$ against $(1-3\cos^2\theta)/r^3$, where r is the distance between Mn and each carbon of pyridine (⊙), quinoline (◬), and isoquinoline (⊡). All the values including the geometric factors are referred to C_4 of pyridine and quinoline, and C_{10} of isoquinoline.

the approximate averaged metal–N distance for these compounds; this value is used in Fig. 2. Since the parameter values relative to a particular γ-carbon resonance are used, the geometric parameters are also normalized to the same carbon. In other words, both the ^{13}C resonance parameters and the geometric values of the γ-carbon are set at unity.

As is shown in Fig. 2, although the linearity is not very good, there are apparent correlations between $1/T_{1M}$ and $1/T_{2M}$ and $1/r^6$, and between $\Delta\delta_M$ and $(1-3\cos^2\theta)/r^3$. This indicates that the ^{13}C resonance parameters induced by $Mn(AA)_2$ are mainly governed by the geometric factors. The scalar interaction is very small, and its extent may be the order of the deviation from the observed correlation between the induced parameters and the geometric factors. This conclusion seems a little surprising when we consider the results of the many studies of the interactions between $Ni(AA)_2$ and various N-heterocyclic compounds,[1–4] which clearly show that the induced ^{13}C shift can be interpreted in terms of the scalar interaction, with the complete neglect of the dipolar term.

The lanthanide shift reagents are also paramagnetic and induce large pseudocontact shifts without any significant line broadening in most cases. The unpaired electrons of the lanthanide metals, which induce the paramagnetic shift, occupy the inner shell. This may be one of the most important reasons why the contact term is negligible.[5]

On the other hand, Mn is a d-transition metal such as Cu, Co, and Ni; therefore we can expect that the paramagnetic effects on the NMR parameters would be induced in a similar way by these metals. However, the present study indicates that the contact interaction is very small in the manganese complexes in the ^{13}C resonance, quite unlike the cases of Cu, Co, and Ni complexes, where the contact interaction is predominant. The negligible contact interaction in the ^{13}C resonance of Mn complexes implies that the unpaired electron spin density does not exist on the carbon atoms of the ligand molecules. From the discussion of $1/T_{1M}$ and $1/T_{2M}$, the Mn metal approaches the nitrogen atom of the ligand molecule and forms the Mn–N bond, which persists for the duration of the dipolar correlation time. In that period the unpaired electron from Mn does not transfer into the ligand molecule through the Mn–N bond. It is not certain why the Mn-complexes are different from other paramagnetic metal complexes, but the difference is evident in the ^{13}C NMR spectra shown in the present study.

This fact is very valuable for the studies of metal binding in biological systems. When a manganous ion is added to an aqueous solution in biological systems, the effects of the paramagnetism on the ^{13}C NMR will appear in the chemical shift, the line width as well as the spin-lattice relaxation time, and their magnitudes will depend upon the distance between the carbon atom and the Mn metal. In other words, Mn is a very useful paramagnetic metal for studying the binding site, and in a favorable case, the averaged distance between the metal and the molecule under study may be estimated.

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