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NMR Studies of the Pyridine Exchange Reaction in the Pyridine Adduct of Bis(salicylaldehydato)nickel(II)

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Synopsis. The pyridine exchange reaction in the pyridine adduct of bis(salicylaldehydato)nickel(II) becomes appreciably slower and its activation energy increases with the decrease of the electron donor properties of the in-plane ligand. However, changes in the spin delocalization onto the coordinated pyridine by the in-plane ligand appear small.

Spin delocalization onto bases interacting with bis(acetylacetonato)nickel(II), Ni(acac)$_2$, has been one of the subjects investigated in great detail through isotropic paramagnetic shifts in NMR.[1] In this system the spin distributions in the bases are directly evaluated from the observed isotropic shifts, since the pseudocontact interaction is negligible and the exchange reaction of the bases which coordinate to Ni(acac)$_2$ is in the limit of the fast exchange rate region. However, whether or not the exchange reaction is in the fast rate region seems to have a critical dependence on the ligands already bound to the nickel. We observed that when bis(salicylaldehydato)nickel(II), Ni(sal)$_2$, is used in place of Ni(acac)$_2$, the relative ratio of contact shifts for the α, β, and γ protons in pyridine appreciably differs from that in the Ni(acac)$_2$ system. This deviation becomes much larger when the nitro derivative of salicylaldehydate ion is used as an in-plane ligand.[2] As is shown later, these changes can be related to the fact that the pyridine exchange reactions in Ni(sal)$_2$ and its derivatives are not in the fast exchange rate region at the measurement temperature, and the observed shifts are not exactly the weighted average between the free and associated forms of pyridine. The main purpose of this note is to show how the exchange reaction of pyridine at the apical position in six-coordinated nickel complexes is affected by the in-plane ligands already bound to the nickel.

Experimental

The nickel(II) complexes used were those with salicylaldehyde and its 5-methyl, 5-chloro, 5-bromo, and 5-nitro derivatives [Ni(sal)$_2$ and Ni(5X-sal)$_2$, X=Me, Cl, Br, and NO$_2$]. These complexes were dried at 110°C *in vacuo* before use. NMR spectra of the bulk solvent protons in pyridine solutions of these complexes were measured with a Jeol JNM PS 100 NMR spectrometer at various temperatures. The magnetic susceptibilities of the complexes in pyridine were determined by the Evans method,[3] using TMS for a reference signal.

Results and Discussion

It was observed that the isotropic shifts and the line widths of pyridine protons change markedly with temperature. Though the ratio of the isotropic shifts of α, β, and γ protons for each nickel complex system at an ambient temperature differs, each approaches the ratio observed for pyridine interacting with Ni(acac)$_2$[1a] and all become the same as the temperature increases. The features of the changes in the line width and in the isotropic shifts are those seen typically in exchanging ligands of transition metal complex solutions.[4] In Fig. 1, the line width changes are shown by the plot of the observed transverse relaxation rates *vs.* $1/T$. It is seen that the pyridine exchange reaction is appreciably affected by the in-plane ligands, and at the ambient temperature ($1/T \approx 3.3 \times 10^{-3}$) the pyridine exchange reaction is in the slow exchange rate region. To consider quantitatively the line width changes in the present system, one needs to take into account effects of spin-spin decoupling as well as effects of changes in the quadrupole relaxation of nitrogen caused by paramagnetic

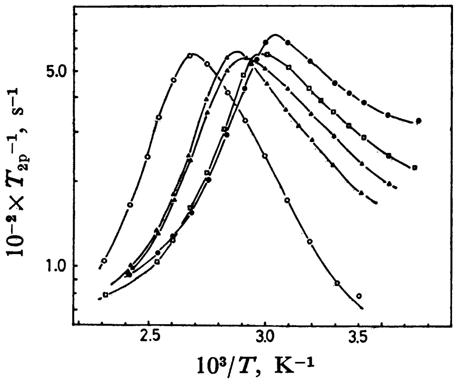

Fig. 1. Temperature dependence of $1/T_2$ for the bulk solvent α proton in the pyridine solutions of the nickel(II) complexes at 0.15 M and at 100 MHz.
—●—: Ni(5 Me-sal)$_2$, —□—: Ni(sal)$_2$, —▲—: Ni(5Cl-sal)$_2$, —△—: Ni(5Br-sal)$_2$, —○—: Ni(5NO$_2$-sal)$_2$.

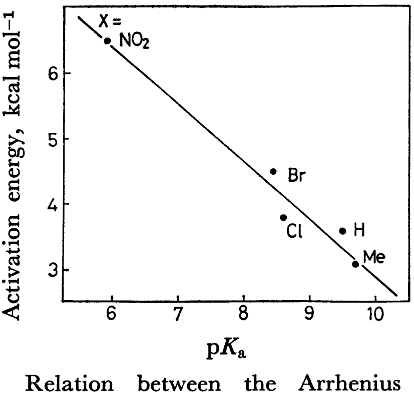

Fig. 2. Relation between the Arrhenius activation energies of pyridine exchange reaction and pK_a values of the in-plane ligands of Ni(5X-sal)$_2$.

pulses due to the presence of the nickel complexes. We assume here that the spin-spin interaction is completely decoupled and the broadening due to the quadrupole relaxation of nitrogen does not contribute any more. As a crude approximation, we further regard the observed line width as arising from only the pyridine exchange reaction.5) The observed relaxation rate, $1/T_2$ for the case satisfying the condition $\Delta\omega_M{}^2 \gg (1/T_{2M})^2$ or $(1/\tau_M)^2$, is hence put equal to P_M/τ_M,4,6) where $\Delta\omega_M$ and $1/T_{2M}$ are the chemical shift and the transverse relaxation rate of the proton in the coordinating pyridine, P_M is the ratio of the solvent bound to the Ni(II) complexes to the free-solvent concentration, and $1/\tau_M$ is the pyridine exchange rate. In Fig. 1 the region where the plots show negative slope satisfies the above rate condition. By the Arrhenius relation, these negative slopes are proportional to the activation energies of the pyridine exchange reactions. The slopes show that the activation energies increase in the order of Ni(5Me-sal)$_2$, Ni(sal)$_2$, Ni(5Cl-sal)$_2$, Ni(5Br-sal)$_2$, and Ni(5NO$_2$-sal)$_2$; their reaction rates at a given temperature also decrease in this order of the complexes. Figure 2 shows that there is a good correlation between the activation energies of the pyridine exchange reactions and the pK_a values7) of the in-plane ligands. Here, the activation energies were evaluated from the slopes of the curves in the slow exchange rate region in Fig. 1, with the approximation $1/T_2 \approx P_M/\tau_M$.5) The results of Fig. 2 suggest that the activation energy of the pyridine exchange reaction decreases with the increase of the electron donor property of the in-plane ligands, since pK_a values may be regarded as a measure of the electron donor properties.

In view of the above result and the fact that acetylacetone has a pK_a value, 9.50,7) larger than salicylaldehyde and its derivatives, it can be understood that the pyridine exchange reaction in the Ni(acac)$_2$ system is much faster than the Ni(sal)$_2$ system.

The hyperfine coupling constants of pyridine protons, $A_H/\hbar$, are obtained from the isotropic shifts in the fast exchange rate region by the relation:

$$\frac{\Delta\omega_{\mathrm{obsd}}}{P_M} = -\left(\frac{A_H}{\hbar}\right)\frac{\omega_0\mu_e\beta\sqrt{S(S+1)}}{3kT\gamma_H}$$

where $\Delta\omega_{\mathrm{obsd}}$ is the observed isotropic shift, ω_0 is the resonant frequency, and μ_e is the effective magnetic moment of nickel in the complexes. The values obtained for the α proton are 10.1±0.5 rad s^{-1} (μ_e=3.1 BM), 9.0±0.5 rad s^{-1} (3.0 BM), 10.1±0.5 rad s^{-1} (2.9 BM), 10.1±0.5 rad s^{-1} (2.8 BM), and 9.7±0.5 rad s^{-1} (2.8BM) for Ni(5Me-sal)$_2$, Ni(sal)$_2$, Ni(5Cl-sal)$_2$, Ni(5Br-sal)$_2$, and Ni(5NO$_2$-sal)$_2$, respectively. Significant changes could not be detected in the hyperfine coupling constants of these complex systems. However, it may be worth noting that the delocalized spin densities on the coordinated pyridine were estimated to be about 0.03 from the comparison with the spin density distribution estimated by the INDO calculation using a phenyl radical as a model compound for pyridine coordinated to nickel.1d)

References

1) For examples: a) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963); b) R. W. Kluiber and W. DeW. Horrocks, Jr., *J. Am. Chem. Soc.*, **88**, 1399 (1966); c) I. Morishima, T. Yonezawa, and K. Goto, *ibid.*, **92**, 6651 (1970); d) W. DeW. Horrocks, Jr., and D. L. Johnston, *Inorg. Chem.* ,**10**, 1835 (1971).

2) The relative ratio of the isotropic shifts for α, β, and γ protons of pyridine was 10 : 4.8 : 1.2 in the system of Ni(sal)$_2$-pyridine at 30°C, but the ratio for the α and β protons in the Ni(5NO$_2$-sal)$_2$-pyridine system was 10 : 19. In the latter case, the isotropic shift of γ proton could not be determined with confidence because of the overlap of its signal with that of the β proton. The ratio reported for the Ni(acac)$_2$-pyridine system is 10.0 : 2.94 : 0.77.1a)

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

4) T. J. Swift, "NMR of Paramagnetic Molecules, Principle and Apprications" ed. by G. N. LaMar, W. DeW. Horrocks, Jr., and R. H. Holm, Academic Press, New York (1973), Chap. 2.

5) Since the line broadening due to the pyridine exchange rection is much larger than the original line width of pyridine or other effects on the line width broadening, the conclusion obtained here is reliable enough in its qualitative meaning, even though the error is estimated to be about 15 — 25% at the maximum in the evaluation of the activation energies for the pyridine exchange reactions.

6) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

7) This value is for 50% dioxan solution and is taken from "Stabilitiy Constants of Metal-Ion Complexes," compiled by L. G. Sillén and A. E. Martell, The Chemical Society, London, Section II (1964), and its supplent No. 1 (1971).