NMR Spectra and Magnetic Exchange Interactions in Nickel(II) Complexes with a Chelated Nitronyl Nitroxide Radical

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^{1}H or ^{2}H NMR contact shifts of the β-diketonate methine in the radical complexes [Ni(β-diketonato)$_2$(NIT2-py)] and [Ni(β-diketonato)(tmen)(NIT2-py)]$^+$ (NIT2-py = 2-(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-3-oxide-1-oxyl and tmen = $N,N,N′,N′$-tetramethylethylenediamine) were found to correlate to a product of the respective ^{1}H or ^{2}H NMR contact shifts of the methine in the nonradical complexes [Ni(β-diketonato)$_2$(tmen)] and the fractional contribution to the Ni(II) moiety arising from the magnetic interaction between nickel(II) ion and NIT2-py radical, proposing a new method to estimate the exchange coupling constant J value from the NMR contact shifts. Variable temperature ^{2}H NMR measurements of the C−D signals in [Ni(acac-d)$_2$(NIT2-py)], [Ni-(acac-d)(tmen)(NIT2-py)]$^+$, and [Ni(acac-d)$_2$(tmen)] suggested the topological discrimination of the acetylacetonates.

Introduction

For more than three decades, much attention has been paid to magnetic resonance spectra in the multispin coupled systems by physical and biochemical chemists.[1-15] Among this, a number of studies on EPR spectra in multispin systems for paramagnetic transition-metal ions with organic radicals[1] or polynuclear structures[2] has been extensively reported. In contrast, though a vast number of NMR investigations for such binuclear paramagnetic metal complexes have been carried out, paramagnetic metal complexes with radical ligands have been studied mainly with limited interests in the coordination effect on the radical ligands concomitant with metal ions.[8-15] During the last two decades, to our knowledge, there have been no NMR studies on coligands in radical complexes. The examination of NMR contact shifts in conjunction with magnetic exchange coupling constants is invaluable to acquiring fundamental insights into the ground-state magnetic interactions between paramagnetic metal ions and radical ligands. This is expected

to afford much information through the coligand or substituent effect, e.g., in two series of the β-diketonato nickel(II) complexes which have been recently synthesized and subsequently explored from both magnetic and electronic spectral points of view.[16] For nonradical paramagnetic octahedral nickel(II) complexes, in general, the contact shifts and line broadening of ^{1}H NMR spectra are usually observed,[3] whereas in radical nickel(II) complexes they would be influenced by coupling with the radical spin. Therefore, such shift changes on coordination of radical ligands could be assessed by the theoretical approach applied to NMR contact shifts in a spin-coupled system for binuclear paramagnetic metal complexes where the spin-coupled contact shifts are expressed through the uncoupled contact shifts for each constituent metal ion.[5-7]

In this paper, correlation between ^{1}H and/or ^{2}H NMR contact of the radical nickel(II) complexes and the exchange coupling constant J will be examined to propose a new method to estimate the J value from the NMR spectra. In addition, the topological discrimination of the acac ligands in [Ni(acac)$_2$(NIT2-py)] will be examined by variable-temperature ^{2}H NMR spectroscopy.

Experimental Section

Preparations of β-Diketonato Nickel(II) Complexes. The preparations of [Ni(β-diketonato)$_2$(NIT2-py)] (β-diketonato = acac (2,4-pentanedionato), bzac (1-phenyl-1,3-butanedionato), dbm (1,3-diphenyl-1,3-propanedionato), tfac (1,1,1-trifluoro-2,4-pentanedionato), hfac (1,1,1,5,5,5-hexafluoro-2,4-pentanedion-ato); NIT2-py = 2-(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-3-oxide-1-oxyl (Chart 1)) and [Ni(β-diketonato)-(tmen)(NIT2-py)]PF$_6$ (acac, bzac, dbm, tfac, bztfac (4,4,4-trifluoro-1-phenyl-1,3-butanedionato); tmen = $N,N,N′,N′$-tetramethylethylenediamine) were described in the previous paper.[16]

The nonradical complexes [Ni(β-diketonato)$_2$(tmen)] (acac, bzac, dbm, tfac, hfac) and [Ni(β-diketonato)(NO$_3$)(tmen)] (acac, bzac, dbm, tfac, bztfac) were synthesized according to the literature methods.[17-19]

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Chart 1

NIT2-py

[Ni(β-diketonato)₂(NIT2-py)]

[Ni(β-diketonato)(tmen)(NIT2-py)]⁺
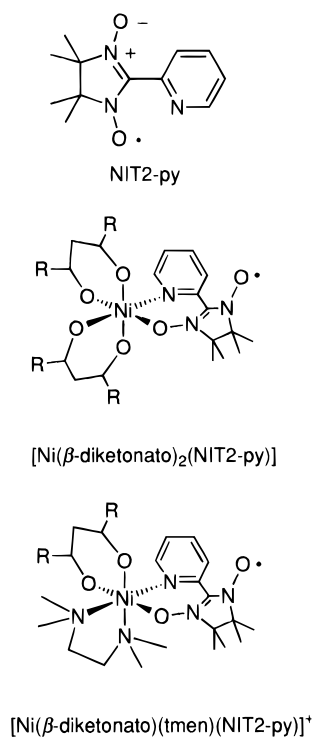
Preparations of Deuterated β-Diketonato Nickel(II) Complexes. Deuteration of β-Diketone. The deuterated β-diketones were prepared according to the modified Egan's method.[20] β-Diketone (0.05 mol) and 2.80 g (0.05 mol) of KOH were dissolved or suspended in 10 mL of 99.9% D_2O, and the mixture was stirred overnight. The white precipitate of potassium β-diketonate-d_n was filtered off and washed with ether. These deuterated ligands were used for the preparations of the radical complexes. Standing overnight, the reaction mixture incorporated detectable amounts of deuterium at the methyl positions of the acetylacetonate, in contrast to the results obtained using the literature method.[20]

[Ni(β-diketonato-d)₂(NIT2-py)] (β-Diketonato-d = acac-d, dbm-d, hfac-d), [Ni(β-diketonato-d)(tmen)(NIT2-py)]PF₆ (acac-d, dbm-d), and [Ni(β-diketonato-d)₂(tmen)] (acac-d, dbm-d, hfac-d). These complexes with the deuterated ligands were prepared according to the methods described elsewhere.[16−19]

Measurements. ¹H NMR spectra were measured on a JEOL JNM-GX270 spectrometer in CDCl₃. The internal standard of TMS was assigned a chemical shift of 0 ppm. ²H NMR spectra were obtained with an internal standard of CDCl₃ (7.2 ppm) on a JEOL JNM-LA500 spectrometer in CHCl₃. The solvents used for the measurement were of spectrograde or reagent grade.

Results and Discussion

General Considerations. ¹H NMR spectra of [Ni(acac)₂-(NIT2-py)] are shown in Figure 1, and the NMR data for [Ni-(β-diketonato)₂(NIT2-py)] and [Ni(β-diketonato)(tmen)(NIT2-py)]⁺ are summarized in Table 1. All the ¹H NMR spectra give isotropic contact shifts with line broadening due to the para-

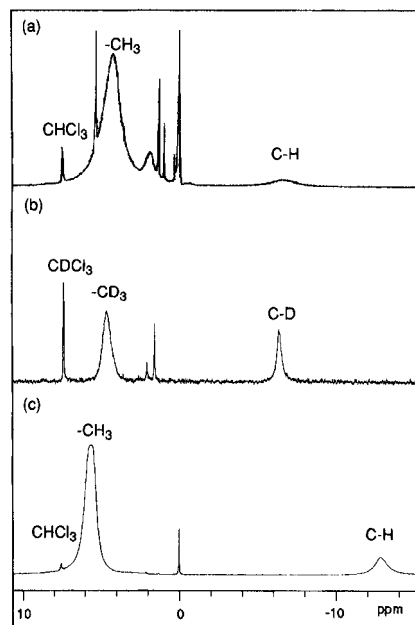(17) Fukuda, Y.; Sone, K. *J. Inorg. Nucl. Chem.* **1972**, *34*, 2315.
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Figure 1. ¹H NMR spectra of [Ni(acac)₂(NIT2-py)] (a) and [Ni(acac)₂-(tmen)] (c) and ²H NMR spectra of [Ni(acac-d)₂(NIT2-py)] (b).

Table 1. ¹H NMR Chemical and Contact Shifts of C−H for [Ni(β-diketonato)₂(NIT2-py)], [Ni(β-diketonato)(tmen)-(NIT2-py)]PF₆, [Ni(β-diketonato)(tmen)], and [Ni(β-diketonato)-(NO₃)(tmen)]PF₆ (270 MHz at 303 K, in CDCl₃) and Exchange Coupling Constants of [Ni(β-diketonato)₂(NIT2-py)] and [Ni(β-diketonato)(tmen)(NIT2-py)]PF₆

compounds	δ/ppm	δ^{con}/ppm	$J^{a,b}$/cm⁻¹
[Ni(acac)₂(NIT2-py)]	−6.74	−9.48	−219.4
[Ni(bzac)₂(NIT2-py)]	−6.15	−10.05	−223.8
[Ni(dbm)₂(NIT2-py)]	−5.80	−10.86	−206.5
[Ni(tfac)₂(NIT2-py)]	−6.24	−8.22	−207.6
[Ni(hfac)₂(NIT2-py)]	−5.38	−6.61	−167^c
[Ni(acac)(tmen)(NIT2-py)]PF₆	−9.85	−12.59	−149.0
[Ni(bzac)(tmen)(NIT2-py)]PF₆	−9.11	−13.01	−110.1
[Ni(dbm)(tmen)(NIT2-py)]PF₆	−9.70	−14.76	−35.5
[Ni(tfac)(tmen)(NIT2-py)]PF₆	−8.60	−10.58	−145.4
[Ni(bztfac)(tmen)(NIT2-py)]PF₆	−8.86	−12.00	−99.8
[Ni(acac)₂(tmen)]	−12.45	−15.19	
[Ni(bzac)₂(tmen)]	−11.81	−15.71	
[Ni(dbm)₂(tmen)]	−11.12	−16.18	
[Ni(tfac)₂(tmen)]	−10.46	−12.44	
[Ni(hfac)₂(tmen)]	−8.69	−9.92	
[Ni(acac)(NO₃)(tmen)]PF₆	−14.71	−17.45	
[Ni(bzac)(NO₃)(tmen)]PF₆	−13.95	−17.85	
[Ni(dbm)(NO₃)(tmen)]PF₆	−13.16	−18.22	
[Ni(tfac)(NO₃)(tmen)]PF₆	−11.79	−13.77	
[Ni(bztfac)(NO₃)(tmen)]PF₆	−11.17	−14.31	

^{a} $H = -2JS_i{\cdot}S_j$. ^{b} Data from ref 16. ^{c} Data from ref 23.

magnetic unpaired electrons in the e_g orbitals of octahedral nickel(II) ion, since the anisotropy of the g values can be neglected due to the orbital nondegeneracy in the $^3A_2$ ground state. The ¹H NMR signals from δ −5.3 to −6.8 for [Ni(β-diketonato)₂(NIT2-py)] are assigned to the 3-methine proton of the β-diketonates by comparison with ¹H NMR of the nonradical acac complexes (Figure 1).[21] This assignment is confirmed by the fact that the methine deuteron chemical shifts of the deuterated β-diketonate for [Ni(β-diketonato-d)₂(NIT2-py)] were observed in the region between δ −5.1 and −6.5. The difference in chemical shifts between the ¹H and ²H NMR spectra is about

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Table 2. ^{2}H NMR Chemical Shifts of C—D for [Ni(β-diketonato-d)$_2$(NIT2-py)], [Ni(β-diketonato-d)(tmen)(NIT2-py)]PF$_6$, and [Ni(β-diketonato-d)$_2$(tmen)] (270 MHz, in CDCl$_3$)

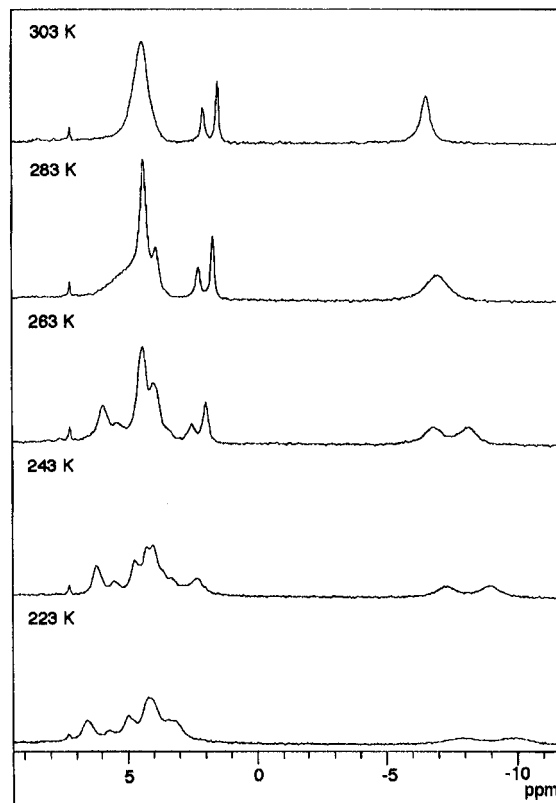|	δ/ppm				
compounds	303 K	283 K	263 K	243 K	223 K
[Ni(acac-d)$_2$(NIT2-py)]	−6.53	−6.93	−6.85	−7.40	−7.99
			−8.19	−8.99	−10.03
[Ni(dbm-d)$_2$(NIT2-py)]	−5.38	−5.52	−5.94	−6.45	−7.53
		−6.04	−6.45	−7.04	
[Ni(hfac-d)$_2$(NIT2-py)]	−5.04	−5.40	−6.01	−6.53	−7.26
[Ni(acac-d)(tmen)(NIT2-py)]PF$_6$	−9.85	−10.39	−11.00	−11.60	−12.40
[Ni(dbm-d)(tmen)(NIT2-py)]PF$_6$	−9.61	−10.16	−10.88	−11.49	−12.14
[Ni(acac-d)$_2$(tmen)]	−12.25	−13.37	−14.69	−16.29	−17.55
[Ni(dbm-d)$_2$(tmen)]	−10.93	−12.07	−13.41	−15.00	−16.63
[Ni(hfac-d)$_2$(tmen)]	−8.63	−9.53	−10.71	−11.98	−13.75

0.2 ppm. Such a lower magnetic field shift on deuteration may be due to an isotope effect. However, since the C—D bond length decreases on deuteration or replacement by the deuteron, the spin density of the deuteron would become larger than that of the proton. This C—D bond-shortening effect may be offset by another factor such as the larger electropositivity for the deuteron as claimed for deuterated acetylacetonato vanadium-(III) complexes.[22]

[Ni(β-diketonato)$_2$(NIT2-py)] has a C_1 symmetry structure with a NIT2-py six-membered chelate as revealed by the X-ray analysis for the hfac complex.[23] Thus, two methine proton signals are predicted for two nonequivalent symmetric β-diketonates, and there could be at most six signals for a mixture of three geometrical isomers of [Ni(β-diketonato)$_2$(NIT2-py)] with asymmetric β-diketonates. However, only one signal of the β-diketonato methine proton was observed. On the other hand, the higher resolution ^{2}H NMR spectra with narrower line widths than that of ^{1}H NMR spectra were obtained as theoretically expected.[24] Nevertheless, the two nonequivalent β-diketonates in [Ni(β-diketonato)$_2$(NIT2-py)] could not be discriminated even by ^{2}H NMR spectra at room temperature. As shown in Figure 2 and Table 2, it is seen that the methine deuteron signal for the acac-d and dbm-d ligands in [Ni(acac-d)$_2$(NIT2-py)] and [Ni(dbm-d)$_2$(NIT2-py)] was split into two signals at 263 and 283 K, but not for the other β-diketonato complexes. Two C—D signals correspond to the nonequivalent acac and dbm methine deuterons as will be examined by the temperature-dependent NMR contact shifts later.

Contact Shifts in Spin Coupled Systems

As shown in Table 1, the C—H contact shifts of the NIT2-py radical complexes lie at the lower magnetic field as compared with those of the corresponding nonradical complexes. The tendency of NMR contact shifts[25] with variation of the β-diketonate ligands in two series of the NIT2-py complexes is similar to that in the nonradical complexes; the C—H contact shifts of β-diketonato ligands were observed in the order of hfac, tfac, acac, bzac, and dbm from the lower magnetic field. However, there is no direct relationship between the C—H contact shifts and the exchange coupling constants J as shown in Table 1. The C—H contact shifts of [Ni(β-diketonato)$_2$(NIT2-py)] are examined by considering both J and the C—H contact shifts of [Ni(β-diketonato)$_2$(tmen)] as follows.

In general, NMR contact shifts in magnetically electron spin-coupled systems are expressed in the following equation (eq

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Figure 2. Variable-temperature ^{2}H NMR spectra of [Ni(acac-d)$_2$(NIT2-py)].

1). Here the spin coupled contact shifts $\delta_i^{con}(T, J)$ are separately expressed in terms of a product of the fractional contributions ($h_i(T, J)$) from each part in paramagnetic moieties (j) and the uncoupled spin density A_j or chemical shifts($\delta_j^{con}(T, 0)$) through

(25) The C—D or C—H contact shifts of the present paramagnetic complexes are determined as the difference of the chemical shifts between the paramagnetic Ni(II) and the diamagnetic chemical shifts obtained from variable temperature ^{2}H NMR measurements and the estimated ones as follows: The C—D chemical shifts of [Ni(acac-d)$_2$(tmen)], [Ni(dbm-d)$_2$(tmen)], and [Ni(hfac-d)$_2$(tmen)] are linearly correlated with the reciprocal of temperature. These intercepts for the linear relations of the temperature dependence are regarded as the chemical shifts of the respective β-diketonato diamagnetic complexes. The diamagnetic chemical shifts of bzac-d and tfac-d complexes are estimated to be an average of the chemical shifts between the acac-d, and dbm-d and between the acac-d and hfac-d ones, respectively, as is also found for the chemical shifts among the diamagnetic palladium-(II) complexes with the respective β-diketonates. (Okeya, S.; Kawaguchi, S.; Matsumoto, K.; Nakamura, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1085.) The diamagnetic chemical shifts of acac, bzac, dbm, tfac, hfac, and bztfac complexes are 2.74, 3.90, 5.06, 1.98, 1.23, and 3.14 ppm.

the theoretical approach employed for the binuclear metal complexes.[5-7]

$$\delta_j^{con}(T, J) = \frac{\Delta\nu}{\nu_o} = \frac{g_e\mu_B}{3h\gamma_N kT} \sum_j A_j C_{ij} S'_i(S'_i + 1) \times$$

$$\frac{(2S'_i + 1)\exp(-E_i/kT)}{\sum_i (2S'_i + 1)\exp(-E_i/kT)} = \sum_j \delta_j^{con}(T, 0)h_j(T, J) \quad (1)$$

The coefficient C_{ij} equals $<S_{jZ}>_{ij}/<S'_Z>_{ij}$ which relates the hyperfine coupling of S_j spin systems in each uncoupled paramagnetic moiety to that in a coupled system for each S'_i level, and the others have the usual meanings. More practical forms for each contribution from paramagnetic centers ($j = 1$ and 2) are given in eqs 2 and 3 where the fractional contributions from coupled paramagnetic origins, Ni(II) ($S_1 = 1$) and NIT2-py ($S_2 = 1/2$), are expressed by functions of the exchange magnetic coupling constant J

$$\delta_1^{con}(T, J) = \delta_1^{con}(T, 0)h_1(T, J) \quad (2)$$

$$\delta_2^{con}(T, J) = \delta_2^{con}(T, 0)h_2(T, J) \quad (3)$$

where

$$h_1(T, J) = \frac{1 + 5\exp(3J/kT)}{2 + 4\exp(3J/kT)} \quad (4)$$

$$h_2(T, J) = \frac{-1 + 10\exp(3J/kT)}{8 + 16\exp(3J/kT)} \quad (5)$$

Here, eqs 2 and 4 are employed, because only the contribution from Ni(II) ion is taken into consideration to compare the contact shifts of the methine proton among the β-diketonato ligands coordinated to Ni(II) ion. Then, these contact shifts $\delta_1^{con}(T, J)$ of the radical complexes are given by $\delta_1^{con}(T, 0) \times h_1(T, J)$ in relation with the exchange coupling constants J, where $\delta_1^{con}(T, 0)$ refers to the contact shifts of nonradical Ni(II) complexes. In the present case, $\delta_1^{con}(T, J)$ and $\delta_1^{con}(T, 0)$ correspond to $\delta^{con}(C-H)$ of [Ni(β-diketonato)$_2$(NIT2-py)] and [Ni(β-diketonato)$_2$(tmen)] or those of [Ni(β-diketonato)(tmen)(NIT2-py)]$^+$ and [Ni(β-diketonato)(NO$_3$)(tmen)], respectively. A plot of the $\delta_1^{con}(T, J)$ against $\delta_1^{con}(T, 0)h_1(T, J)$ at 303.15 K, according to eqs 2 and 4, exhibits a good linear correlation for the mono- and bis(β-diketonato) complexes as shown in Figure 3, leading to the following equations

$$\delta^{con}(303, J) = 0.507 \times \delta^{con}(303, 0)h_1(303, J) + 6.52 \quad (6)$$

$$\delta^{con}(303, J) = 1.28 \times \delta^{con}(303, 0)h_1(303, J) + 1.09 \quad (7)$$

for [Ni(β-diketonato)$_2$(NIT2-py)] and [Ni(β-diketonato)(tmen)-(NIT2-py)]$^+$, respectively. It is seen that the C-H contact shifts of [Ni(β-diketonato)(tmen)(NIT2-py)]$^+$ and [Ni(β-diketonato)$_2$-(NIT2-py)] at room temperature are determined by the contribution from the contact shifts of the nonradical complexes [Ni(β-diketonato)(NO$_3$)(tmen)] and [Ni(β-diketonato)$_2$(tmen)], respectively, and the exchange coupling constant J between a nickel(II) ion and NIT2-py radical. Furthermore, it is found that this relationship is appropriate for the low-temperature case. Since it is difficult to determine the positions of the ^{1}H NMR signals due to line broadening upon lowering temperature, ^{2}H NMR contact shifts[25] with narrower line widths are used for
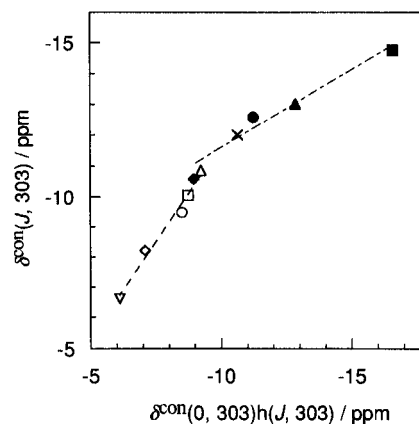

Figure 3. Plots of ^{1}H NMR contact shifts in the form of $\delta^{con}(303, J)$ vs $\delta^{con}(303, 0)h(303, J)$ at 303 K for [Ni(β-diketonato)$_2$(NIT2-py)] (acac (○), bzac (□), dbm (△), tfac (◇), and hfac (▽)) and [Ni(β-diketonato)-(tmen)(NIT2-py)]PF$_6$ (acac (●), bzac (■), dbm (▲), tfac (◆), and bztfac (×)). Lines for [Ni(β-diketonato)$_2$(NIT2-py)] (- - -) and [Ni(β-diketo-nato)(tmen)(NIT2-py)]PF$_6$ (− · −) are the least-squared-fits.

this case. The functions $\delta_1^{con}(T, J)$ and $\delta_1^{con}(T, 0)$ correspond to the contact shifts $\delta^{con}(C-D)$ of [Ni(β-diketonato-d)$_2$(NIT2-py)] and [Ni(β-diketonato-d)$_2$(tmen)], respectively. A plot of the $\delta_1^{con}(T, J)$ against $\delta_1^{con}(T, 0)h_1(T, J)$ at low temperature, according to equations 2 and 4, gives a fairly good linear correlation for the bis complexes as did the room-temperature case.

By using the above relations (eqs 6 and 7), the exchange coupling constant J is estimated through knowledge of the contact shifts of both the radical and nonradical complexes with the identical β-diketonato ligands. This offers an alternative semiempirical means to simply estimate the J value from the NMR measurements only. This is applicable only to these types of complexes thus far, but more advantageous over the elaborate traditional one from variable-temperature magnetic-susceptibility measurements.

Discrimination of the acac Methines in [Ni(acac-d)$_2$(NIT2-py)]. A plot of the C-D contact shifts for the acac complexes against the reciprocal of temperature gives linear lines with negative slopes as shown in Figure 4. These slopes for the linear relations with the temperature dependence are compared on the basis of the following considerations.

The two C-D signals for the acac-d in [Ni(acac-d)$_2$(NIT2-py)] are labeled as C-D$_a$ and C-D$_b$ (Chart 2). These contact shifts $\delta_a^{con}(T, J_a)$ and $\delta_b^{con}(T, J_b)$ of C-D$_a$ and C-D$_b$, respectively, in [Ni(acac-d)$_2$(NIT2-py)] are given according to eq 2 as follows

$$\delta_a^{con}(T, J_a) = \delta_a^{con}(T, 0)h(T, J_1) \quad (8)$$

$$\delta_b^{con}(T, J_b) = \delta_b^{con}(T, 0)h(T, J_2) \quad (9)$$

where $\delta_a^{con}(T,0) = A_a\delta_0^{con}(T,0)$ and $\delta_b^{con}(T,0) = A_b\delta_0^{con}(T, 0)$.

The functions $\delta_a^{con}(T, 0)$ and $\delta_b^{con}(T, 0)$ correspond to the contact shifts for the C-D$_a$ and C-D$_b$ in the hypothetical uncoupled complex with the same chromophore as the NIT2-py complex.

A_a and A_b are coefficients representing the deviations in the spin density of the C-D on going from the bis(acac)tmen complex to the hypothetical one. $\delta_0^{con}(T, 0)$ stands for the C-D contact shifts of nonradical complex [Ni(acac-d)$_2$(tmen)]. The exchange coupling constants J_1 and J_2 are labeled for anticipated

Chart 2

[Ni(β-diketonato-d)₂(NIT2-py)]

[Ni(β-diketonato-d)(tmen)(NIT2-py)]⁺

[Ni(β-diketonato-d)₂(tmen)]
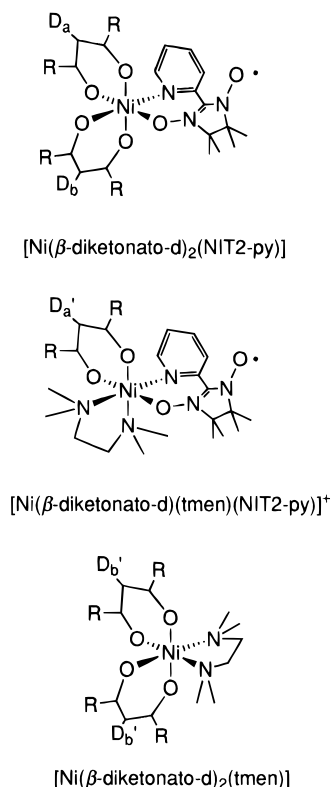
magnetic interactions between two different $e_g(d)$ orbitals and NIT2-py SOMO, of which the difference may lead to distinguishing the C−D$_a$ and C−D$_b$, respectively. The A_a and A_b in the hypothetical uncoupled systems are presumed to be unchanged in the coupled systems, i.e., the difference between A_a and A_b (eq 10 derived from eqs 8 and 9) being constant.

$$A_a - A_b = \frac{1}{\delta_0^{con}(T, 0)} \left(\frac{\delta_a^{con}(T, J_1)}{h(T, J_1)} - \frac{\delta_b^{con}(T, J_2)}{h(T, J_2)} \right) \quad (10)$$

When the contact shifts of the nonradical tmen complex and the NIT2-py complex are substituted together with $h(T, J)$ ($J = J_1 = J_2 = -219.4$ cm⁻¹ from the magnetic-susceptibility measurement[16]) into the right member of eq 10, the obtained values are found not to be constant at different temperatures in disaccordance with the above presumption. Since this suggests that J_1 are not equal to J_2, the contact shifts depend on the differences not only in A_a and A_b but also in exchange coupling between two different $e_g(d)$ orbitals and NIT2-py SOMO.

As shown in Figure 4, one of two lines for that of [Ni(acac-*d*)₂(NIT2-py)] is similar in slope and intercept to that of the radical complex [Ni(acac-*d*)(tmen)(NIT2-py)]⁺, whereas the other is similar to the nonradical complex [Ni(acac-*d*)₂(tmen)]. The former gives gentler slopes in contrast to the steeper slopes for the latter. One of the oxygens of the acetylacetonate in [Ni-(acac-*d*)(tmen)(NIT2-py)]⁺ binds at the trans position of the
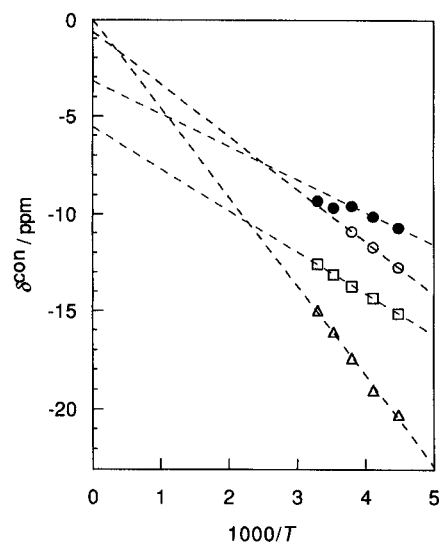

Figure 4. Inverse temperature dependence of ²H NMR for [Ni(acac-*d*)₂(NIT2-py)]; C−D$_a$ (○), C−D$_b$ (●), [Ni(acac-*d*)(tmen)(NIT2-py)]PF₆; C−D$_a$′ (□) and [Ni(acac-*d*)₂(tmen)]; C−D$_b$′ (△). Lines are the least-squared-fits.

NIT2-py N−O group as shown in Chart 2, which was revealed by the X-ray analysis.[16] Therefore, the signal giving a gentler slope for the C−D contact shifts of [Ni(acac-*d*)₂(NIT2-py)] corresponds to the methine deuteron (C−D$_a$) in the acac bound at the trans position of the NIT2-py coordinated oxygen.

It is plausible that the slopes become gentler as a result of the antiferromagnetic interaction with the coordinated NIT2-py. This distinct behavior arises from the difference in the magnetic interactions between NIT2-py and two different e_g orbitals. That is, the NIT2-py coordinated oxygen exerts a larger influence on the C−D$_a$ than on the C−D$_b$, probably in terms of trans influence, implying a topological discrimination of the acac ligands with respect to the disposition of the NIT2-py oxygen ligator.

Conclusions

The C−H contact shifts of the radical complexes [Ni(β-diketonato)₂(NIT2-py)] or [Ni(β-diketonato)(tmen)(NIT2-py)]⁺ are determined by the contribution of the antiferromagnetic interaction between nickel(II) ion and NIT2-py radical as well as the C−H contact shifts of the nonradical β-diketonato complexes. The linear relation affords a new method to estimate the exchange coupling constants from only the NMR contact shifts at room temperature.

From variable-temperature NMR measurements of [Ni(acac-*d*)₂(NIT2-py)], two C−D NMR contact shifts could be topologically discriminated by the different influences from the NIT2-py SOMO.