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Nitrogen-14 Magnetic Resonance Studies of the Exchange of Solvent Pyridine on Bis(β-diketonato)bis(pyridine)nickel(II) and -cobalt(II) Complexes

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The analysis of linewidth and shift data of the nitrogen-14 magnetic resonance gave the following activation parameters for the exchange reaction of pyridine (py) on $CoA_2(py)_2$ (A=acac, tfa, and tta) and $Ni(acac)_2(py)_2$ with a pyridine molecule as bulk solvent: $\Delta H^{\ne}$=41.4, 51.1, 48.3, and 47.2 kJ mol^{-1}, $\Delta S^{\ne}$=18, 17, 3, and 10 JK^{-1} mol^{-1}, and k_1 (298K)=2.9×10^6, 5.3×10^4, 2.9×10^4, and 1.3×10^5 s^{-1}. Here acac=acetylacetonate, tfa=trifluoroacetylacetonate and tta=thenoyltrifluoroacetonate. The electron-withdrawing power of substituent groups on the β-diketonate rings was correlated with more favorable activation of the exchange, that is, the stronger electron withdrawal causes less dissociative activation. This explains qualitatively even the negative $\Delta S^{\ne}$ values observed for similar pyridine exchange in the cases of $Co(hfa)_2(py)_2$ (hfa=hexafluoroacetylacetonate) and $Ni(tta)_2(py)_2$.

Exchange reactions of a coordinated solvent molecule (S) on bis(β-diketonato) complexes of Ni^{II} and Co^{II}(M), represented by Eq. 1, have been kinetically studied by several authors[1—7] using NMR techniques.

$$MA_2S_2 + S^* \longrightarrow MA_2SS^* + S. \tag{1}$$

In most of the cases, the exchange rates were discussed in terms of the nature of β-diketone rings; that is, electron-withdrawing substituents on the rings were shown to be a major factor retarding the exchange and the trend was described quantitatively by the Hammet equation. On the other hand, only a few attempts have been made[4—7] to clarify the reaction mechanism, mainly because observed activation parameters contained rather large uncertainties. The FT-NMR systems enables us to reduce the uncertainties originated from previous instrumental problems and ^{14}N NMR is more favorable; its advantage has already been pointed out.[8] In the present work, we first focus our attention on a series of bis(β-diketonato)cobalt(II) complexes in pyridine solvent, since ^{14}N NMR studies of an analogous series of Ni^{II} were already reported by Lincoln *et al.* using CW wideline spectrometer.[6] Nickel(II) complexes with acac and tta are also examined; the former is considered as a standard complex for comparison to other works. The tta complexes of both Co^{II} and Ni^{II} appear in similar solvent exchange studies.

Experimental

Materials. Anhydrous $M(acac)_2$ and $M(tta)_2$ were prepared by the method of Cotton *et al.*[9] or by a slightly modified version of it. $Co(tfa)_2(py)_2$ and $Co(hfa)_2(py)_2$ were obtained by repeated recrystalization of the corresponding diaqua complexes from pyridine solution. The values of chemical analysis of all products were in good agreement with the theoretical values. Pyridine used as a solvent was dried over pottasium hydroxide for several days and then doubly distilled in the presence of a small amount of suspended barium oxide. Deuterated pyridine was obtained in ampules from CEA France and an ampule was freshly opened just before each use,without any purification.

Solutions for NMR experiments were prepared under a nitrogen atmosphere by dissolution of complexes into pyridine which contained 13 v.% of pyridine-d_5. The concentration range of the paramagnetic ions was 0.01—0.15 mol dm^{-3}; this was quantitatively determined by EDTA titration. The water content of the solutions was found by the GC method[10] to be less than 2ppm, which means the content was negligible.

The electronic absorption spectra of the solution were recorded and the molecular weight measurements were carried out for the preliminary characterization of the solvated complexes in pyridine: a JASCO UVDEC-1 spectrometer and a Corona-117 apparatus for vapor pressure depression method were used.

NMR Measurements. A JEOL FX-90Q FT-NMR spectrometer operated at 6.42 MHz for ^{14}N was used in the ^{2}H lock mode. Typically,the free induction decay(FID) spectrum was accumulated over 1000 to 4000 pulses of 20 μs with a spectral width of 6 kHz. Since a WIND function was applied, linewidths of plotted spectra were necessarily corrected with subtraction by the corresponding broadening factors in Hz. The temperatures(−18—113 °C) were measured by using a copper-constantan thermocouple in a 10ϕ o.d. NMR tube with silicone oil before and after pulsing; while accumulation was being performed, temperature drift was monitored by a thermocouple installed inside JEOL temperature control unit; correspondence between temperature readings from two thermocouples had been investigated before accumulation. The accumulated FID's were used for data analysis only when the temperature deviation during the accumulations had been less than ±0.3 °C.

Results

Relaxation Data. The ^{14}N transverse relaxation time due to the interaction between pyridine solvent and a paramagnetic β-diketonato complex (T_{2p}) is defined as Eq. 2:

$$T_{2p} = (1/T_2 - 1/T_{2A})^{-1} P_m (1 - P_m)^{-1}. \tag{2}$$

Here T_2 is the observed relaxation time of paramagnetic solution and T_{2A} is that of the pure solvent, both derived from the observed half-height widths in Hz, $W(=\pi^{-1}T_2^{-1})$ and $W_A(=\pi^{-1}T_{2A}^{-1})$. P_m is the mole fraction of the solvent in the first coordination sphere, assuming an additional coordination number of 2. The values of it were small enough in the present work to treat $(1-P_m)$ in Eq. 2 as 1. According to Swift and Connick,[11] T_{2p} can be represented in a reduced form as follows:

$$T_{2p}^{-1} = [\tau_m + \{\tau_m(\Delta\omega_m)^2\}^{-1}]^{-1} + (T_2^*)^{-1}. \tag{3}$$

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Here τ_m is the mean lifetime of coordinated pyridine and $\Delta\omega_m$ is the chemical shift in radian/s of ^{14}N of complexed solvent relative to free solvent.

$$\tau_m = h(k_B T)^{-1} \exp\{\Delta H^{\neq}(RT)^{-1} - \Delta S^{\neq}R^{-1}\} \quad (4)$$

$$\Delta\omega_m = (2\pi)^2(A/h)\omega\mu_{eff}\mu_B\{S(S+1)\}^{1/2}T^{-1}(3k_B\gamma_N). \quad (5)$$

Here A/h is the scalar coupling constant, μ_{eff} the effective magnetic moment (3.13 and 4.82 BM for Ni and Co complexes), **S** the net electron spin of the paramagnetic ions, ω the radio frequency(Hz) of operation, k_B the Boltzman constant and γ_N the gyromagnetic ratio of ^{14}N; other symbols have their usual meanings. The first term of Eq. 3 is a reduced form of the full equation of Swift and Connick assuming that $\Delta\omega_m{}^2 \gg T_{2m}{}^{-2}$, $\tau_m{}^{-2}$, in the relatively lower temperature range and that $\tau_m{}^{-2} \gg \Delta\omega_m{}^2 \gg (T_{2m}\tau_m)^{-1}$, in the higher temperature range, where T_{2m} is the relaxation time of ^{14}N in pyridine coordinated to M in the absence of chemical exchange. The former condition was experimentally confirmed by the constant chemical shift of the bulk pyridine peak. The latter was not sure since the pyridine peak was not recognized while coordinated to the paramagnetic ion, even at the lowest temperature, because of the small P_m and the broadening of the line. It seemed reasonable, however, that T_{2m} in pyridine case could be replaced by that in acetonitrile, which had been already found to meet the latter condition.[8] The T_2* term of Eq. 3 is the additional contribution from the outer coordination sphere or the fast exchange region.

The circles in Figs. 1 to 6 are the observed T_{2p}'s and they are shown along with full lines of the computed best fits. The full lines in Figs. 2 and 3 were obtained by use of the SALS (Statistical Analysis with Least-Squares Fittings)[17] program applied to Eq. 3 in which $\Delta H^{\neq}$, $\Delta S^{\neq}$, and A/h were treated as parameters and the T_2* term was ignored. In Figs. 1 and 5, SALS computation was first performed about the temperature range in which the T_2* was negligible. The term was treated as an additional parameter which caused the deviation of the observed points; it affected the first term in brackets at the lowest temperature and/or $\tau_m(\Delta\omega_m)^2$ in the highest temperature range. In Figs. 4 and 6, only the τ_m term in brackets of Eq. 3 was used for the computation. The activation parameters and the A/h values obtained

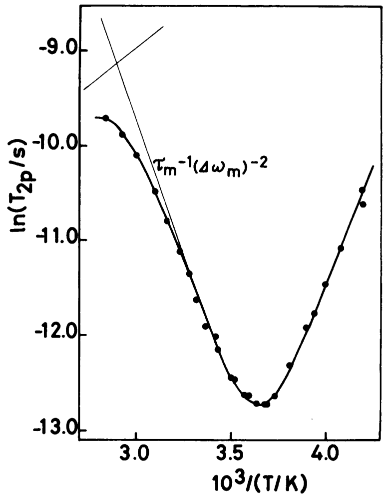

Fig. 1. Temperature dependence of the reduced ^{14}N NMR linewidth(T_{2p}) for the bulk-solvent pyridine resonance in the Co(acac)$_4$(py)$_2$ system.

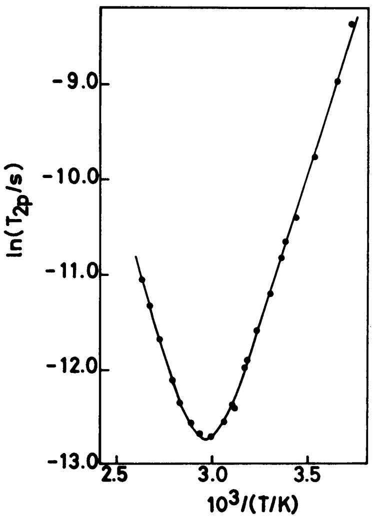

Fig. 2. Temperature dependence of T_{2p} in the Co(tfa)$_2$(py)$_2$ system.

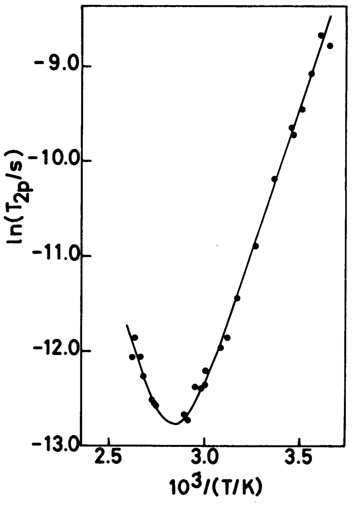

Fig. 3. Temperature dependence of T_{2p} in the Co(tta)$_2$(py)$_2$ system.

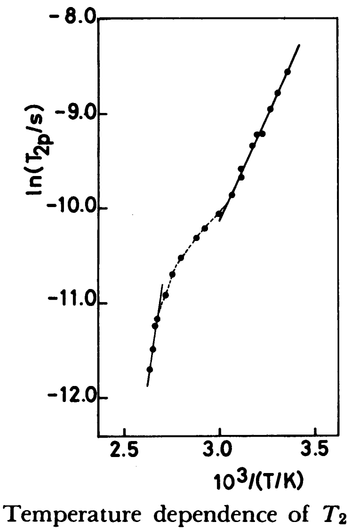

Fig. 4. Temperature dependence of T_{2p} in the Co(hfa)$_2$(py)$_2$ system.

from the computation are summarized in Table 1.

Shift Data. The chemical shift of the paramagnetic solutions is represented also in terms of τ_m, $\Delta\omega_m$, and T_{2m} by Swift and Connick.[11] Assuming the same two conditions as in the case of the T_{2p} data analysis, Eq. 6 can be derived:

$$S_p = (S-S_0)P_m{}^{-1}$$
$$= -(\Delta\omega_m/2\pi)\{1+(\Delta\omega_m\tau_m)^2\}^{-1}. \quad (6)$$

Here S(in Hz) is the observed chemical shift of the paramagnetic solution and S_0(in Hz) is that of the pure solvent. The observed shift data of the present systems are illustrated in Figs. 7 and 8 along with the calculated one(full lines in the Figs.). The latter were obtained from Eq. 6 by using the results of the relaxation data analysis already mentioned. The agreement between them indicated the validity of the relaxation data analysis again. The dashed lines denote cases in which the prediction by Eq. 6 was impossible, since the relaxation data lacked any contribution from the $\tau_m(\Delta\omega_m)^2$ term. (See Figs. 4 and 6.)

It should be noted that A/h values could be also obtained, roughly but absolutely independently from the relaxation data, from the observed S_p values. In the Figs. 7 and 8, the values of S_pT on the ordinate become constant as the temperature approaches the highest values, except in Co(hfa)$_2$(py)$_2$ and Ni(tta)$_2$(py)$_2$ cases. The constant values must be $-\Delta\omega_mT/2\pi$. That is because the $(\Delta\omega_m\tau_m)^2$ term in the Eq. 6 was negligible at temperature high enough for τ_m to be very small. A/h values were, therfore, derived from Eq. 5; they are shown in parentheses in Table 1.

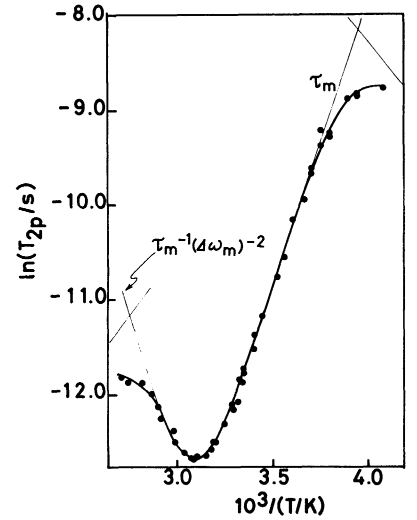

Fig. 5. Temperature dependence of T_{2p} in the Ni(acac)$_2$(py)$_2$ system.

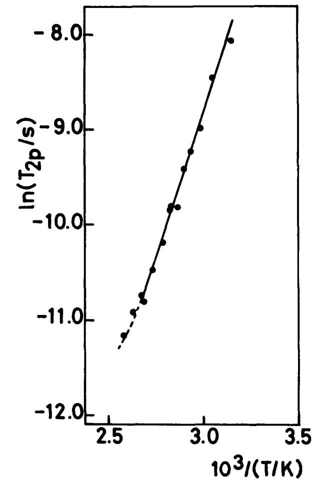

Fig. 6. Temperature dependence of T_{2p} in the Ni(tta)$_2$(py)$_2$ system.

TABLE 1. KINETIC PARAMETERS FOR PYRIDINE EXCHANGE

	$\Delta H^{\ast}$	$\Delta S^{\ast}$	$k_{1,298}$*a	A/h
	kJ mol^{-1}	JK^{-1}mol^{-1}	s^{-1}($\sum\sigma^*$)*b	10^6Hz
Co(acac)$_2$(py)$_2$	41.4(0.5)*c	17.7(2.1)*c	2.9X10^6(0)	6.7(6.9)*d
Co(tfa)$_2$(py)$_2$	51.1(0.6)	16.9(1.9)	5.3X10^4(2.75)	8.2(7.9)
Co(tta)$_2$(py)$_2$	48.3(0.8)	2.6(2.7)	2.9X10^4(3.55)	9.0(9)
Co(hfa)$_2$(py)$_2$	33.8(3.0)	−60.1(9.7)	5.4X10^3(5.50)	[~7]*e
Ni(acac)$_2$(py)$_2$	47.2(0.8)	10.3(2.5)	1.3X10^5(0)	18(18)
Ni(tta)$_2$(py)$_2$	48.6(1.4)	−27.4(3.9)	7.1X10^2(3.55)	[~11]

*a: Defined as $\tau_m{}^{-1}$ at 298K and evaluated from $\Delta H^{\ast}$ and $\Delta S^{\ast}$ results. *b: Sum of Taft parameters. *c: Standard deviation. *d: Values in parenthses from shift data. *e: Values in brackets are estimated(see text).

TABLE 2. ABSORPTION SPECTRA OF PYRIDINE SOLUTION OF COMPLEXES: λ_{max} IN cm^{-1} WITH ε IN mol^{-1}cm^{-1} IN PARENTHESES

	$^4T_{2g}\leftarrow{}^4T_{1g}$	$^4A_{2g}\leftarrow{}^4T_{1g}$	$^4T_{1g}(P)\leftarrow{}^4T_{1g}$	
Co(acac)$_2$(py)$_2$*	9730(6.06)	18420(18.63)	19800(26.24)	20880(33.84)
Co(tfa)$_2$(py)$_2$	9600(5.48)	18520(23.51)	19760(36.87)	21370(43.84)
Co(tta)$_2$(py)$_2$	9600(10.54)	18400(70.66)	**	
Co(hfa)$_2$(py)$_2$	9380(6.50)	**	**	
	$^3T_{2g}\leftarrow{}^3A_{2g}$	$^1E_g\leftarrow{}^3A_{2g}$	$^3T_{1g}\leftarrow{}^3A_{2g}$	
Ni(acac)$_2$(py)$_2$	10000(7.30)	12990(1.45)	16900(8.17)	
	9750(6.8)	13100(v.w.)	16650(8.0)***	
Ni(tta)$_2$(py)$_2$	10000(9.78)	12950(1.97)	16890(17.25)	

* The crystal shows isomorphism with Ni(acac)$_2$(py)$_2$ (Ref. 12). ** Overlapped by intense UV absorption. *** Ref. 12.

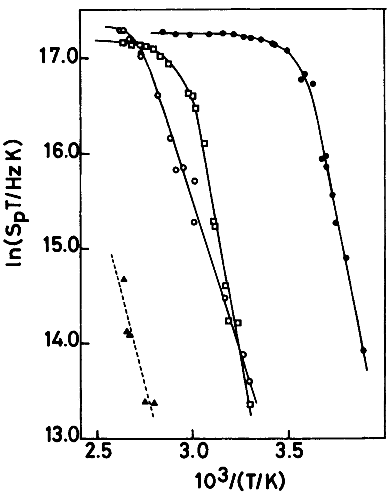

Fig. 7. Temperature dependence of the shift for the pyridine solutions containing Co(II) complexes.

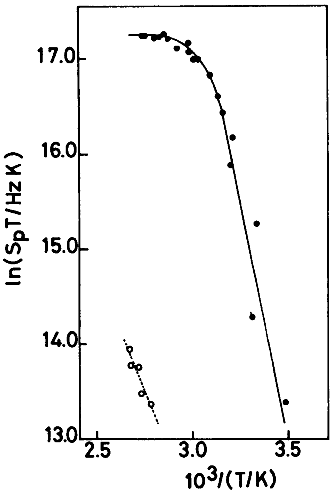

Fig. 8. Temperature dependence of the shift for the pyridine solutions of Ni(II) complexes.

In the case of either $Co(hfa)_2(py)_2$ or $Ni(tta)_2(py)_2$, A/h was only estimated from the observed S_p and the τ_m value derived from the relaxation data, by the use of Eq. 6. The results are shown in brackets in Table 1.

Discussion

Table 1 reveals that the pyridine exchange is retarded by electron-withdrawing substituents of chelate rings, which can be described by the Hammett equation:[1] $\log(k/k_0)=\rho\sigma$, where σ is the sum of the Taft σ^* parameters for the substituents of β-diketons. The trend is consistent with other authors' observations.[1,2,6] The σ^* values of tta was obtained by interpolation of the present observations, resulting in the value of 0.9 for σ^* of thienyl group. This seems quite suitable,in comparison with the value of 0.6 of the phenyl group.

The $\Delta S^{\neq}$ values listed in Table 1 suggest that, among a series of β-diketonato complexes of the metals, the electron-withdrawing power of the substituents have an effect also on the activation mechanism of the pyridine exchange. The stronger electron withdrawal causes the lower electron density within a chelate ring and the larger effective oxidation number of a central metal. It is reasonable in an activated state that the central metal with a larger effective oxidation number would interact with both leaving and entering pyridine molecules to form virtually two bonds. This case might be called an "associatively" activated mechanism. When the effective oxidation number is much smaller, the interaction between the central metal and any leaving or entering solvent is weak enough to lead all the present complexes, except $Co(hfa)_2(py)_2$ and $Ni(tta)_2(py)_2$, to dissociative activation. It should be noted here that actual activated states cannot be clearly visualized as either associative(ly) or dissociative. There might be possibilities of β-diketonates as unidentate ligands at an activated state and/or of a *trans-cis* equiliblium with their mutual conversion. A straight comparison, therefore, between the cases of simply solvated ions by six solvent molecules[13,14] and the present case is of little significance.

Taking into account the fact that the $\Delta H^{\neq}$ values reflect the crystal field theory activation energies (C.F.A.E),[15,16] the $\Delta H^{\neq}$ values in Table 1 support partly the trend of the activation mechanism already suggested by the $\Delta S^{\neq}$ values. The smaller effective oxidation number of a central ion causes the smaller C.F.A.E., assuming a dissociatively activated state. Assuming an associatively activated one, the circumstances are exactly the reverse. (The smaller C.F.A.E. must be the reflection of either the easier bond rupture or the more difficult bond formation.) In the actual series of Co complexes, the acac complex has a smaller $\Delta H^{\neq}$ compare to the tfa analogue, which has a larger effective oxidation number. This behavior is consistent with their dissociative activations predicted by $\Delta S^{\neq}$ values. That the $\Delta H^{\neq}$ value of the hfa analogue is smaller than the tta one can be explained as follows: The activation mechanism of the former complex is associative and that of the latter has a transient feature. They are consistent with what the $\Delta S^{\neq}$ values suggested. Furthermore, the differences in the $\Delta H^{\neq}$ values between $Co(acac)_2(py)_2$ and the Ni analogue and between $Co(tta)_2(py)_2$ and its Ni analogue are roughly parallel to C.F.A.E. calculated by Basolo and Pearson,[15] assuming a trigonal bipyramidal five coordinate and an octahedral wedge seven coordinate transition state.

Since it proved significant that solvent molecules interact with the effective charge of a central metal ion, not only the nature of the ligand but also the basicity of the solvents should be one of the alternate factors to predict the nature of activation. Trimethyl phosphate seems suitable as a solvent with small basicity and enough affinity to solvate to bis(β-diketonato) complexes in the present work. In any case, even a strong electron-withdrawing substituent induces an effective charge on a central ion which is not large enough to cause "associative" activation. A precise report will be submitted soon.

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