noted that the presentation of the data in Figure 2 does not necessarily imply a relationship between d-electron population and chemical shift values. For example, it will be noted that the chemical shifts fall into groups depending on whether the stereochemistry of the complex is tetrahedral, square planar, or octahedral. Unfortunately, rationalizations such as those examined for [acac]⁻ complexes and outlined at the commencement of this discussion do not singularly account for the observed groupings of the chemical shift values of the 1,3-dithio chelates.

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Registry No. *cis*-Co(OEt-SacSac)$_3$, 54340-43-1; *trans*-Co(OEt-SacSac)$_3$, 54382-40-0; *cis*-Rh(OEt-SacSac)$_3$, 54340-44-2; *trans*-Rh(OEt-SacSac)$_3$, 54382-41-1; *cis*-Ir(OEt-SacSac)$_3$, 54365-68-3; *trans*-In(OEt-SacSac)$_3$, 54422-35-4; Fe(OEt-SacSac)$_3$, 54365-69-4; Ru(OEt-SacSac)$_3$, 54365-70-7; Os(OEt-SacSac)$_3$, 54365-71-8.

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Kinetics and Mechanism of the Chloride Anation of *trans*-Diaquobis(ethylenediamine)rhodium(III) Complex Ion in Aqueous Solution

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The kinetics of the chloride anation of *trans*-Rh(en)$_2$(H$_2$O)$_2^{3+}$ in aqueous solution have been studied at 40, 50, and 65° with 0.02 $M <$ (H$^+$) < 0.2 M and 0.2 $M <$ (Cl$^-$) < 1.0 M at unit ionic strength. Under all conditions *trans*-Rh(en)$_2$Cl$_2^+$ is the only observed product indicating that the substitution of the first Cl$^-$ is rate determining. The rate shows a strong inverse dependence on (H$^+$) indicating that the base form of the complex, *trans*-Rh(en)$_2$(OH)(H$_2$O)$^{2+}$, is some 10^3 times more reactive than the conjugate acid form, *trans*-Rh(en)$_2$(H$_2$O)$_2^{3+}$. This behavior allows a kinetic distinction to be made between two possible explanations of the less than first-order dependence of the rate on (Cl$^-$). It is found that the data cannot be fitted to an interchange stoichiometric mechanism rate law but can be fitted to a dissociative stoichiometric mechanism rate law. Therefore, by default, it is assumed that *trans*-Rh(en)$_2$(H$_2$O)$_2^{3+}$ and/or *trans*-Rh(en)$_2$(OH)(H$_2$O)$^{2+}$ anates *via* a dissociative stoichiometric mechanism. Comparing this result with those obtained for related complexes indicates that the substitution mechanism of an octahedral complex is far more sensitive to the nature of the inert ligands when the central atom is rhodium(III) than when the central atom is cobalt(III).

Introduction

Studies of the substitution reactions of octahedral complexes have been extensive and have yielded a fairly clear picture of the general mechanisms by which these complexes undergo reaction.[1,2] They seem to react either *via* a dissociative or an interchange stoichiometric mechanism, with either associative or dissociative activation occurring in an interchange mechanism.[3] However, our knowledge of the specific factors that determine which of these mechanisms is used by a complex is still extremely shallow. It is believed that such a knowledge can be obtained if the reaction mechanisms of a series of related complexes are known. For example, data indicate that Rh(NH$_3$)$_5$H$_2$O^{3+} anates *via* an associative interchange mechanism[4-6] while RhCl(H$_2$O)$_5^{2+}$ and/or RhCl(OH)(H$_2$O)$_4^+$ anates *via* a dissociative mechanism.[7] Some idea as to what is causing this difference in mechanism between these fairly dissimilar complexes could be obtained if the substitution mechanism employed by *trans*-Rh(en)$_2$(H$_2$O)$_2^{3+}$ were known. This latter complex can be thought of as intermediate between the others since it predominantly contains amine ligands as does Rh(NH$_3$)$_5$H$_2$O^{3+} but does have an inert oxygen-bonded ligand as do the chloroaquo complexes. This particular example prompted the present research which is an attempt to elucidate the substitution mechanism of *trans*-Rh(en)$_2$(H$_2$O)$_2^{3+}$.

Three experimental approaches are available which allow a fairly unambiguous distinction to be made between the interchange and dissociative stoichiometric mechanisms for anation reactions of octahedral complexes. These are the independent determination of apparent ion-pair constants,[5,8] a reverse kinetic saturation technique,[9] and the determination of the kinetic behavior of diaquo complexes as a function of acidity.[7] It is this last approach that is used in the present study to judge the mechanism of the Cl$^-$ anation of *trans*-Rh(en)$_2$(H$_2$O)$_2^{3+}$ and its conjugate base *trans*-Rh(en)$_2$(OH)(H$_2$O)$^{2+}$.

Experimental Section

Materials. Deionized water with a specific resistance greater than 100 megohm cm was obtained by passing tap water through a commercial charcoal and mixed-bed ion exchanger. Stock solutions of HClO$_4$, HCl, NaOH, and NaCl were prepared by dissolving reagent grade chemicals in deionized water. The concentrations of the NaCl solutions were determined from the weight of reagent added whereas those of the HClO$_4$, HCl, and NaOH solutions were de-

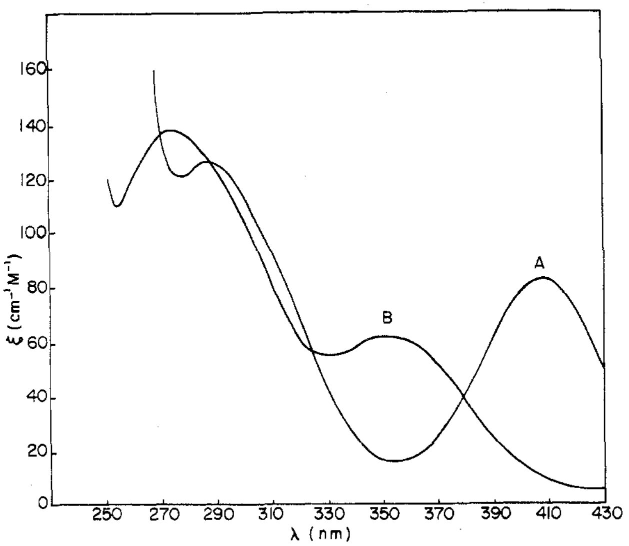

Figure 1. Visible-ultraviolet absorption spectra at $I = 1.00\ M$: A, *trans*-$Rh(en)_2Cl_2^+$; B, *trans*-$Rh(en)_2(H_2O)_2^{3+}$, $(H^+) \geqslant 0.02\ M$.

termined by titration using potassium acid phthalate as a primary standard. The preparation and standardization of stock $NaClO_4$ solutions were accomplished as previously outlined.[7] $AgClO_4$ solutions were prepared by passing solutions of $AgNO_3$ through a column of Bio-Rad AG1-X4, 50–100 mesh resin in the ClO_4^- form. The solutions were standardized by the Mohr method.

Solid *trans*-$Rh(en)_2Cl_2(ClO_4)$ was prepared by the published method.[10a] The visible–ultraviolet spectrum of the complex in aqueous solutions maintained at an ionic strength, I, of 1.00 M with $NaClO_4$ and/or NaCl is shown in Figure 1. The absorption maxima at 287 and 407 nm with extinction coefficients of 126.4 ± 1.4 and 82.5 ± 0.6 (cm $M)^{-1}$, respectively, are in close agreement with those previously reported.[11] Within the precision of the measurements, the spectrum of the complex is unaffected by changes in the relative amounts of $NaClO_4$ and NaCl used to maintain the ionic strength or by changes in the ionic strength itself.

Solid *trans*-$Rh(en)_2(OH)(H_2O)(ClO_4)_2$ was prepared, with some variations, by the method outlined by Poë and Shaw.[11] One-half gram of *trans*-$Rh(en)_2Cl_2(ClO_4)$ and 2 equiv of NaOH made up to a volume of 15 ml with water was placed in a flask attached to a reflux condenser. The solution was gently heated and agitated until all the complex had dissolved. Heating was continued to boil the solution for 15 min (the solution paled within the first minute of boiling). The solution was then combined with 20 ml of water in an ice bath and allowed to cool to room temperature. The pH of the solution was adjusted to 4–6 (all pH adjustments were made with 0.5 M $HClO_4$ or 0.2 M NaOH and were monitored with pHydrion paper), 0.1 M $AgClO_4$ was added in 10% excess, and the solution was filtered. The pH was adjusted to 10–11 and the solution was filtered to remove excess Ag^+ ions. The pH was then adjusted to 5–6. At this point the solution volume was 75–80 ml; this was reduced to 10–15 ml on a steam bath. While standing overnight at room temperature, pale yellow, needle-shaped crystals formed. These were collected by filtration, washed with ethanol and ethyl ether, and air-dried. They were further purified by one recrystallization from water. The average yield was 0.35 g. *Anal.* Calcd for $Rh(en)_2(OH)(H_2O)(ClO_4)_2$: C, 10.5; N, 12.3; H, 4.2; Cl, 15.5. Found: C, 10.4; N, 12.4; H, 4.2; Cl, 15.3.

The visible–ultraviolet spectrum of the acid form of the complex, *trans*-$Rh(en)_2(H_2O)_2^{3+}$, in aqueous solutions where $(H^+) \geq 0.02\ M$ and $I = 1.00\ M$ with $NaClO_4$ and/or NaCl is shown in Figure 1. The maxima occur at 274 and 351 nm with extinction coefficients of 138.1 ± 0.8 and 61.6 ± 0.6 (cm $M)^{-1}$, respectively. This is similar to the spectrum previously reported[11] except that the maxima are found at about 10 nm higher wavelength. The spectrum of the diaquo complex is unaffected by changes in the relative amounts of $NaClO_4$ and NaCl used to maintain the ionic strength, I, although the ultraviolet region is affected by its value. With $I \leq 0.3\ M$, the extinction coefficient of the 274-nm maximum becomes 130.0 ± 0.9 (cm $M)^{-1}$.

pH Titrations. The pH of the solutions was monitored with an Accumet Model 420 digital pH meter using a glass electrode and a calomel electrode filled with saturated NaCl solution. This apparatus was standardized as follows. A solution of 1.00 M sodium salt was placed in a cell thermostated to ±0.1°. The electrodes were inserted, the cell covered as much as possible with sheets of parafilm, and a stream of N_2 inserted above the solution. After thermal equilibrium had been established, the solution was titrated with 0.1 M $HClO_4$ or HCl solution made up to an ionic strength of 1.00 M with the corresponding sodium salt. The data plotted as pH (calculated) *vs.* pH (observed) gave straight lines over a pH (calculated) range of about 2.0–4.2, with individual titration points being within ±0.01 pH unit of the best fit straight line. It can be seen that this titration standardization procedure allows the calculation of hydrogen ion concentrations at $I = 1.00\ M$ rather than hydrogen ion activities. In one instance the applicability of the acid range standardization data to the entire pH range was checked by titrating the acid solution with 0.1 M NaOH, $I = 1.00\ M$. The data points in the pH (calculated) range of 9.5–10.8 fell within ±0.03 pH unit of the standardization line established by the data in the 2.0–4.2 pH (calculated) range.

Table I. Acid-Base Hydrolysis Constants of *trans*-$Rh(en)_2(H_2O)_2^{3+}$ Ion at 1.00 M Ionic Strength[a]

Temp, °C	Salt	$-\log P_1$	$-\log P_2$
65.0	$NaClO_4$	(3.82)[b]	
50.5	$NaClO_4$	3.99	7.47
50.0	$NaClO_4$	4.05	7.57
39.5	$NaClO_4$	4.17	7.47
39.5	$NaClO_4$	4.17	7.37
26.4	$NaClO_4$	4.40	7.64
26.4	$NaClO_4$	4.34	7.63
26.4	NaCl	4.51	
26.4	NaCl	4.47	

[a] (Complex) = 0.0015 M. [b] Extrapolated from measured data.

Immediately after the acid standardization titration solid *trans*-$Rh(en)_2(OH)(H_2O)(ClO_4)_2$ was added to the solution. The pH change that accompanied the dissolution of the complex indicated the uptake of 1 mol of H^+/mol of complex. After dissolution the solution was titrated with 0.1 M NaOH, $I = 1.00\ M$. The titration curves show two well-separated buffering regions interpreted as being caused by the equilibria

$$[trans\text{-}Rh(en)_2(H_2O)_2^{3+}] \overset{P_1}{\rightleftharpoons} [trans\text{-}Rh(en)_2(OH)(H_2O)^{2+}] + H^+ \quad (1)$$

$$[trans\text{-}Rh(en)_2(OH)(H_2O)^{2+}] \overset{P_2}{\rightleftharpoons} [trans\text{-}Rh(en)_2(OH)_2^{+}] + H^+ \quad (2)$$

In these equations the formulas of the variously protonated species are bracketed to indicate that a portion of each species may be ion paired in solution.

A value for P_1 or for P_2 was calculated from each titration point in the corresponding buffer region. The average values obtained from each titration curve are listed as $-\log P$ values in Table I. Where the background salt was $NaClO_4$ ten titration points from each buffer region were used in the analysis. The average deviation of $-\log P_1$ in a given titration was ±0.01 unit, while that for $-\log P_2$ was ±0.02 unit. Plots of $-\log P_1$ *vs.* the reciprocal absolute temperature were analyzed by a nonweighted least-squares treatment.[12] This gives $\Delta H° = 6.5 \pm 0.6$ kcal/mol and $\Delta S° = 2 \pm 2$ cal/(deg mol) for P_1 in 1.00 M $NaClO_4$ media.

Where the background salt was NaCl, seven titration points in the first half of the P_1 buffer region were obtained within 3 min. The use of longer times or more extensive titrations is complicated by the Cl^- anation of the complex. The average deviation of the $-\log P_1$ for a given titration in NaCl medium is ±0.01 log unit.

It was found that the *trans*-$Rh(en)_2(OH)(H_2O)^{2+}$ complex undergoes some unknown, possibly polymerization, reaction in solution. Neutral solutions of the complex were allowed to stand at room temperature for 1–5 days at which time they were acidified and their visible–ultraviolet spectra recorded. The spectra are quite unlike that of *trans*-$Rh(en)_2(H_2O)_2^{3+}$ (see Figure 1), having two maxima below 320 nm with extinction coefficients ranging up to 600 (cm $M)^{-1}$. The features of the spectra depend on the storage time and possibly on the $NaClO_4$ concentration. Solutions of the diaquo and dihydroxy forms of the complex treated in an identical fashion showed no reaction. Although this reaction of *trans*-$Rh(en)_2(OH)(H_2O)^{2+}$ seems similar to that observed with other hydroxyrhodium complexes,[7] it was not investigated further, except to establish that this reaction does not interfere with the experiments that are pertinent to the goals of this study. Upon completion of the 50.5° pH titration (see Table I), the solution was acidified and its spectrum obtained. The spectrum was identical with that of *trans*-$Rh(en)_2(H_2O)_2^{3+}$ shown in Figure 1. Also, the spectra of the kinetic runs (see below) indicate no reaction taking place other than the Cl^- anation of mononuclear complexes.

Kinetics. Solutions containing the desired amounts of $HClO_4$ or HCl, $NaClO_4$, NaCl, and deionized water were made up volumetrically at room temperature. To these were added aliquots of a freshly prepared solution of *trans*-$Rh(en)_2(OH)(H_2O)(ClO_4)_2$ and $HClO_4$ or HCl. The concentration ranges for the final solutions were (complex)[13] = 0.001 *M*, $I = 1.00$ *M*, 0.2 *M* < (Cl^-) < 1 *M*, and 0.02 *M* < (H^+) < 0.2 *M*. The solutions were placed in a bath controlled to ± 0.02° and allowed 20–30 minutes to become thermally equilibrated. Periodically aliquots of the solution were removed, cooled in an ice bath, and stored at 5°. Five samples were extracted from each solution. Subsequently the samples were allowed to warm to room temperature and their visible–ultraviolet spectra were obtained.

Under all conditions studied the reaction solutions clearly showed the four isosbestic points (at 271, 288, 324, and 379 nm) indicated in Figure 1. Thus the only complexes observable in solution are *trans*-$Rh(en)_2(H_2O)_2^{3+}$ and *trans*-$Rh(en)_2Cl_2^+$. It will be assumed that the substitution of the first Cl^- is rate determining and that the chloroaquo complex thus formed rapidly reacts with a second Cl^- to give the observed dichloro product. The pseudo-first-order rate constant, k_{obsd}, for the disappearance of *trans*-$Rh(en)_2(H_2O)_2^{3+}$ was evaluated for each run from the slope of a plot of log $(A_\infty - A_t)$ *vs.* time. A_∞ is the calculated absorbance of the solution at 407 nm for the condition where all the complex has been converted to *trans*-$Rh(en)_2Cl_2^+$ and A_t is the actual absorbance of the solution at 407 nm at time *t*. These plots were linear under all conditions studied over at least 2 half-lives of the reaction. The reaction will go to completion under the conditions used.[10b]

All visible–ultraviolet spectra in this study were obtained on a Cary 118C spectrophotometer.

Results

A study was first made of the dependence of k_{obsd}, the pseudo-first-order rate constant for the disappearance of *trans*-$Rh(en)_2(H_2O)_2^{3+}$, on the proton concentration. The data at 50 and 65° are plotted in Figure 2 as k_{obsd} *vs.* the reciprocal proton concentration. It can be seen that at both temperatures the data describe straight lines with positive slopes and intercepts. This behavior can be interpreted according to the reactions and rate expression

$$[ML_4(H_2O)_2] \overset{P_1}{\rightleftharpoons} [ML_4(OH)(H_2O)] + H^+ \qquad (1)$$

$$[ML_4(H_2O)_2] \xrightarrow[(Cl^-)]{F_a} \text{product} \qquad (3)$$

$$[ML_4(OH)(H_2O)] \xrightarrow[(Cl^-)]{F_b} \text{product} \qquad (4)$$

$$k_{obsd} = F_a + F_b[P_1/(H^+)] \qquad (5)$$

where ML_4 is *trans*-$Rh(en)_2$, F_a is the pseudo-first-order rate expression describing the reaction of the acid form of the complex with Cl^-, and F_b is the corresponding expression for the reaction of the base form of the complex. The formulas of the complexes are written without charges for convenience and are bracketed to indicate that a portion of each complex is ion-paired in solution. Equation 5 holds where $(H^+) >> P_1$ which is the condition of this study.

The data in Figure 2 indicate that the base form of the complex, *trans*-$Rh(en)_2(OH)(H_2O)^{2+}$, is orders of magnitude more reactive to Cl^- anation than is the acid form of the complex, *trans*-$Rh(en)_2(H_2O)_2^{3+}$. For example at $1/(H^+) = 50$ M^{-1} the data in Table I indicate that less than 1% of the complex is in the basic form; however, this basic form accounts for more than 95% of the observed rate.

Data showing the dependence of k_{obsd} on the concentration of Cl^- at various temperatures and acidities is given in Figures 3–5. At each temperature and acidity the data do not describe a straight line but one that is curving downward. This less than first-order dependence of k_{obsd} on (Cl^-) can be described by an equation of the form

$$k_{obsd} = \frac{R(Cl^-)}{1 + S(Cl^-)} \qquad (6)$$

where *S* will be referred to as the saturation parameter and is responsible for the curvature of the plot. Two mechanisms, the interchange and the dissociative stoichiometric mechanisms, have been put forth to explain this type of behavior.[2] For systems, such as the present one, where the basic form of the complex is orders of magnitude more reactive than the acid form, a distinction between these two possible mechanisms can be made from kinetic data alone.[7]

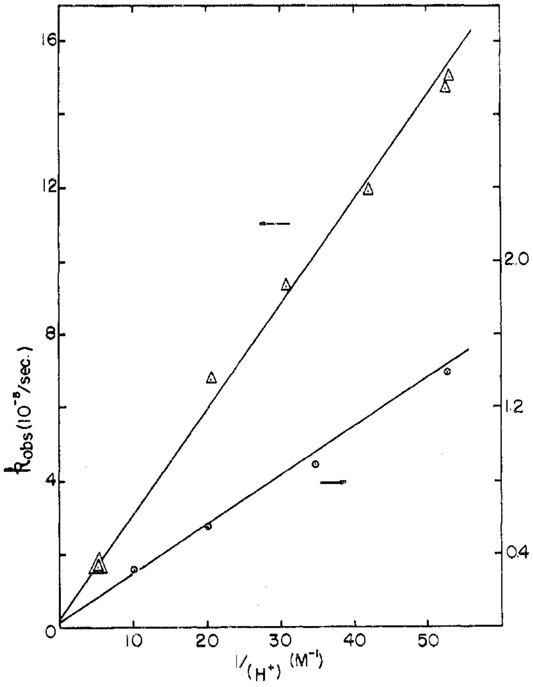

Figure 2. Dependence of k_{obsd} on reciprocal concentration of H^+, with $I = 1.00$ *M*, (complex) = 0.001 *M*: △, 65°, (NaCl) = 0.801 *M*; ○, 50°, (NaCl) = 0.641 *M*. Arrows indicate the corresponding ordinate.

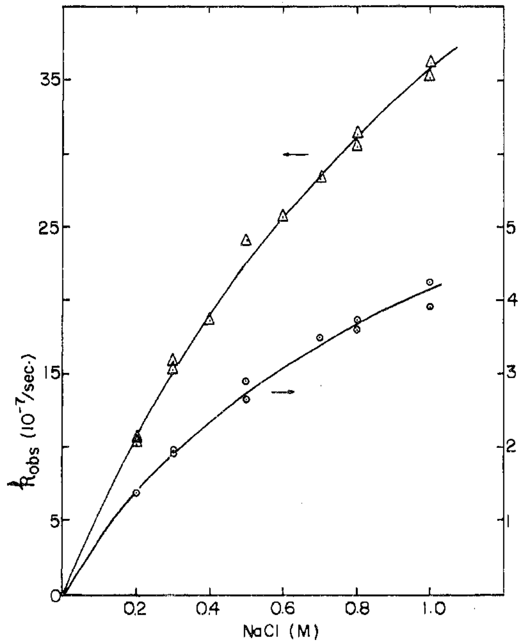

Figure 3. Dependence of k_{obsd} on concentration of chloride with $T = 40°$, $I = 1.00$ *M*, and (complex) = 0.001 *M*: △, $(H^+) = 0.0190$ *M*; ○, $(H^+) = 0.199$ *M*. Arrows indicate the corresponding ordinate.

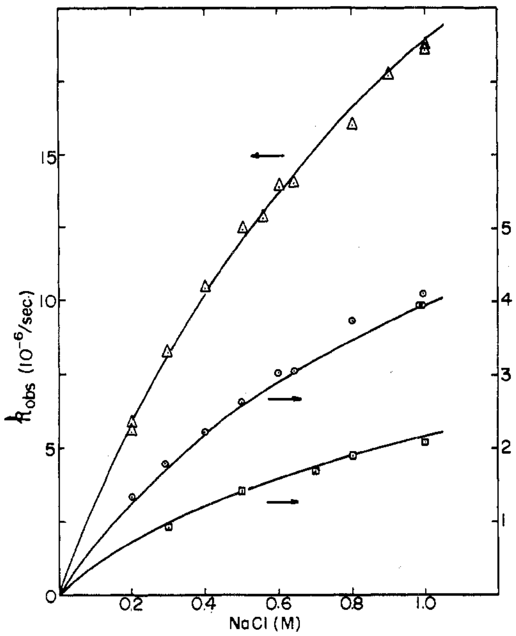

Figure 4. Dependence of k_{obsd} on concentration of chloride with $T = 50°$, $I = 1.00\ M$, and (complex) = 0.001 M: △, (H^+) = 0.0190 M; ○, (H^+) = 0.099 M; □, (H^+) = 0.199 M. Arrows indicate the corresponding ordinate.

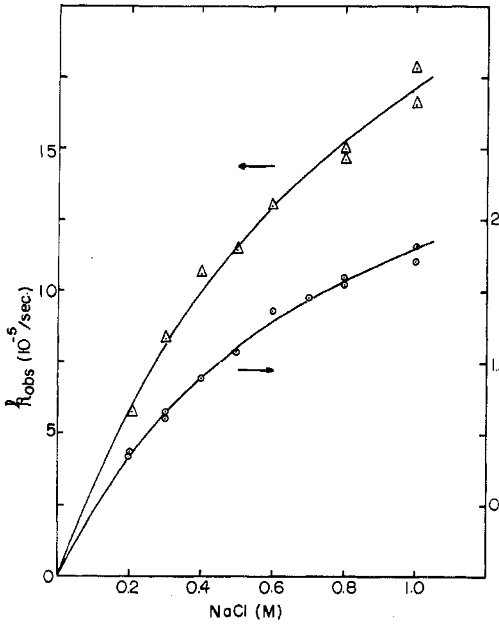

Figure 5. Dependence of k_{obsd} on concentration of chloride with $T = 65°$, $I = 1.00\ M$, and (complex) = 0.001 M: ○, (H^+) = 0.199 M; △, (H^+) = 0.0190 M. Arrows indicate the corresponding ordinate.

In solutions containing cationic complexes and high concentrations of anions, it must be assumed that ion pairs exist. The fact that ion pairs exist in the present case is indicated by the variation in the ultraviolet spectrum of the diaquo complex with ionic strength (see Experimental Section). Thus the continuously and simultaneously maintained equilibria 7–10

$$ML_4(H_2O)_2 + Y \overset{K_Y}{\rightleftharpoons} ML_4(H_2O)_2{\cdot}Y \tag{7}$$

$$ML_4(H_2O)_2 + Z \overset{K_Z}{\rightleftharpoons} ML_4(H_2O)_2{\cdot}Z \tag{8}$$

$$ML_4(OH)(H_2O) + Y \overset{K_Y'}{\rightleftharpoons} ML_4(OH)(H_2O){\cdot}Y \tag{9}$$

$$ML_4(OH)(H_2O) + Z \overset{K_Z'}{\rightleftharpoons} ML_4(OH)(H_2O){\cdot}Z \tag{10}$$

must be assumed, where Y is the reactive anion Cl^-, Z is the unreactive anion ClO_4^-, and the species on the right side of the equations represent outer-sphere ion pairs. The presence of these ion pairs can affect the value of the overall hydrolysis constant, P_1 (eq 1). Where the hydrolysis constant for the nonpaired species is defined as Q

$$ML_4(H_2O)_2 \overset{Q}{\rightleftharpoons} ML_4(OH)(H_2O) + H^+ \tag{11}$$

P_1 becomes

$$P_1 = K_h\left[\frac{1 + K'(Y)}{1 + K(Y)}\right] \tag{12}$$

where $K_h = Q(1 + K_Z'I)/(1 + K_ZI)$ and is the overall hydrolysis constant, P_1, in pure ClO_4^- media; I is the ionic strength; $K = (K_Y - K_Z)/(1 + K_ZI)$ and $K' = (K_Y' - K_Z')/(1 + K_Z'I)$. The data in Table I show a small variation in P_1 as (Y) = (Cl^-) is changed from 0 to 1 M.

In the interchange stoichiometric mechanism it is assumed that the only species in solution that can give rise to products are the Y ion-paired species. Reaction occurs *via* the interchange of outer-sphere Y with inner-sphere water

$$ML_4(H_2O)_2{\cdot}Y \xrightarrow{k} ML_4(H_2O)Y + H_2O \tag{13}$$

$$ML_4(OH)(H_2O){\cdot}Y \xrightarrow{k'} ML_4(OH)Y + H_2O \tag{14}$$

From eq 7, 8, and 13, the rate expression for the acid form of the complex is

$$F_a = \frac{k_{in}K(Y)}{1 + K(Y)} \tag{15}$$

where $k_{in} = kK_Y/(K_Y - K_Z)$ and K is as defined for eq 12. An analogous primed expression can be derived for the reaction of the base form of the complex, F_b. Substituting for F_a, F_b, and P_1 into eq 5 gives

$$k_{obsd} = \frac{k_{in}K(Y) + k'_{in}K'(Y)K_h/(H^+)}{1 + K(Y)} \tag{16}$$

In the dissociative stoichiometric mechanism it is assumed that each of the species in eq 7–10 can give rise to product. Reaction occurs *via* the dissociation of a water ligand creating steady-state amounts of a five-coordinate intermediate which is stable enough to react selectively with either Y or H_2O. For the free diaquo complex this is represented by

$$ML_4(H_2O)_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ML_4(H_2O) + H_2O \tag{17}$$

$$ML_4(H_2O) + Y \xrightarrow{k_3} ML_4(H_2O)Y \tag{18}$$

A similar set of equations with different rate constants must be written for the five other species in eq 7–10. The complete set of equations yield

$$F_a = \frac{A(Y) + C(Y)^2 + E(Y)^3 + G(Y)^4}{1 + B(Y) + D(Y)^2 + F(Y)^3 + H(Y)^4} \tag{19}$$

$$F_b = \frac{A'(Y) + C'(Y)^2 + E'(Y)^3 + G'(Y)^4}{1 + B'(Y) + D'(Y)^2 + F'(Y)^3 + H'(Y)^4} \tag{20}$$

where the parameters A, A', B, B', etc. are complicated combinations of the ion-pair constants (eq 7–10), various rate constants (*i.e.*, eq 17 and 18), and the ionic strength.

If it is assumed that only the terms that are first power in (Y) are experimentally significant in eq 19 and 20 and that $P_1 = K_h$ (see eq 11), substitution into eq 5 gives eq 21 as a rate law for the dissociative mechanism.[14]

$$k_{obsd} = \frac{A(Y)}{1 + B(Y)} + \frac{A'(Y)K_h/(H^+)}{1 + B'(Y)} \tag{21}$$

Table II. Test of the Interchange Rate Law

Temp, °C	$(H^+), M$	Obsd saturation parameter, S, M^{-1}
40.0	0.0190	0.65 ± 0.08
	0.199	1.06 ± 0.10
50.0	0.0190	0.79 ± 0.05
	0.0990	0.91 ± 0.08
	0.199	0.89 ± 0.12
65.0	0.0190	1.13 ± 0.12
	0.199	1.33 ± 0.06

Table III. Kinetic Parameters for a Dissociative Rate Law[a]

Temp, °C	$10^6A, M^{-1}$ sec^{-1}	B, M^{-1}	$10^3A', M^{-1}$ sec^{-1}	B', M^{-1}
40.0	0.35 ± 0.10	3.4 ± 1.6	1.61 ± 0.06	0.67 ± 0.08
50.0	1.26 ± 0.58	2.3 ± 1.9	6.4 ± 0.2	0.76 ± 0.09
65.0	10.6 ± 5.0	3.6 ± 2.7	44 ± 2	1.08 ± 0.11

[a] Ionic strength 1.00 *M*.

Inspection of eq 16 and 21 shows how these rate laws may be distinguished experimentally. Equation 21, even though it is a heavily simplified rate law, is less restrictive than the nonsimplified eq 16. It has four adjustable parameters as opposed to only three in eq 16. Thus a distinction between the two rate laws can be made by judging whether the more restrictive eq 16 gives an adequate fit to the data. The approach to be used in the present case employs the following reasoning. The difference between the two rate laws lies in their saturation parameters. In the interchange rate law the expression for the reaction of the acid complex and that for the base complex have the same saturated parameter, K. In the dissociative rate law the acid and base expressions have different saturation parameters, B and B'. Thus the fit of the data to eq 16 can be tested by determining the observed saturation parameter (S of eq 6) at each individual acidity. If eq 16 is adequate, the observed saturation parameter will not vary with acidity at a given temperature, being equal to K at each acidity. If a more complex relationship such as eq 21 is necessary, the observed saturation parameter will vary with acidity, predominantly reflexing the value of B' at low acidity and moving toward the value of B at high acidity.

The data at each individual acidity in Figures 3–5 were fitted to eq 6 using a nonlinear weighted least-squares method.[15] The best fit values of R and S generate curves that are nearly identical with the solid lines in the figures. The analysis gives the standard deviation of the individual k_{obsd} values as 3–4%. The values and standard deviations of S, the observed saturation parameter, are listed in Table II as a function of temperature and acidity. At 50° the S values are identical within experimental error. However, at 65° the saturation parameters at the two acidities differ by more than one standard deviation, while those at 40° differ by more than two standard deviations. If a statistical "t" test is applied[16] to the difference between the S values at both 65 and 40°, it is found that there is a less than 20% probability that the S values at 65° are identical and a less than 0.1% probability that the 40° S values are identical. Therefore it must be concluded that the data at 65 and 40°, but especially those at 40°, do not give an adequate fit to eq 16, the interchange mechanism rate law.

The data do give an adequate fit to eq 21, the dissociative mechanism rate law. This is not surprising as the equation has four adjustable parameters allowing the observed saturation parameter to vary with acidity. Due to its complexity eq 21 would probably fit any set of anation data. The data at each temperature in Figure 2–5 were fitted to eq 21 using a nonlinear weighted least-squares method.[15] The best fit values of A, B, A', and B' along with their standard deviations are listed in Table III. The solid lines in Figures 2–5 are plots of eq 21 using these best fit values and K_h ($=P_1$ in $NaClO_4$ media) values from Table I. The analysis gives the standard deviation of the individual k_{obsd} values as 3–4%. The temperature dependences of the four kinetic parameters were analyzed according to transition-state theory. For the purpose of this analysis A and A' were viewed as second-order rate constants; B and B', as ratios of second-order to first-order rate constants.[17] The activation parameters and their standard deviations listed in Table IV were evaluated by a nonweighted linear least-squares treatment.[12] The intrinsic uncertainties listed in Table III were not considered in evaluating the standard deviations of the activation parameters. Thus these standard deviations simply reflect the linearity of the three point temperature plots.

Table IV. Temperature Parameters for a Dissociative Rate Law[a]

Kinetic parameter	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(deg mol)	$\Delta(\Delta H^{\ddagger})$, kcal/mol	$\Delta(\Delta S^{\ddagger})$, cal/(deg mol)
A	28.6 ± 1.5	3 ± 5		
B			1 ± 4	5 ± 12
A'	27.2 ± 0.4	16.8 ± 1.4		
B'			4.1 ± .7	12.4 ± 2.2

[a] Ionic strength 1.00 *M*.

Some comments should be made concerning attempts to judge the fit of the data to eq 16, the interchange rate law, by using the parameters in Table III. It can be seen that eq 16 holds if B and B' of eq 21 are experimentally indistinguishable. However, a simple inspection of the values and standard deviations of B and B' in Table III is not the most critical test of the adequacy of eq 16. The standard deviations listed in Table III are overly large for this purpose due to the strong coupling of the standard deviations of A, A', B, and B' in the least-squares analysis. The four parameters cannot be independently varied.[18] If one parameter is allowed to vary within its standard deviation range, the other parameters must be varied in a systematic manner in order to maintain an adequate fit. Therefore the interrelationships, or coupling, of the standard deviations of A, A', B, and B' must be understood before a critical judgement can be made on whether the condition $B = B'$ gives an adequate fit to the data. Such an understanding is difficult to achieve. However, this whole problem is circumvented in Table II where the data are analyzed in such a manner that the parameters to be compared are not coupled in the analysis.

Discussion

It was assumed that the kinetic data obtained in this study measure the rates of formation of *trans*-$Rh(en)_2Cl(H_2O)^{2+}$ and *trans*-$Rh(en)_2Cl(OH)^+$. The observed product, *trans*-$Rh(en)_2Cl_2^+$, results from the rapid anation of these first formed products. The validity of this interpretation depends on the relative Cl^- anation rate of *trans*-$Rh(en)_2Cl(H_2O)^{2+}$ since the acid–base equilibrium of the monochloro species will be rapidly established and should be pushed to the acid side with $(H^+) > 0.019$ *M*. It has been found[19] that the second-order rate constant for the Cl^- anation of *trans*-$Rh(en)_2Cl(H_2O)^{2+}$ is 7.2×10^{-4} M^{-1} sec^{-1} at 50° and $I = 0.2$ *M*. The highest anation rates observed at 50° in the present study are those at $(H^+) = 0.019$ *M* where $k_{obsd}/(Cl^-)$ varies from 0.19×10^{-4} M^{-1} sec^{-1} at $(Cl^-) = 1$ *M* to 0.29×10^{-4} M^{-1} sec^{-1} at $(Cl^-) = 0.2$ *M*. Obviously, with the second Cl^- adding at a rate that is more than 20 times faster than that of the first Cl^-, no buildup of the monochloro species is observed. This behavior can be attributed to the strong trans-labilizing ability of a Cl^- ligand in the complex. The fact that *trans*-$Rh(en)_2(OH)(H_2O)^{2+}$ anates some 10^3 times faster than *trans*-$Rh(en)_2(H_2O)_2{}^{3+}$ can also be attributed to a trans effect of the OH^- ligand. Such trans-labilizing effects are commonplace in octahedral rhodium complexes.[7,11]

Table V. Observed Rate Parameters[a] at (Y) = 0.2 *M* for *trans*-$Rh(en)_2(OH)(H_2O)^{2+}$ + Y → *trans*-$Rh(en)_2(OH)Y^+$ + H_2O

Temp, °C	$k_{obsd}/(I^-)$[b]	$k_{obsd}/(Cl^-)$[c]	$k_{obsd}/(Br^-)$[d]	$k_{obsd}/(Cl^-)$[e]
50	72	52	1.5	0.54
40			0.29	0.10
35	11	6.3		
20	1.2	0.65		

[a] $k_{obsd}/(Y)$ in units of 10^{-4} M^{-1} sec^{-1}. [b] Reference 11; $I = 0.2$ *M*, pH 6.1. [c] This paper; $I = 1$ *M*, calculated for pH 6.1 from values in Tables III and IV taking $k_{obsd}/(Cl^-) = A'/(1 + B'(Cl^-))$. [d] Reference 11; $I = 0.2$ *M*, pH 2.0. [e] This paper; $I = 1$ *M*, calculated for pH 2.0 from values in Tables I and III taking $k_{obsd}/(Cl^-) = A'K_h/(1 + B'(Cl^-))(H^+)$.

Poe and Shaw[11] have studied the anation of *trans*-$Rh(en)_2(OH)(H_2O)^{2+}$ by I^- at pH 6.1. Their data at $(I^-) = 0.2$ *M* are compared with the calculated Cl^- anation rates of the basic complex at pH 6.1, $(Cl^-) = 0.2$ *M*, in Table V. As can be seen from the second and third columns of the table, the reaction rates of the two anions are quite similar at 50, 35, and 20°, with the I^- rates being 1.3–1.9 times those of Cl^-.

Poë and Shaw[11] also studied the Br^- anation of the complex at pH 2. They assumed that the data measured the anation rate of *trans*-$Rh(en)_2(H_2O)_2^{3+}$ since at this pH more than 99% of the complex is in this diaquo form. However, the Cl^- anation data of the present study (see eq 5 and Figure 2) indicate that the basic form of the complex, *trans*-$Rh(en)_2(OH)(H_2O)^{2+}$, accounts for more than 95% of the observed rate even at pH 2. That the Br^- anation data actually refer to the hydroxyaquo complex can be seen from comparisons of the fourth and fifth columns of Table V. The observed Br^- anation rates are only about 3 times larger than the corresponding Cl^- anation rates of the hydroxyaquo complex. This similarity in rates is expected since I^- and Cl^- have similar anation rates. In contrast, the observed Br^- anation rates are some 100 times greater than the Cl^- anation rates of *trans*-$Rh(en)_2(H_2O)_2^{3+}$. (At $(Cl^-) = 0.2$ *M*, $k_{obsd}/(Cl^-)$ for the diaquo complex is slightly smaller than the *A* values given in Table III.) The interpretation of Poë and Shaw's data at pH 2 as being the Br^- anation of *trans*-$Rh(en)_2(OH)(H_2O)^{2+}$ also explains the relatively high activation parameters they observed: $\Delta H^‡_{obsd} = 32$ kcal/mol and $\Delta S^‡_{obsd} = 23$ cal/(deg mol). According to eq 21, $k_{obsd}/(Br^-)$ has the approximate form $A'K_h/(H^+)$ when $(Br^-) \leq 0.2$ *M* at pH 2. This is true regardless of which stoichiometric mechanism is most appropriate to the reaction. Thus $\Delta H^‡_{obsd} = \Delta H^‡(A') + \Delta H°(K_h)$ and $\Delta S^‡_{obsd} = \Delta S^‡(A') + \Delta S°(K_h) - R[\ln (H^+)]$. Assuming that the activation parameters for A' and K_h found in the present study approximate those for the Br^- anation and taking $(H^+) = 0.01$ *M* yield $\Delta H^‡_{obsd} = 34$ kcal/mol and $\Delta S^‡_{obsd} = 28$ cal/(deg mol).

One might be tempted to try to explain the relative differences in the rates listed in Table V for the anation of the hydroxyaquo complex by Cl^-, Br^-, and I^-. The explanation would concern the intimate mechanism of the reaction, *i.e.*, how changes in the attacking anion affect one or more of the fundamental constants of the rate law. Such an exercise is unwarranted, however, even if the differences in the ionic strengths of the data could be overcome. The problem is twofold. As pointed out below, the available data do not allow the assigning of a stoichiometric mechanism to the reaction of the hydroxyaquo complex alone. Second, with either stoichiometric mechanism, the measurable kinetic parameters are complicated composites of fundamental rate and equilibrium constants. Thus with the present data it is impossible to determine which elementary reaction steps are being affected by the change in attacking anion.

The comparisons in Table II, especially that at 40°, show that the kinetic data do not give an adequate fit to eq 16, the interchange rate law. My conclusion will be that *trans*-$Rh(en)_2(H_2O)_2^{3+}$ and/or *trans*-$Rh(en)_2(OH)(H_2O)^{2+}$ does not anate *via* a strict interchange stoichiometric mechanism. (If only one of the complexes anates *via* an interchange mechanism, an inadequate fit to eq 16 will be observed.) The conclusion does depend on the validity of the assumptions used in deriving eq 16. The first was that eq 7–10 give the forms of the complex present in solution. It was assumed that ion triplets do not exist to a kinetically noticeable extent under the conditions of the study. The second assumption was that the measurable parameters, $k_{in}K$, $k'_{in}K'K_h$, and *K* were unaffected by medium changes at $I = 1$ *M*. It will be recalled that $(H^+)/(Na^+)$ and $(Cl^-)/(ClO_4^-)$ varied from run to run. Unfortunately the data available do not allow an unequivocal evaluation of these assumptions. However, it does not seem unreasonable to assume that the difference in the curvature of k_{obsd} *vs.* (Cl^-) at the two acidities at 40° (see Table II) arose at least in part from the inherent inadequacy of the mechanism.

Table VI. Indicated Substitution Mechanisms of Some Related Octahedral Complexes

Complex no.	Complex	Indicated mechanism[a]	Ref
1	$Co(NH_3)_5H_2O^{3+}$	I_d	8
2	*trans*-$Co(en)_2(OH)(H_2O)^{2+}$	I	9
3	$Rh(NH_3)_5H_2O^{3+}$	I_a	4–6
4	$RhCl(H_2O)_5^{2+}$ and/or $RhCl(OH)(H_2O)_4^+$	D	7
5	*trans*-$Rh(en)_2(H_2O)_2^{3+}$ and/or *trans*-$Rh(en)_2(OH)(H_2O)^{2+}$	D	This work

[a] Key: I_a, interchange with associative activation; I_d, interchange with dissociative activation; D, dissociative. See ref 3.

The data do give a good fit to the simplified dissociative rate law, eq 21, due to the relative complexity of this expression. Therefore, by default, it will be assumed that *trans*-$Rh(en)_2(H_2O)_2^{3+}$ and/or *trans*-$Rh(en)_2(OH)(H_2O)^{2+}$ anates *via* a dissociative stoichiometric mechanism.

Table VI lists some related d^6 octahedral complexes for which data allow an assignment of either an interchange or dissociative stoichiometric mechanism. The complexes have been numbered to facilitate discussion. Where the data allow, the intimate mechanism of the interchange step is indicated by the subscripts a (associative, bond formation in the transition state) or d (dissociative, primarily bond rupture in the transition state).[3] If the assigned mechanisms do conform to reality, insight into some of the factors controlling the substitution mechanisms of octahedral complexes can be gained. Complexes **3** and **5** indicate that the inert ligands have a profound effect on the substitution mechanism of rhodium complexes. Replacing a trans amine ligand with an oxygen-bonded ligand changes the mechanism from one where a five-coordinate species is not formed even as an activated transition-state complex to one where a five-coordinate species is a relatively stable intermediate of the reaction. Comparing **3** and **5** with the analogous cobalt complexes, **1** and **2**, indicates that the substitution mechanism is far less sensitive to such a change in inert ligand when cobalt is the central atom.

It is worth speculating on the reasons for these effects if only to point the direction for further research. The three mechanisms will be viewed as indicating the varying stability of five-coordinated species: I_a, five-coordinated species is too unstable to be formed along the reaction coordinate; I_d, species is formed but reacts with the first group it encounters; D, species is stable enough to react selectively. If both forms of complex **5** anate *via* a D mechanism, the stabilization of the five-coordinate intermediate could be due to donation to the metal of unshared electrons on the oxygen atom. This would be consistent with the D mechanism for complex **4** since all the ligands in 4 have unshared electrons. But how this donation would occur is unclear. The aquation rates of *trans*-Co(en)$_2$LCl$^+$ complexes have been explained[1] 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)$_2$Cl$_2$$^+$ in the anation 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 σ 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$_3$)$_5$H$_2$O^{3+} and Cr(H$_2$O)$_6$$^{3+}$ substitute *via* I$_a$ mechanisms;[6,20] however, very few data are available on iridium complexes.

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Registry No. *trans*-Rh(en)$_2$(H$_2$O)$_2$$^{3+}$, 21863-10-5; *trans*-Rh(en)$_2$(OH)(H$_2$O)$^{2+}$, 27842-81-5; Cl$^-$, 16887-00-6; *trans*-Rh(en)$_2$Cl$_2$$^+$, 18539-17-8.

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

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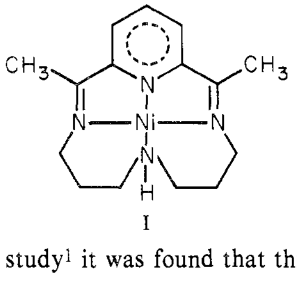
The temperature dependence of the solvent proton nmr spectra has been measured for the Schiff base complex (2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene)nickel(II), referred to as NiCR^{2+} dissolved in methanol and acetonitrile. Chemical-exchange effects are observed for both the line broadening and shifts. The rate constant (25°) for exchange of one solvent molecule, $\Delta H^\ddagger$ (kcal mol^{-1}), and $\Delta S^\ddagger$ (cal mol^{-1} deg^{-1}) in methanol are 1.1 $\times$ 10^7 sec^{-1}, 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 $>7 \times 10^5$ sec^{-1}. The kinetic results show that NiCR^{2+} 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^{2+}.



I

In a previous study[1] it was found that this complex, in a number of nonaqueous solvents, underwent a diamagnetic–paramagnetic equilibrium, represented in general by

$$\underset{\text{diamagnetic}}{\mathrm{NiA_4}^{2+}} + 2(\text{solvent}) \rightleftarrows \underset{\text{paramagnetic}}{\mathrm{NiA_4(solvent)_2}^{2+}} \quad (1)$$

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.[2] 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^{2+} salts have been described previously.[1]

The nmr samples were prepared by weight on a standard vacuum