

the ligands in **4** have unshared electrons. But how this donation would occur is unclear. The aquation rates of *trans*-Co(en)<sub>2</sub>LCl<sup>+</sup> complexes have been explained<sup>1</sup> in terms of lone-pair donation by L, but the donation requires a trigonal-bipyramidal structure for the five-coordinate intermediate. The exclusive formation of *trans*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> in the aquation of complex **5** strongly indicates that the intermediate has a square-planar geometry in this case. If only the hydroxy form of complex **5** anates *via* a D mechanism, the stability of the intermediate might be due to a strong donation of electron density through the O-Rh  $\sigma$  bond. This would be consistent with both the mechanism and stereochemistry of the products for complexes **4** and **5**. Clearly our understanding of this oxygen-bonded inert ligand effect would be increased if the individual mechanisms of the acid and base forms of **5** were elucidated.

The relative insensitivity of the substitution mechanism of cobalt complexes to the nature of the inert ligands may be due to cobalt being harder, less polarizable, than rhodium. If this be true, the substitution mechanism of iridium complexes should strongly depend on the nature of the inert ligands whereas that of chromium complexes should not. Data do indicate that both Cr(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>3+</sup> and Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> substitute *via* I<sub>a</sub> mechanisms;<sup>6,20</sup> however, very few data are available on iridium complexes.

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**Registry No.** *trans*-Rh(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup>, 21863-10-5; *trans*-Rh(en)<sub>2</sub>(OH)(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup>, 27842-81-5; Cl<sup>-</sup>, 16887-00-6; *trans*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>, 18539-17-8.

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- (13) This low concentration of complex is dictated by the observation that the solubility product for *trans*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> and ClO<sub>4</sub><sup>-</sup> is about 10<sup>-3</sup> M<sup>2</sup> at room temperature.
- (14) For a more detailed derivation of the rate laws used in this paper see the Appendix to ref 7.
- (15) The computer fitting program was developed by S. D. Christian and coworkers of this department and uses the procedure of D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, **2**, 431 (1963). Standard deviations were estimated from the elements of the inverse matrix.
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Contribution from the Department of Chemistry,  
University of Alberta, Edmonton, Alberta, Canada

## Solvent Proton Magnetic Resonance Study of a Nickel(II)-Schiff Base Complex in Methanol and Acetonitrile

L. L. RUSNAK and R. B. JORDAN\*

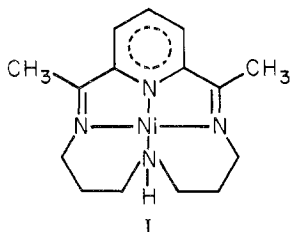
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The temperature dependence of the solvent proton nmr spectra has been measured for the Schiff base complex (2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene)nickel(II), referred to as NiCR<sup>2+</sup> dissolved in methanol and acetonitrile. Chemical-exchange effects are observed for both the line broadening and shifts. The rate constant (25°) for exchange of one solvent molecule,  $\Delta H^\ddagger$  (kcal mol<sup>-1</sup>), and  $\Delta S^\ddagger$  (cal mol<sup>-1</sup> deg<sup>-1</sup>) in methanol are 1.1 × 10<sup>7</sup> sec<sup>-1</sup>, 9.4, and 5.2. The exchange-controlled region in acetonitrile is not well defined and it can only be said that the rate is >7 × 10<sup>5</sup> sec<sup>-1</sup>. The kinetic results show that NiCR<sup>2+</sup> is much more labile than hexasolvated nickel(II) in these solvents. The magnitude, sign, and temperature dependence of the shift of the OH proton in methanol are found to be unusual but can be attributed to a significant pseudocontact shift of opposite sign to the contact shift.

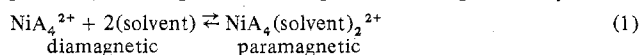
### Introduction

This work presents the results of studies of the solvent proton line broadening and chemical shifts in methanol and acetonitrile, caused by the nickel(II) complex of 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (I), subsequently referred to as NiCR<sup>2+</sup>.



In a previous study<sup>1</sup> it was found that this complex, in a

number of nonaqueous solvents, underwent a diamagnetic-paramagnetic equilibrium, represented in general by



The results of the earlier work are used here to calculate the concentration of the paramagnetic species which causes the line broadening and chemical shift effects.

The results for methanol and acetonitrile reported here are similar to those found previously for *N,N*-dimethylformamide.<sup>2</sup> However, the hydroxy proton shifts in methanol show several unusual features which are explained by a pseudocontact contribution to the shift.

### Experimental Section

The preparation and characterization of the NiCR<sup>2+</sup> salts have been described previously.<sup>1</sup>

The nmr samples were prepared by weight on a standard vacuum

line using published methods.<sup>1</sup> The solvents were doubly vacuum distilled and stored under vacuum over molecular sieves. Internal standards for chemical shift measurements, cyclopentane in methanol and tetramethylsilane in acetonitrile, were vacuum distilled into the nmr sample tube before it was sealed off.

In acetonitrile NiCR(PF<sub>6</sub>)<sub>2</sub> was studied at concentrations of 0.630 and 0.525 *m*. A wider concentration range could not be studied because of solubility limitations at higher values and because much lower values would produce significant broadening only at the low-temperature extreme.

In methanol seven solutions of NiCR(BF<sub>4</sub>)<sub>2</sub> were studied in the concentration range 0.075–0.22 *m*. The shifts and line broadenings were always found to depend linearly on the NiCR<sup>2+</sup> concentration at a given temperature. For the more dilute solutions a small amount of 2,4-dinitrobenzenesulfonic acid (Eastman Organic Chemicals) was added in order to collapse the coupling of the OH and CH<sub>3</sub> protons. Blank methanol samples were prepared similarly. A change in the acid concentration had no effect on the line broadenings or shifts. Shifts were also measured in samples with no added acid and were found to agree with those measured in the presence of acid. Shifts measured in the presence of NiCR(NO<sub>3</sub>)<sub>2</sub> and NiCR(SbF<sub>6</sub>)<sub>2</sub> in methanol, in the absence of acid, agree with those obtained from NiCR(BF<sub>4</sub>)<sub>2</sub>. All of these results were used in the data analysis.

The nmr spectra were obtained on Varian Associates A-56/60 and HA-100 spectrometers. Temperatures were controlled and measured using standard methods described previously.<sup>2</sup>

## Results

The solvent proton nmr line broadening caused by the paramagnetic ion will be discussed in terms of the relaxation time  $T_{2P}$ , defined by

$$\frac{1}{T_{2P}P_M} = \frac{\pi(\Delta\nu_{\text{obsd}} - \Delta\nu_{\text{solv}})}{P_M} \quad (2)$$

where  $\Delta\nu_{\text{obsd}}$  and  $\Delta\nu_{\text{solv}}$  are the full widths at half-height of the solvent nmr resonance in the presence and absence, respectively, of the paramagnetic species, and  $P_M$  is the ratio of the concentration of solvent bound to the paramagnetic ion to the concentration of the free solvent. It has been shown<sup>1</sup> that NiCR<sup>2+</sup> undergoes a diamagnetic-paramagnetic equilibrium described by eq 1; therefore

$$P_M = \frac{nX_P[\text{NiCR}^{2+}]_{\text{total}}}{S_O - nX_P[\text{NiCR}^{2+}]_{\text{total}}} \quad (3)$$

where  $n$  is the number of solvent molecules in the first coordination sphere of paramagnetic NiCR<sup>2+</sup> ( $n = 2$  has been assumed),  $S_O$  is the molal solvent concentration, and  $X_P$  is the mole fraction of NiCR<sup>2+</sup> in the paramagnetic form. Values of  $X_P$  were calculated from the  $\Delta H^\circ$  and  $\Delta S^\circ$  for reaction 1 determined previously.<sup>1</sup>

The temperature dependence of  $(T_{2P}P_M)^{-1}$  is described by the equation<sup>3</sup>

$$\frac{1}{T_{2P}P_M} = \frac{1}{\tau_M} \left\{ \frac{(T_{2M})^{-2} + (\tau_M T_{2M})^{-1} + \Delta\omega_M^2}{(\tau_M^{-1} + T_{2M}^{-1})^2 + \Delta\omega_M^2} \right\} + \frac{1}{T_{2O}} \quad (4)$$

where the temperature dependence of the lifetime of the solvent molecule in the first coordination sphere of the paramagnetic ion is given by

$$\frac{1}{\tau_M} = \frac{kT}{h} \exp\left(-\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right) \quad (5)$$

The temperature dependence of the transverse relaxation time in the first coordination sphere of the paramagnetic ion ( $T_{2M}$ ) is assumed to be a simple exponential

$$T_{2M}^{-1} = C_M \exp(E_M/RT) \quad (6)$$

and the outer-sphere relaxation time ( $T_{2O}$ ) is assumed to have the form

$$T_{2O}^{-1} = C_O \exp(E_O/RT) \quad (7)$$

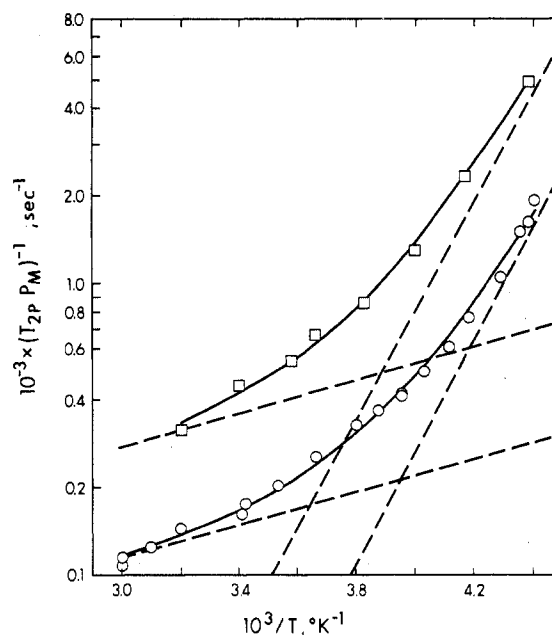


Figure 1. Temperature dependence of  $-\log(T_{2P}P_M)$  for NiCR(PF<sub>6</sub>)<sub>2</sub> in acetonitrile at 100 MHz (□) and 60 MHz (○).

The shift between a solvent proton in the bulk solvent minus that in the first coordination sphere of the paramagnetic ion is given by<sup>4</sup>

$$\Delta\omega_M = -\left(\frac{A}{h}\right) \frac{\omega_O \mu_{\text{eff}} \beta(S(S+1))^{1/2}}{3\gamma_N kT} \quad (8)$$

and, if  $\mu_{\text{eff}}$  is independent of temperature, then

$$\Delta\omega_M = -C_\omega/T \quad (9)$$

It has been shown by Swift and Connick<sup>3</sup> that the observed shift of the solvent resonance in the presence of the paramagnetic ion minus that in the pure solvent is given by

$$\Delta\omega_{\text{obsd}} = \frac{-P_M \Delta\omega_M}{(1 + (\tau_M/T_{2M}))^2 + (\tau_M \Delta\omega_M)^2} \quad (10)$$

**NiCR(PF<sub>6</sub>)<sub>2</sub> in Acetonitrile.** The temperature dependences of  $(T_{2P}P_M)^{-1}$  and  $(\Delta\omega_{\text{obsd}}/P_M)$  for this system are shown in Figures 1 and 2, respectively. The experimental points have been corrected for the formation of the diamagnetic species using values<sup>1</sup> of  $-4.16$  kcal mol<sup>-1</sup> for  $\Delta H^\circ$  and  $-10.8$  cal mol<sup>-1</sup> deg<sup>-1</sup> for  $\Delta S^\circ$  for reaction 1. The complex is 66% paramagnetic at 60° and >90% paramagnetic below 0°.

The temperature dependence of  $(T_{2P}P_M)^{-1}$  has been fitted to the equation

$$(T_{2P}P_M)^{-1} = T_{2M}^{-1} + \tau_M \Delta\omega_M^2 + T_{2O}^{-1} \quad (11)$$

which is obtained from eq 4 if  $\tau_M^{-1} \gg T_{2M}^{-1}$  and  $\tau_M^{-2} \gg \Delta\omega_M^2$ . The results do not show a region only controlled by  $T_{2O}^{-1}$  so that parameters for this term cannot be determined independently. It has been assumed that  $E_O = E_M$ ,<sup>5</sup> in which case, after appropriate substitution from eq 5, 6, 7, and 9, it is found that

$$(T_{2P}P_M)^{-1} = (C_M + C_O) \exp(E_M/RT) + \left(\frac{C_\omega}{T}\right)^2 \frac{h}{kT} \exp\left(\frac{\Delta H^\ddagger}{RT} - \frac{\Delta S^\ddagger}{R}\right) \quad (12)$$

The results in Figure 1 at 60 and 100 MHz were fitted by a least-squares method<sup>6</sup> to eq 12, with  $C_\omega$  held constant at values calculated from the shift results.

Table I. Least-Squares Best-Fit Parameters for  $(T_2\rho P_M)^{-1}$  for  $\text{NiCR}(\text{PF}_6)_2$  in Acetonitrile

	60 MHz			100 MHz		
	A	B	C	D	E	F
$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	11.0	6.96	9.07	9.09	6.93	11.0
$\Delta S^\ddagger$ , cal mol <sup>-1</sup> deg <sup>-1</sup>	14.8	-3.38	6.06	5.97	-3.80	14.6
$(C_M + C_O)$ , sec <sup>-1</sup>	2.87	15.2	5.22	6.26	36.9	2.48
$E_M = E_O$ , kcal mol <sup>-1</sup>	2.40	1.33 <sup>a</sup>	2.03	2.44	1.33 <sup>a</sup>	3.00 <sup>a</sup>
$10^{-6}C_\omega$ , radians sec <sup>-1</sup> deg	3.56 <sup>b</sup>	3.56	3.56 <sup>b</sup>	5.94 <sup>b</sup>	5.94 <sup>b</sup>	5.94 <sup>b</sup>

<sup>a</sup> The value of  $E_M$  was obtained as explained in the text and held constant. <sup>b</sup> Values determined from the 60- and 100-MHz chemical shift measurements and held constant.

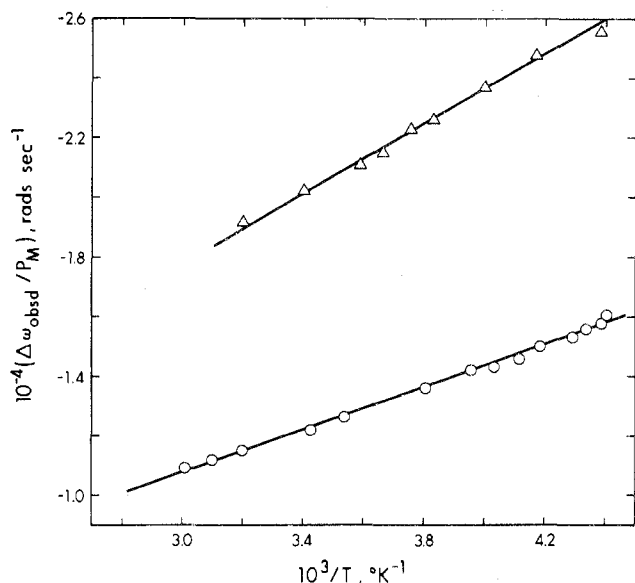


Figure 2. Temperature dependence of  $(\Delta\omega_{\text{obsd}}/P_M)$  for  $\text{NiCR}(\text{PF}_6)_2$  in acetonitrile at 100 MHz ( $\Delta$ ) and 60 MHz ( $\circ$ ).

The parameters resulting from the least-squares analysis are summarized in Table I. In fits A and D the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values from the 60- and 100-MHz data are in significant disagreement. If  $E_M = E_O$  is fixed at 1.33 kcal mol<sup>-1</sup> for both frequencies, then self-consistent  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values are obtained as seen from fits B and E in Table I. On the other hand  $E_M = E_O$  might be lower at 60 MHz than at 100 MHz judging from the previous study in DMF.<sup>2</sup> If this is the case, a whole range of self-consistent  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values can be obtained, as seen by comparing fits A-F and C-D in Table I. Clearly the system is underdetermined; the data in Table I predict an exchange rate from  $7.5 \times 10^5$  to  $9.3 \times 10^6$  sec<sup>-1</sup> at 25°.

The dashed lines of lesser slope in Figure 1 represent the  $(T_2M^{-1} + T_2O^{-1})$  contribution calculated from fits B and E. The values show the same type of variation with frequency as was observed for  $\text{NiCR}^{2+}$  in DMF and water.<sup>2</sup> This variation is attributed to the magnetic field dependence of the electron spin relaxation time.

Substantial upfield shifts of the order of 100 Hz are observed in this system. The temperature dependence of the shifts shown in Figure 2 is consistent with eq 9, and the  $C_\omega$  values show the expected ratio of 10:6 for the 100- and 60-MHz values. If  $\mu_{\text{eff}}$  is taken as 3.00 BM,<sup>1</sup> then eq 8 can be used to calculate a hyperfine coupling constant ( $A/\hbar$ ) of  $-2.66 \times 10^6$  radians sec<sup>-1</sup>.

**$\text{NiCR}^{2+}$  in Methanol.** The temperature dependence of  $(T_2\rho P_M)^{-1}$  for the  $\text{CH}_3$  and OH protons of methanol are shown in Figures 3 and 4, respectively, and the temperature dependence of the shifts are shown in Figures 5 and 6, respectively. All of the data have been corrected for the formation of the diamagnetic species using values of  $\Delta H^\circ = -4.26$  kcal mol<sup>-1</sup> and  $\Delta S^\circ = -11.5$  cal mol<sup>-1</sup> deg<sup>-1</sup> for reaction 1.1

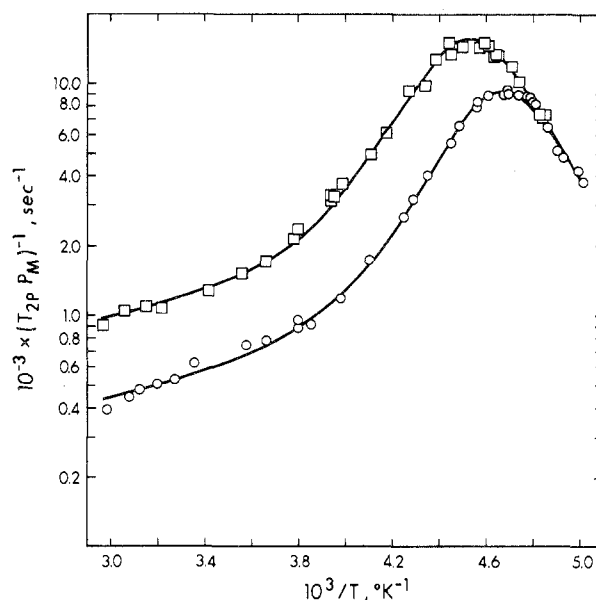


Figure 3. Temperature dependence of  $-\log(T_2\rho P_M)^{-1}$  for the  $\text{CH}_3$  protons of methanol solutions of  $\text{NiCR}^{2+}$  at 100 MHz ( $\square$ ) and 60 MHz ( $\circ$ ).

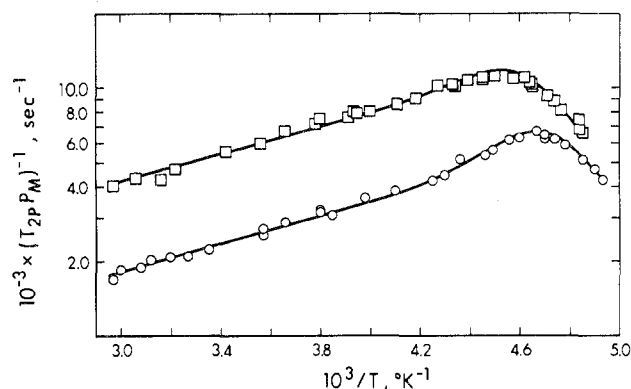


Figure 4. Temperature dependence of  $-\log(T_2\rho P_M)^{-1}$  for the OH proton of methanol solutions of  $\text{NiCR}^{2+}$  at 100 MHz ( $\square$ ) and 60 MHz ( $\circ$ ).

The complex is  $\sim 60\%$  in the paramagnetic form at 60° and  $>90\%$  below 0°.

The  $(T_2\rho P_M)^{-1}$  results for this system appear to be unusual in that the OH and  $\text{CH}_3$  proton temperature variation seems much different. The central region with a positive slope in Figure 3 is barely observable for the OH proton data in Figure 4. This observation is understandable however when it is recognized that this region is primarily controlled by  $\tau_M \Delta\omega_M^2$  and when the shifts in Figures 5 and 6 are considered. It should be noted that for  $10^3/T < 4.4$  the shifts for the OH proton are 2-3 times smaller than those for the  $\text{CH}_3$  protons. This explains why the  $\tau_M \Delta\omega_M^2$  region is smaller for the OH proton, but it remains to be explained why the OH proton shifts are so much smaller than and of opposite sign to the shifts of the  $\text{CH}_3$  protons.

Table II. Least-Squares Best-Fit Parameters for NiCR<sup>2+</sup> in Methanol

Data	Proton	Freq, MHz	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , cal mol <sup>-1</sup> deg <sup>-1</sup>	$C_M$ , sec <sup>-1</sup>	$E_M$ , kcal mol <sup>-1</sup>	$10^{-6} C_\omega$ , radians sec <sup>-1</sup> deg
$(T_2PPM)^{-1}$	CH <sub>3</sub>	60	9.21	4.65	59.5	1.15 <sup>a</sup>	3.81
		100	9.52	5.12	58.9	1.15 <sup>a</sup>	3.96 <sup>b</sup>
		100	9.28 <sup>c</sup>	4.61	130.9	1.15 <sup>a</sup>	6.65
$\Delta\omega_{\text{obsd}}/P_M$	CH <sub>3</sub>	60	9.70	6.68	58.9 <sup>d</sup>	1.15 <sup>a</sup>	3.96
		100	9.28 <sup>c</sup>	4.53	130.9 <sup>d</sup>	1.15 <sup>a</sup>	6.57
		100	9.28 <sup>c</sup>	4.66	284.3	1.17	e
$(T_2PPM)^{-1}$	OH	60	9.28 <sup>c</sup>	4.57	639.8	1.18	e
		100	9.28 <sup>c</sup>	4.57	639.8	1.18	e
		100	9.28 <sup>c</sup>	5.36	284.3 <sup>d</sup>	1.17 <sup>d</sup>	e
$\Delta\omega_{\text{obsd}}/P_M$	OH	60	9.28 <sup>c</sup>	5.36	284.3 <sup>d</sup>	1.17 <sup>d</sup>	e
		100	9.28	5.52	639.8 <sup>d</sup>	1.18 <sup>d</sup>	e
		100	9.28	5.52	639.8 <sup>d</sup>	1.18 <sup>d</sup>	e

<sup>a</sup> Value obtained from  $(T_2PPM)^{-1}$  OH data with  $\Delta H^\ddagger$  fixed at 9.52 kcal mol<sup>-1</sup> and held constant. <sup>b</sup> Value obtained from  $\Delta\omega_{\text{obsd}}/P_M$  data and held constant. <sup>c</sup> Value obtained from 100-MHz  $\Delta\omega_{\text{obsd}}/P_M$  data and held constant. <sup>d</sup> Value obtained from appropriate  $(T_2PPM)^{-1}$  data and held constant. <sup>e</sup> Temperature dependence given by eq 13.

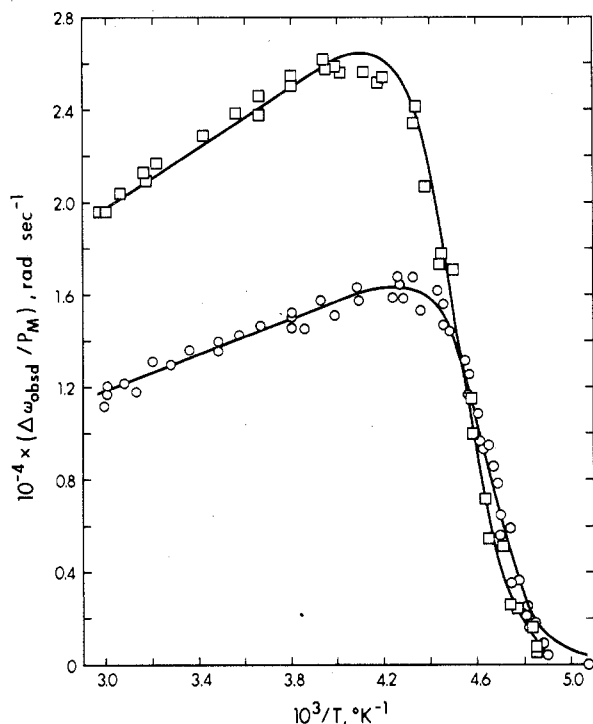


Figure 5. Temperature dependence of  $(\Delta\omega_{\text{obsd}}/P_M)$  for the CH<sub>3</sub> protons of methanol solutions of NiCR<sup>2+</sup> at 100 MHz (□) and 60 MHz (○).

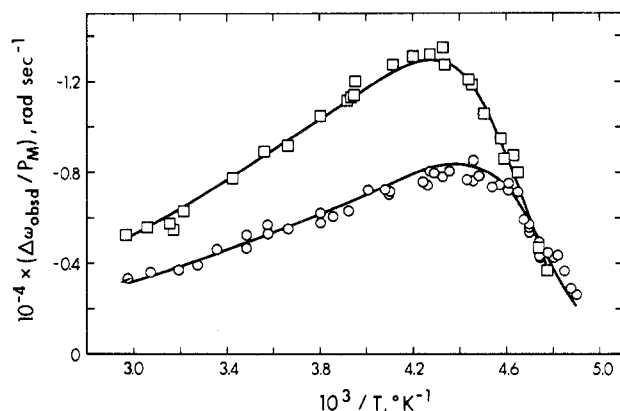


Figure 6. Temperature dependence of  $(\Delta\omega_{\text{obsd}}/P_M)$  for the OH proton of methanol solutions of NiCR<sup>2+</sup> at 100 MHz (□) and 60 MHz (○).

It is also found that the OH proton shifts decrease more rapidly with temperature than predicted by eq 9 and are consistent with

$$(\Delta\omega_M)_{\text{OH}} = \frac{C_1}{T} + \frac{C_2}{T^2} \quad (13)$$

An explanation for these unusual aspects of the OH proton shifts is given in a separate section of this paper.

The temperature dependence of  $(T_2PPM)_{\text{CH}_3}^{-1}$  has been fitted to eq 4. Since the outer-sphere contribution  $(T_2O)_{\text{CH}_3}^{-1}$  is not actually observed, it has been estimated from the  $T_1$  results of Luz and Meiboom<sup>7a</sup> on Ni(CH<sub>3</sub>OH)<sub>6</sub><sup>2+</sup>, after correction for the differing  $n$  values.<sup>8</sup> It is estimated that  $(T_2M)_{\text{CH}_3}^{-1}/(T_2O)_{\text{CH}_3}^{-1} \approx 3.1$ , so that  $C_O = C_M/3.1$  if  $E_O = E_M$ . Then, within the limitations of these assumptions  $(T_2O)_{\text{CH}_3}^{-1}$  can be defined in terms of the parameters for  $(T_2M)_{\text{CH}_3}^{-1}$ . The value of  $(E_M)_{\text{CH}_3}$  was fixed at 1.15 kcal mol<sup>-1</sup>, the value given by the OH proton data. The latter give a much more precise value of  $E_M$  because of the much longer temperature region over which  $(T_2M)^{-1}$  controls  $(T_2PPM)^{-1}$  for the OH proton. The OH proton data are also more accurate in this region because of the larger experimental line widths.

The results of various fits of the CH<sub>3</sub> proton data are summarized in Table II. The agreement of  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ , and  $C_\omega$  from various fits is satisfactory and provides some justification for the assumptions made.

In order to fit the OH proton data it was necessary to obtain values for  $C_1$  and  $C_2$  in eq 13. These were determined from the linear plot of  $T(\Delta\omega_{\text{obsd}}/P_M)$  vs.  $T^{-1}$  for  $10^3/T < 4.2$ . At 100 MHz the constants are  $C_1 = -2.0 \times 10^6$  radians sec<sup>-1</sup> deg and  $C_2 = 1.25 \times 10^9$  radians sec<sup>-1</sup> deg<sup>2</sup>. The values at 60 MHz were taken to be 60/100 of the above values and were found to be consistent with the observed shifts as can be seen from the calculated curve in Figure 6.

In order to analyze the  $(T_2PPM)_{\text{OH}}^{-1}$  data the outer-sphere contribution was estimated from previous work<sup>7</sup> which indicates that  $(T_2O)_{\text{OH}}^{-1}/(T_2O)_{\text{CH}_3}^{-1} \approx 1.6$ , and  $(T_2O)_{\text{CH}_3}^{-1}$  was estimated as described previously. It should be noted in Figure 4 that the  $\tau_M$ -controlled region appears only at the low-temperature extreme where the somewhat uncertain outer-sphere effects are also likely to be significant. Therefore it did not seem reasonable to attempt to determine independent  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values from the OH proton  $T_2P$  data. Therefore  $\Delta H^\ddagger$  was fixed at values indicated by the CH<sub>3</sub> proton results, and best fit values of  $\Delta S^\ddagger$ ,  $C_M$ , and  $E_M = E_O$  were obtained. The results of these fits are given in Table II. The agreement of the  $\Delta S^\ddagger$  values with those obtained from the CH<sub>3</sub> proton data indicates that the OH and CH<sub>3</sub> protons exchange at the same rate.

The shift results for the CH<sub>3</sub> protons (Figure 5) have been fitted to eq 10, with  $(\Delta\omega_M)_{\text{CH}_3}$  taken to have the temperature dependence given by eq 9. The values of  $C_M$  and  $E_M$  were held constant in these fits and  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ , and  $C_\omega$  were allowed to vary. The resulting best fit parameters, summarized in Table II, are in good agreement with those obtained from the  $(T_2PPM)_{\text{CH}_3}^{-1}$  data. The value of  $C_\omega = 3.96 \times 10^6$  radians sec<sup>-1</sup> deg at 60 MHz, combined with a  $\mu_{\text{eff}}$  of 3.00 BM,<sup>1</sup> can be used to calculate a hyperfine coupling constant ( $A/\hbar$ ) of  $2.96 \times 10^6$  radians sec<sup>-1</sup> for the CH<sub>3</sub> protons.

The OH proton shifts were fitted to eq 9; however ( $\Delta\omega_M$ )<sub>OH</sub> was taken to have the temperature dependence given by eq 13, and  $C_1$  and  $C_2$  were held fixed at the values given above for the 100-MHz data. In all cases  $E_M$  and  $C_M$  were held fixed at values obtained from the ( $T_2PM$ )<sub>OH</sub><sup>-1</sup> results. For the more accurate 100-MHz data both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were allowed to vary and the best fit values, given in Table II, are found to be in good agreement with those from other data sets. In the case of the 60-MHz chemical shifts it was necessary to restrain  $\Delta H^\ddagger$ , and only  $\Delta S^\ddagger$  was allowed to vary to obtain the calculated curve in Figure 6. Although a number of data points lie ~10% below the calculated curve in the region  $3.9 < 10^3/T < 4.55$ , the quality of the fit is considered to be satisfactory since the 60-MHz OH proton chemical shifts observed were generally less than 10 Hz. From the average of the several independent determinations of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  indicated in Table II, it is concluded that  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are 9.4 kcal mol<sup>-1</sup> and 5.2 cal mol<sup>-1</sup> deg<sup>-1</sup>, respectively, for methanol exchange from NiCR<sup>2+</sup>. Error limits are difficult to establish because of the assumptions about the outer-sphere contributions.

**Hydroxy Proton Shift.** In previous work on nickel(II) in methanol it has been found that the shifts of the solvent OH and CH<sub>3</sub> protons are of the same sign and of similar magnitude and show the normal temperature dependence described by eq 9. The OH proton shifts for the NiCR<sup>2+</sup>-CH<sub>3</sub>OH system are quite unusual therefore in that (a) they are of opposite sign to those of the CH<sub>3</sub> protons, (b) they are much smaller in magnitude than those of the CH<sub>3</sub> protons, and (c) they show a more complicated temperature dependence while the CH<sub>3</sub> protons appear normal in this and all other respects.

The OH proton results may be explained if it is assumed that there is a large pseudocontact contribution to the chemical shift. It has been shown by Kurland and McGarvey<sup>9</sup> that the pseudocontact contribution would have the temperature dependence indicated by eq 13, so that the temperature dependence of the total shift will be given by

$$(\Delta\omega_M)_{OH} = \left(-\frac{C_\omega}{T}\right)_{\text{contact}} + \left(-\frac{C_1'}{T} + \frac{C_2}{T^2}\right)_{\text{pseudocontact}} \quad (14)$$

or

$$(\Delta\omega_M)_{OH} = -\left(\frac{C_\omega + C_1'}{T}\right) + \frac{C_2}{T^2} = -\frac{C_1}{T} + \frac{C_2}{T^2} \quad (15)$$

Normally  $|C_1/T| \gg |C_2/T^2|$  and the latter is not observed. The temperature dependence of  $\Delta\omega_M$  is not able to distinguish contact and pseudocontact contributions in such cases. However, for NiCR<sup>2+</sup> in methanol it appears that  $C_\omega$  and  $C_1'$  are of similar magnitude and opposite sign. As a result the OH proton shifts are much smaller than those for the CH<sub>3</sub> protons and the  $C_2/T^2$  term becomes significant. In addition, since the observed OH proton shifts are of opposite sign to those for the CH<sub>3</sub> protons, it appears that  $C_1'$  is slightly larger in magnitude than  $C_\omega$ .

It was of interest to determine if this explanation was qualitatively reasonable. Therefore the expression for the pseudocontact shift of a nonaxially symmetric system was developed from the general expression for the pseudocontact shift given as eq 17 by Kurland and McGarvey.<sup>9</sup> It was found that the pseudocontact shift is given by

$$\frac{\Delta\omega_M}{\omega_O} = \frac{2\beta^2}{9kR^3T} \left\{ (3 \cos^2 \Omega - 1) \left[ \left( g_z^2 - \frac{g_x^2 + g_y^2}{2} \right) - \frac{1}{6kT} \left( 2Dg_z^2 + \frac{g_x^2(D-3E) + g_y^2(D-E)}{2} \right) \right] - (\sin^2 \Omega \times \cos 2\Psi) \left[ \frac{g_y - g_x}{2} + \frac{1}{12kT} (g_y(D+3E) - g_x(D-3E)) \right] \right\} \quad (16)$$

**Table III.** Parameters and Results of  $T_{2O}$  and  $T_{2M}$  Calculations for NiCR<sup>2+</sup> in Methanol and Acetonitrile

	Methanol		Acetonitrile
	CH <sub>3</sub>	OH	
$10^2(T_{2O})^{-1}$ , sec <sup>-1</sup> <sup>a</sup>	1.34	2.20	0.43
	2.97	5.05	0.99
$d_o$ , Å	6.75	5.71	9.4
$10^{-2}(T_{2M})_{\text{obsd}}$ <sup>-1</sup> , sec <sup>-1</sup> <sup>b</sup>	4.11	20.6	1.00
	9.13	47.3	2.48
$10^{-2}(T_{2M})_{\text{calcd}}$ <sup>-1</sup> , sec <sup>-1</sup> <sup>b</sup>	4.12	20.6	1.01
	9.13	44.8	2.47
$10^{-2}(T_{2M})_{\text{sc}}$ <sup>-1</sup> , sec <sup>-1</sup> <sup>c</sup>	0.38	0.55	0.34
	1.08	1.51	0.93
$10^{11}\tau_c$ , sec		3.7	5.8
$10^{11}T_{1e}$ , sec		0.66	0.71
$10^{13}T_{2e}$ , sec		1.0	0.46
$10^{-22}C_e$ , sec <sup>-1</sup>		17.5	25.1
$r_i$ , Å	3.90	2.95	5.3

<sup>a</sup> Values estimated as described in the text. <sup>b</sup> Calculated sum of the scalar and dipolar interaction mechanisms. <sup>c</sup> Calculated scalar contribution using experimental coupling constants.

where  $g_x$ ,  $g_y$ , and  $g_z$  are the components of the  $g$  tensor,  $D$  is the zero field splitting arising from the tetragonal distortion,  $E$  is the additional zero-field parameter characterizing the rhombic distortion,  $R$  is the magnitude of the metal ion to proton radius vector,  $\Omega$  is the angle between the symmetry axis and the radius vector, and  $\Psi$  is the angle between the  $x$  axis and the projection of the unit vector which joins the metal ion and ligand proton onto the  $xy$  plane.

The zero-field splitting parameters are taken to be related to the  $g$  tensor components by<sup>10</sup>

$$D = \frac{\lambda}{2} \left( g_z - \frac{g_x + g_y}{2} \right) \quad (17)$$

$$E = \frac{\lambda}{4} (g_x - g_y)$$

where  $\lambda$  is the spin-orbit coupling constant.

The structure of NiCR<sup>2+</sup> indicates that the major symmetry axis or  $z$  axis should pass through the pyridine nitrogen, nickel(II), and amine nitrogen atoms. The  $y$  axis is taken to be that passing through the azomethine nitrogens and nickel(II) and the  $x$  axis passes through the solvent oxygen atoms. In order to maximize the pseudocontact shift of appropriate sign the angle  $\Omega$  should be ~90°. Therefore, the solvent molecule is assumed to be oriented so that the OH proton lies over one of the azomethine nitrogens. With this model  $\Psi$  is ~35°, and calculations with estimated  $g$  components indicate that the  $\sin^2 \Omega \cos(2\Psi)$  term in eq 16 will contribute little to the final result. The value of  $(A/\hbar)_{OH}$  is assumed to be 19% larger than  $(A/\hbar)_{CH_3}$ <sup>11</sup> as observed for nickel(II) in methanol,<sup>6</sup> and  $R$  is taken to be 2.95 Å from models. It is estimated that  $\lambda \approx -300$  cm<sup>-1</sup>, somewhat less negative than the free-ion value of -322 cm<sup>-1</sup>. It is then found that one set of parameters which give the experimental  $C_1$  and  $C_2$  values is  $g_x = 2.00$ ,  $g_y = 2.63$ ,  $g_z = 2.68$ ,  $D = -54.9$  cm<sup>-1</sup>, and  $E = 47.1$  cm<sup>-1</sup>. The magnitudes of the  $g$  values are reasonable and  $g_z$  and  $g_y$  are similar, as expected, since nitrogen atoms are on both of these axes.

Clearly no great significance should be attached to the above-estimated values. However, they do show that the explanation of the OH proton chemical shifts in terms of the pseudocontact contribution is a reasonable one.

It may also be noted that the apparent absence of a significant pseudocontact shift for the CH<sub>3</sub> protons is consistent with this model. Of course the increased interaction distance ( $R \approx 3.9$  Å) decreases the pseudocontact contribution by about a factor of 2, but the angle  $\Omega$  for the CH<sub>3</sub> protons will be close to 55°. At the latter value  $(3 \cos^2 \Omega - 1) \approx 0$  and the pseudocontact contribution would disappear.

Table IV. Summary of Results for Related Systems

Complex	$k(25^\circ)$ , sec <sup>-1</sup>	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , cal mol <sup>-1</sup> deg <sup>-1</sup>	$10^{-6} A/h$ , radians sec <sup>-1</sup>
Ni(CH <sub>3</sub> OH) <sub>6</sub> <sup>2+</sup> <sup>a</sup>	$1 \times 10^3$	15.8	8.0	4.2 (OH), 3.6 (CH <sub>3</sub> )
NiCR(CH <sub>3</sub> OH) <sub>2</sub> <sup>2+</sup> <sup>b</sup>	$1.1 \times 10^7$	9.4	5.2	-1.0 (OH), <sup>c</sup> 3.0 (CH <sub>3</sub> )
Ni(CH <sub>3</sub> CN) <sub>6</sub> <sup>2+</sup> <sup>d</sup>	$2.7 \times 10^3$	15.0	8.5	-3.3
NiCR(CH <sub>3</sub> CN) <sub>2</sub> <sup>2+</sup> <sup>b</sup>	$>7 \times 10^5$			-2.66
Ni(DMF) <sub>6</sub> <sup>2+</sup> <sup>e</sup>	$3.8 \times 10^3$	15.0	8	4.28 (CH)
NiCR(DMF) <sub>2</sub> <sup>2+</sup> <sup>f</sup>	$1.9 \times 10^6$	9.5	2.2	2.3
NiTAAB(DMF) <sub>2</sub> <sup>2+</sup> <sup>g</sup>	$7.3 \times 10^4$	11.5	2.5	2.3
NiTRI(DMF) <sub>3</sub> <sup>2+</sup> <sup>g</sup>	$5.9 \times 10^2$	15.6	6.5	2.9
Ni(OH <sub>2</sub> ) <sub>6</sub> <sup>2+</sup> <sup>h</sup>	$3.4 \times 10^4$	13.9	8.7	1.3 <sup>i</sup>
NiCR(OH <sub>2</sub> ) <sub>2</sub> <sup>2+</sup> <sup>f</sup>	$4.5 \times 10^4$	6.8	-14	-1.1

<sup>a</sup> Reference 6. <sup>b</sup> This work. <sup>c</sup> Calculated from observed chemical shift at 25°. <sup>d</sup> Reference 12. <sup>e</sup> N. A. Matwiyoff, *Inorg. Chem.*, 5, 788 (1966). <sup>f</sup> Reference 2. <sup>g</sup> L. L. Rusnak, et al., *Inorg. Chem.*, 11, 199 (1972). <sup>h</sup> Reference 13. <sup>i</sup> Z. Luz and R. G. Shulman, *J. Chem. Phys.*, 43, 3750 (1965).

**Magnetic Field Dependence of  $T_{2M}$  and  $T_{2O}$ .** It was observed previously<sup>2</sup> for NiCR<sup>2+</sup> in DMF and water that  $T_{2M}$  and  $T_{2O}$  decreased as the magnetic field strength increased. Similar observations have since been made for nickel(II) in acetonitrile<sup>12</sup> and for nickel(II) in water,<sup>13</sup> and the systems reported here also show this effect.

A more detailed discussion of this field dependence has been given in our earlier work<sup>2</sup> where it is attributed to the variation of the longitudinal ( $T_{1e}$ ) and transverse ( $T_{2e}$ ) electron spin relaxation times. These times are contributing correlation times for the electron-nuclear dipole-dipole and scalar interactions. Following McLachlan,<sup>14</sup> the average electron spin relaxation times for an electron spin system with  $S = 1$  are

$$\langle T_{1e} \rangle^{-1} = C_e \left\{ \frac{\tau_c}{1 + \omega_S^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_S^2 \tau_c^2} \right\} \quad (18)$$

$$\langle T_{2e} \rangle^{-1} = \frac{C_e}{2} \left\{ 3\tau_c + \frac{5\tau_c}{1 + \omega_S^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_S^2 \tau_c^2} \right\}$$

where  $C_e$  is a field-independent constant,  $\tau_c$  is an unspecified correlation time, and it is assumed that  $\tau_c < T_{1e}$ .<sup>15</sup>

The experimental values of  $T_{2M}^{-1}$  and  $T_{2O}^{-1}$  are consistent with a dominant dipole-dipole interaction mechanism. The results at the two frequencies 60 and 100 MHz have been treated iteratively, using well-known equations (see ref 2, for example) to calculate  $\tau_c$ ,  $C_e$ , the inner-sphere interaction distance ( $r_i$ ), and outer sphere interaction distance ( $d_o$ ).<sup>16</sup> The  $r_i$  values are in reasonable agreement with estimates which can be made from structural models.

The  $\tau_c$  values agree with rotational tumbling times of  $4.1 \times 10^{-11}$  and  $6.2 \times 10^{-11}$  sec determined<sup>17</sup> from the epr spectrum of the vanadyl ion in methanol and acetonitrile, respectively. This result is consistent with an electron spin relaxation mechanism in which the modulation of the zero-field splitting of the complex is governed by tumbling of the complex in solution. However, unpublished results for vanadyl and low-spin cobalt(II) complexes indicate that the activation energy for tumbling should be 2.7–3.0 kcal mol<sup>-1</sup>. But if this value is used along with other parameters in Table III, then effective  $E_M$  values of 2.6 and 2.7 kcal mol<sup>-1</sup>, at 60 and 100 MHz, respectively, are obtained. This analysis would appear to rule out fits B and E in Table I. However, a problem arises if this analysis is extended to methanol. Here tumbling is expected to have an activation energy of 3–3.5 kcal mol<sup>-1</sup>, yet the measured  $E_M$  is about 1.15 kcal mol<sup>-1</sup>. This value is well defined experimentally by the hydroxy proton line broadening. The same difficulty arose in our earlier study in DMF,<sup>2</sup> where  $E_M$  is expected to be about 2.8 kcal mol<sup>-1</sup>, compared to the observed value of 1–1.5 kcal mol<sup>-1</sup>.

It appears anomalous that a rotational correlation time in eq 18 accounts for the frequency dependence of  $T_{2M}$  but does not account for the activation energy which is always lower

than expected. Investigations of the frequency dependence of  $T_1$  are under way to clarify this problem. It seems that the difficulty lies in the limitations of eq 18<sup>15</sup> and that the agreement with rotational correlation times is a coincidence.

### Conclusion

The kinetic parameters for solvent exchange and the scalar coupling constants for several related nickel(II) systems are summarized in Table IV. A comparison of the scalar coupling constants reveals that in DMF and acetonitrile and for the CH<sub>3</sub> protons in methanol the values are of the same sign and similar magnitude, but slightly smaller, for the Schiff base complexes than for the hexasolvated nickel(II) ion. The apparent scalar coupling with the OH proton for NiCR<sup>2+</sup> in methanol is then clearly anomalous in that it is of opposite sign to that for Ni(CH<sub>3</sub>OH)<sub>6</sub><sup>2+</sup>. As already discussed, this anomaly can be explained by a pseudocontact contribution to the OH shift for NiCR<sup>2+</sup> in methanol. It should be noted further that the NiCR<sup>2+</sup>-OH<sub>2</sub> system is anomalous in the same sense. In our earlier study<sup>2</sup> no significance was attributed to this negative coupling constant, but in the light of the structural similarity of the methanol OH proton and water protons it now seems likely that a pseudocontact effect was also observed for NiCR<sup>2+</sup> in H<sub>2</sub>O. Unfortunately the latter system could not be studied over a wide enough temperature range to reveal any  $T^{-2}$  dependence of the shift and a detailed analysis is not possible.

In the previous study<sup>2</sup> it was found that DMF exchange is much faster from NiCR<sup>2+</sup> than from Ni<sup>2+</sup>. The present results for methanol and acetonitrile also show the much greater lability of NiCR<sup>2+</sup> and indicate that the effect is almost entirely due to a more favorable  $\Delta H^\ddagger$  for NiCR<sup>2+</sup>. However, it is not clear whether the faster exchange from NiCR<sup>2+</sup> is due to the effect of the nonreacting ligand CR or whether exchange is coupled to the diamagnetic-paramagnetic equilibrium.<sup>18</sup> This possibility was discussed more fully in our previous work.<sup>2</sup> It is interesting to note that there is a reasonable linear free energy relationship between the exchange rates and the diamagnetic-paramagnetic equilibrium constant. Such a correlation is not surprising since both processes would involve removal of a solvent molecule from the coordination sphere of nickel(II) if the exchange mechanism is dissociative.

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**Registry No.** NiCR(PF<sub>6</sub>)<sub>2</sub>, 34109-89-2; NiCR(CH<sub>3</sub>OH)<sub>2</sub><sup>2+</sup>, 54181-79-2; NiCR(CH<sub>3</sub>CN)<sub>2</sub><sup>2+</sup>, 54181-80-5.

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Contribution from the Department of Chemistry,  
University of Cincinnati, Cincinnati, Ohio 45221

## Ligand-Exchange Reactions and Isomerization of an Isoquinoline-Platinum(II) Complex

FREDERICK PESA and MILTON ORCHIN\*

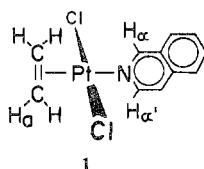
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The  $^1\text{H}$  nmr spectrum of a freshly prepared  $\text{CDCl}_3$  solution of *trans*- $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{iquin})]$ , **1**, shows no  $^3J_{\text{Pt-NCH}}$  owing to fast exchange with a small amount of adventitious free isoquinoline (iquin). However, after storage at room temperature in the dark for several days, the spectrum of the solution clearly shows the  $^3J_{\text{Pt-NCH}}$ . During the elapsed time, the uncomplexed isoquinoline is slowly consumed by reaction with **1** to form *trans*- $[\text{PtCl}_2(\text{iquin})_2]$ . Irradiation of a  $\text{CHCl}_3$  solution of **1** with ultraviolet light results in the isomerization of **1** to its *cis* isomer, probably *via* the bridged dimer  $[\text{PtCl}_2(\text{iquin})_2]$ .

### Introduction

We have shown earlier<sup>1</sup> that the  $^1\text{H}$  nmr spectrum of a freshly prepared  $\text{CDCl}_3$  solution of *trans*- $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{iquin})]$ , **1**, does not exhibit  $^3J_{\text{Pt-NCH}}$ . However, this coupling appears



when the solution is allowed to stand at room temperature for several days. We originally thought this behavior to be a consequence of a slow conformational conversion of the isoquinoline (iquin) moiety to a rigid rotamer. It was assumed that, owing to steric shielding of the empty  $p$  orbital on Pt, such a rotamer would be resistant to solvolysis and hence its  $^1\text{H}$  nmr spectrum would exhibit the observed  $^3J_{\text{Pt-NCH}}$ . Subsequently this interpretation was shown to be incorrect.<sup>2</sup> Instead it was suggested that the complex was exchanging with free ligand and the latter gradually disappeared with time. However, it was claimed that the exchange was accompanied by a slow isomerization of the *trans* complex **1** to its *cis* isomer. The *cis* isomer, **2**, was assumed to be responsible for the inhibition of isoquinoline exchange and hence the gradual appearance of coupling. The increase in the concentration of **2** was monitored by the appearance of a new ethylene proton signal.

We confirm that the initial presence, followed by the gradual disappearance of free isoquinoline, rather than conformational change, accounts for the coupling phenomena in the  $^1\text{H}$  nmr spectra. However, we find that the reported<sup>2</sup> *trans*  $\rightarrow$  *cis* rearrangement in solution probably is an adventitious photochemical reaction and the presence of the *cis* isomer is irrelevant to the pertinent coupling behavior. We also clarify the source and the eventual fate of the free ligand.

### Results and Discussion

The 90-MHz  $^1\text{H}$  nmr spectrum of **1** (Figure 1a) taken promptly in  $\text{CDCl}_3$  solution at room temperature shows no coupling of  $^{195}\text{Pt}$  with either of the  $\alpha$  protons of isoquinoline.

Although not shown in Figure 1, on cooling to about  $0^\circ$ , coupling with  $\text{H}_\alpha$  ( $J = 41$  Hz) becomes clearly apparent and on further cooling ( $\sim -40^\circ$ ) coupling with the second  $\alpha$  proton,  $\text{H}_{\alpha'}$ , also becomes apparent ( $J = 30$  Hz). On warming to room temperature and again determining the  $^1\text{H}$  nmr spectrum, the original spectrum is reproduced. In order for spin-spin coupling to be observed,<sup>3</sup> the average lifetime of the coordinated complex,  $\text{PtL}$ , must be larger than  $1/J$  and apparently the rate of exchange of L at the intermediate temperature is accidentally such that only coupling with the proton having the higher coupling constant is readily discernible.

Although no  $^3J_{\text{Pt-NCH}}$  is present in the spectrum of the fresh solution, after about 3 or more days of standing at room temperature in  $\text{CDCl}_3$  solution, the spectrum of the solution of **1** clearly shows coupling of both  $\text{H}_\alpha$  and  $\text{H}_{\alpha'}$  at room temperature. A typical spectrum of an aged solution is shown in Figure 1b. The coupling constants and chemical shifts of  $\text{H}_\alpha$  and  $\text{H}_{\alpha'}$  are virtually the same as those observed in the nmr spectrum of the fresh solution of  $-40^\circ$ .

When the freshly prepared  $\text{CDCl}_3$  solution is extracted with either  $\text{HBF}_4$  or passed over a cation-exchange resin,<sup>4</sup> free ligand is removed and the solution now exhibits  $^3J_{\text{Pt-NCH}}$ . The recovery of pure isoquinoline from the extract has been demonstrated.<sup>4</sup> Addition of a small quantity of isoquinoline to the treated solution results in the loss of coupling. The generality of this behavior and its quantitative aspects are under study.

It is clear from the above facts that free ligand is responsible for fast exchange and the absence of coupling in the freshly prepared solution of **1**. However, the fate of the ligand in aged solutions remains to be demonstrated. We believe that the free ligand gradually disappears by irreversible formation of *trans*- $[\text{PtCl}_2(\text{iquin})_2]$ , **3**. The presence of **3** is difficult to show because it is present in such small amounts. However, if a small quantity of additional isoquinoline is added to the aged  $\text{CHCl}_3$  solution of **1**, **3** is precipitated. The properties of this precipitate correspond to those of **3** separately prepared in good purity and yield by adding stoichiometric quantities of isoquinoline to a chloroform solution of **1**. We find no evidence for the formation of the *cis* isomer **2** in the absence of ultraviolet light.