Nuclear Magnetic Resonance Line Broadening by a Tridendate Schiff-Base Complex of Nickel(II), Triaquotribenzo[*b,f,j*][1,5,9]triazacyclododecinenickel(II)

John E. Letter, Jr., and R. B. Jordan*

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. *Received June 2, 1970*

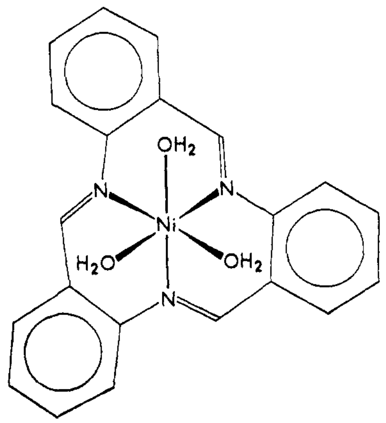
Abstract: The temperature dependence of solvent water proton line broadening by $Ni(TRI)(OH_2)_3^{2+}$ has been measured. The kinetic parameters for water exchange are $k = 3.8 \times 10^4$ sec^{-1} (25°), $\Delta H^* = 10.9$ kcal mol^{-1}, and $\Delta S^* = -1.9$ eu. Comparison to water exchange on other nickel(II) complexes indicates that the fused-ring tridendate chelate has no unusual effect on the water exchange rate. It is concluded that no large change in bond angles at nickel occurs in the transition state for water exchange.

There have been several recent studies of the effect of nonexchanging ligands on the water exchange rate from hydrated nickel(II) complexes. Dodgen, Hunt, and coworkers have studied the water exchange rate of SCN^-,[1] Cl^-,[2] $NH_2-(CH_2)_2-NH_2$,[3] and NH_3[4] complexes of nickel(II) using $^{17}OH_2$ nmr line broadening. It was generally found that the water exchange rate increased on complex formation and with increasing number of amine ligands. Margerum and coworkers have studied the rate of NH_3 complexation to a wide variety of nickel(II)-amine and -carboxylate complexes.[5] If it is assumed that the rate of NH_3 complex formation is controlled by the water exchange rate then the same general trends as found from the $^{17}OH_2$ work are observed.

In contrast to these trends Rablen and Gordon[6] found the water exchange rate on $Ni(terpy)(H_2O)_3^{2+}$ (terpy = terpyridyl) to be very similar to that on $Ni(OH_2)_6^{2+}$. It would appear that terpyridine decreases the water exchange rate when compared to other amine type ligands. These conclusions are reinforced by the recent study of Grant, Dodgen, and Hunt[7] on $Ni(dipy)(H_2O)_4^{2+}$ and $Ni(dipy)_2(OH_2)_2^{2+}$. Water exchange in both of these systems is also similar to that in $Ni(OH_2)_6^{2+}$.

As a result of these studies it is now possible to at least qualitatively anticipate the water exchange rates for various nickel(II) complexes. It therefore seemed possible that some mechanistic information might be gained by studying a fused ring tridendate ligand complex. Such a ligand would prevent significant changes in the bond angles at nickel in the transition state for water exchange. Then if such changes are normally required, the fused-ring ligand complex should show slower exchange and a higher ΔH^* than expected.

The system chosen for study, triaquotribenzo[*b,f,j*][1,5,9]triazacyclododecinenickel(II), $Ni(TRI)(OH_2)_3^{2+}$, is shown in structure I. The $Ni(TRI)OH_2(NO_3)_2$ complex was prepared by Melson and Busch[8] and has been partially resolved by Taylor and Busch.[9] The structure of $Ni(TRI)(OH_2)_2(NO_3)_2$ has been determined by Fleischer and Klem.[10]



I

Experimental Section

The nickel complex was prepared following the procedure outlined by Melson and Busch.[8] The *o*-aminobenzaldehyde was prepared from *o*-nitrobenzaldehyde as described by Smith and Opie.[11] $Ni(TRI)(H_2O)_3(NO_3)_2$ was prepared by self-condensation of *o*-aminobenzaldehyde in the presence of $Ni(NO_3)_2 \cdot 6H_2O$ as described by Melson and Busch.[12] The perchlorate salt was prepared from the nitrate as described in ref 8.

The nickel salts were air dried. *Anal.* Calcd for $Ni(TRI)(H_2O)_3(ClO_4)_2$: C, 40.70; N, 6.78; H, 3.39. Found: C, 40.89; N, 7.07; H, 3.71. Calcd for $Ni(TRI)(H_2O)_3(NO_3)_2$: C, 47.75; N, 13.27; H, 3.60. Found: C, 47.10; N, 13.22; H, 3.55.

The complex was also identified by comparison of the infrared and visible spectra to spectral results previously published.[8]

The nmr line-broadening studies were carried out mainly with the nitrate salt because of its greater solubility. The nickel concentration was varied between 0.0277 and 0.0400 *M*. The insolubility of the compound limits the magnitude of the broadenings which can be observed. Several samples of the less soluble perchlorate salt were prepared and were found to produce the same amount of broadening with the same temperature dependence. From six different samples, 39 data points were obtained at 60 MHz over the temperature range 3–94°. At 100 MHz, 16 data points were obtained from three samples over the temperature range 5–80°.

---

[1] R. B. Jordan, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **5**, 1906 (1966).

[2] S. F. Lincoln, F. Aprile, H. W. Dodgen, and J, P. Hunt, *ibid.*, **7**, 929 (1968).

[3] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **91**, 5001 (1969).

[4] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *ibid.*, **92**, 798 (1970).

[5] J. P. Jones, E. J. Billo, and D. W. Margerum, *ibid.*, **92**, 1875 (1970), and references quoted therein.

[6] D. Rablen and G. Gordon, *Inorg. Chem.*, **8**, 395 (1969).

[7] M. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **92**, 2321 (1970).

[8] G. A. Melson and D. H. Busch, *ibid.*, **87**, 1706 (1965).

[9] L. T. Taylor and D. H. Busch, *ibid.*, **89**, 5372 (1967).

[10] E. B. Fleischer and E. Klem, *Inorg. Chem.*, **4**, 637 (1965).

[11] L. I. Smith and J. W. Opie, *Org. Syn.*, **28**, 11 (1948).

[12] G. A. Melson and D. H. Busch, *J. Amer. Chem. Soc.*, **86**, 4834, (1964).

The nmr spectra were recorded on Varian A-56/60 and HA-100 spectrometers equipped with Model V-4343 temperature controllers and standard temperature probes. Temperatures were measured using the ethylene glycol and methanol standards supplied by Varian Associates.

Chemical shifts were measured at 100 MHz using *tert*-butyl alcohol (1.010 *M*, 10% by volume) as an internal standard. The same concentration of *tert*-butyl alcohol was used in the solvent blank and in the sample containing the nickel complex in order to overcome the solvent dependence of the shift of *tert*-butyl alcohol.[13]

Results and Discussion

The solvent proton relaxation time may be expressed as

$$(T_{2P}')^{-1} = \frac{(T_{2P})^{-1}}{P_m} = \pi\frac{(\Delta\nu_{obsd} - \Delta\nu_{sol})}{P_m} \qquad (1)$$

where $\Delta\nu_{obsd}$ is the full width at half height of the solvent proton resonance in the presence of the paramagnetic ion and $\Delta\nu_{sol}$ is the analogous line width in the absence of paramagnetic ion. P_m is the ratio of bound to free solvent molecules, which for $Ni(TRI)(OH_2)_3^{2+}$ is $3[Ni]/([H_2O]_{total} - 3[Ni])$.

Some typical experimental results from the line-broadening study at 60 and 100 MHz are given in Tables I and II, respectively. Figure 1 shows a plot of log $(T_{2p}')^{-1}$ *vs.* the reciprocal of the absolute temperature for the data in Tables I and II. The smooth curves in Figure 1 are based on a least-squares fit of all the data as described below.

Table I. Typical[a] Line-Broadening Results for $Ni(TRI)(OH_2)_3^{2+}$ in Water at 60 MHz

Temp, °C	Full width, Hz $\Delta\nu_{obsd}$	Full width, Hz $\Delta\nu_{obsd} - \Delta\nu_{sol}$	$10^{-3} \times (T_{2P}')^{-1}$, sec^{-1} Obsd	$10^{-3} \times (T_{2P}')^{-1}$, sec^{-1} Calcd[b]
3	7.50	5.25	7.66	7.58
9	7.85	6.10	8.92	8.42
16	8.80	7.20	10.52	10.34
21	9.55	7.95	11.60	11.13
27	9.85	8.35	12.20	11.64
35	9.65	8.20	11.97	11.64
40	9.25	7.85	11.45	11.38
46	8.90	7.49	10.90	10.94
56	8.18	6.88	10.02	10.11
66	7.82	6.61	9.60	9.34
76	7.10	6.00	8.72	8.67
86	6.39	5.39	7.84	8.08

[a] Data from two of the six samples studied at 60 MHz. From 3 to 40°, a sample with $[Ni(TRI)(OH_2)_3^{2+}] = 0.0398$ *M* and $P_m = 2.15 \times 10^{-3}$ was used. From 46 to 86° the sample had $[Ni(TRI)(OH_2)_3^{2+}] = 0.0400$ *M* and $P_m = 2.16 \times 10^{-3}$. [b] Calculated from the 60-MHz, fit-C parameters in Table IV.

Table II. Typical[a] Line-Broadening Data Results for $Ni(TRI)(OH_2)_3^{2+}$ in Water at 100 MHz

Temp, °C	Full width, Hz $\Delta\nu_{obsd}$	Full width, Hz $\Delta\nu_{obsd} - \Delta\nu_{sol}$	$10^{-3} \times (T_{2P}')^{-1}$, sec^{-1} Obsd	$10^{-3} \times (T_{2P}')^{-1}$, sec^{-1} Calcd[b]
15	10.20	8.52	12.52	12.50
21	10.70	9.34	13.73	14.36
30	11.50	10.30	15.17	15.68
40	11.76	10.60	15.61	14.90
50	9.28	8.28	12.20	13.22
60	8.56	7.94	11.68	11.66
72	8.36	7.36	10.83	10.21
80	7.20	6.20	9.13	9.46

[a] Data from one of the three samples studied at 100 MHz; $[Ni(TRI)(OH_2)_3^{2+}]$ 0.0358 *M*; $P_m = 1.07 \times 10^{-3}$. [b] Calculated from the 100-MHz, fit-C parameters in Table IV.

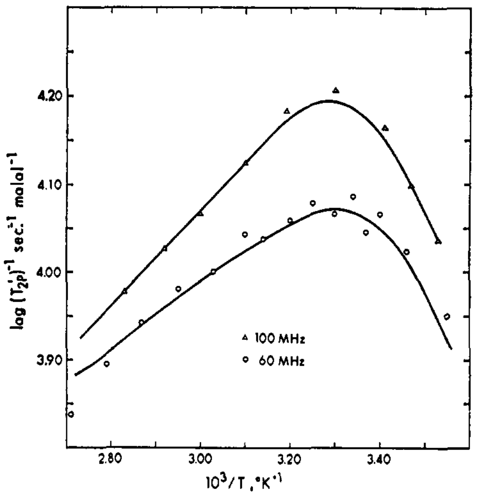


Figure 1. Variation of log $(T_{2P}')^{-1}$ with reciprocal of the absolute temperature. The smooth curves represent the best fit C of Table IV for all the data. Points are the results given in Tables I and II.

The chemical shifts of the solvent in the presence of $Ni(TRI)(OH_2)_3^{2+}$, measured at 100 MHz using *tert*-butyl alcohol as an internal standard, are given in Table III. Shifts were also observed at 60 MHz, but the maximum value was only ~3 Hz with an uncertainty of ±1 Hz, and the values were not used in the subsequent analysis.

Table III. Solvent-Water Proton Chemical Shift for $Ni(TRI)(OH_2)_3^{2+}$ in Water[a] at 100 MHz

Temp, °C	Chemical shift ($\Delta\omega/2\pi$), Hz Obsd	Chemical shift ($\Delta\omega/2\pi$), Hz Calcd[b,c]
15	2.2	1.74
21	0.2	2.90
30	3.0	4.86
40	4.6	5.49
60	5.4	6.11
72	5.9	5.90
80	5.9	5.76

[a] Sample was 0.0358 *M* in $Ni(TRI)(OH_2)_3(NO_3)_2$, with 10% by volume *tert*-butyl alcohol; $[H_2O] = 50.3$ *M*; $P_m = 2.14 \times 10^{-3}$. [b] Calculated from eq 8 with $\Delta\omega_m = 5.960 \times 10^3/T$ sec^{-1}, $\Delta H^* = 11.55$ kcal mol^{-1}, and $\Delta S^* = +0.25$ eu, as given in fit C, Table IV. [c] The agreement of calculated and observed values is considered to be satisfactory since the observed values have an uncertainty of ~±1 Hz.

The temperature dependence of the line broadening as shown in Figure 1 should be described by the equation

$$(T_{2P}')^{-1} = \frac{1}{\tau_m}\left(\frac{(1/T_{2m})^2 + (1/T_{2m}\tau_m) + \Delta\omega_m^2}{[(1/T_{2m} + (1/\tau_m)]^2 + \Delta\omega_m^2}\right) + (T_{2O})^{-1} \qquad (2)$$

The first term in eq 2 was developed by Swift and Connick[14] with the symbols having their usual meaning. The second term, $(T_{2O})^{-1}$, is added to account for outer-sphere line broadening. Although there is no direct

---

(13) R. G. Anderson and M. C. R. Symons, *Trans. Faraday Soc.*, **65**, 2550 (1969).

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

Table IV. Least-Squares Best-Fit Parameters

Fit[a]	Frequency, MHz	ΔH^*, kcal mol^{-1}	ΔS^*, eu	C_m, sec^{-1}	E_m, kcal mol^{-1}	$10^{-6} \times C_\omega$, sec^{-1} deg
A	60	8.81	−7.97	4.93×10^2	1.99	3.08
	100	8.36	−9.95	2.72×10^3	0.76	8.51
B	60	8.47	−9.23	5.45×10^2	1.92	3.58[b]
	100	10.15	−3.37	2.98×10^2	2.39	5.96[b]
C[c]	60	10.36	−3.37	6.66×10^2	1.61	3.58[b]
	100	11.55	0.25	5.20×10^2	1.81	5.96[b,d]

[a] The standard error on the fits did not change significantly with an average value of $3.64 \pm 0.02 \times 10^3$ for the 60-MHz data using 39 data points. [b] C_ω held constant at value indicated by 100-MHz shift data. [c] Outer-sphere line-broadening term $(T_{2O})^{-1} = 1.723 \times 10^2 \exp(E_m/RT)$ was added as described in text. [d] The hyperfine coupling constant calculated from eq 6, (A/h), is 2.84×10^6 Hz.

indication of this effect in the results, comparison of the 60- and 100-MHz data shows that it is contributing to the observed line broadening.

The temperature dependence of τ_m is assumed to follow transition-state theory

$$(\tau_m)^{-1} = \frac{kT}{\hbar} \exp((-\Delta H^* + T\Delta S^*)/RT) \tag{3}$$

A simple exponential temperature dependence with the same activation energy has generally been found satisfactory for T_{2m} and T_{2O}, *i.e.*

$$(T_{2m})^{-1} = C_m \exp(E_m/RT) \tag{4}$$

$$(T_{2O})^{-1} = C_0 \exp(E_0/RT) \tag{5}$$

It has been shown by Bloembergen[15] that

$$\Delta\omega_m = \left(\frac{A}{\hbar}\right) \frac{\omega_0 g\beta(S)(S+1)}{3kT\gamma_H} \tag{6}$$

where (A/h) is the electron–proton hyperfine coupling constant and a spin-only magnetic moment is assumed. From eq 6 the temperature variation of $\Delta\omega_m$ is given by

$$\Delta\omega_m = C_\omega/T \tag{7}$$

Initially there did not appear to be any need for the outer-sphere term and the $(T_{2P}')^{-1}$ data were fitted to eq 2 after substitution from eq 3, 4, and 7. The five parameters ΔH^*, ΔS^*, C_m, E_m, and C_ω were allowed to vary to give a least-squares best fit.[16] The results are shown as fit A in Table IV. A comparison of the parameters from the 60- and 100-MHz data shows that ΔH^* and ΔS^* agree quite well but C_m and E_m are very different. The C_ω values also are not consistent since at 60 MHz C_ω should be 0.60 of the value at 100 MHz; that is it should be 5.11×10^6 instead of 3.08×10^6.

In view of these results it was decided to fix C_ω at a value consistent with the shift measurements and then allow ΔH^*, ΔS^*, C_m, and E_m to vary to give the least-squares best fit. The value of C_ω was determined by fitting the observed shift to the expression[14]

$$\Delta\omega_{\text{obsd}} = \frac{P_m\Delta\omega_m}{1 + (\tau_m\Delta\omega_m)^2} \tag{8}$$

At higher temperatures $(\tau_m\Delta\omega_m)^2 \ll 1$ and C_ω can be calculated directly from the observed shift without knowing τ_m. With the value of C_ω at 100 MHz fixed at 5.96×10^6 the line-broadening data were refitted to give the parameters shown for fit B in Table IV. Comparison of the 60- and 100-MHz results shows that none of the parameters except possibly E_m is in satisfactory agreement.

It was then concluded that to make the shift and broadening data internally consistent it would be necessary to add an outer-sphere line-broadening contribution. The magnitude of this term was estimated, from the work of Luz and Meiboom[17] on the nickel(II)–methanol system, to be about a factor of 3 less than the inner-sphere relaxation rate $(T_{2m})^{-1}$. A value for C_0 of 1.723×10^2 was estimated from the average C_m values at 60 MHz from fits A and B.

The data were then refitted using ΔH^*, ΔS^*, C_m, and E_m as adjustable parameters and holding C_ω and C_0 constant at the values given above. The results are given as fit C in Table IV. The agreement of the parameters from the 60- and 100-MHz data was judged to be satisfactory in all cases.

It should be noted that the C_m and E_m differences are such that the T_{2m} values calculated from either set of parameters are in good agreement. For example, at 70° $(T_{2m})^{-1}$ is calculated to be 7.20×10^3 and 7.55×10^3 cm^{-1} from the 60- and 100-MHz parameters, respectively. The analogous values at 25° are 10.0×10^3 and 10.9×10^3 sec^{-1}. If the inner-sphere T_{2m} is completely due to a dipolar relaxation then the correlation time (τ_c) is 1.4×10^{-11} sec if r(Ni–H) is 2.6 Å. The τ_c value seems qualitatively consistent with the expected value for the electron-spin relaxation time on nickel(II).

A similar type of compensating difference is evident in the ΔH^* and ΔS^* values. In fact the calculated ΔG^* at 25° is 11.48 kcal mol^{-1} from both sets of data, giving a rate constant for exchange of one water molecule, k_1, of 3.75×10^4 sec^{-1}.

The analysis outlined above illustrates very clearly the necessity of considering all the terms which may be contributing to the line broadening and of making as many independent measurements as possible. In this study the main criteria for a satisfactory fit are agreement of the 60- and 100-MHz studies and consistency of the line-broadening and shift results. The surprising feature is that the addition of the outer-sphere term has such a large effect on ΔH^* and ΔS^*, even though qualitative observation of Figure 1 does not indicate that any outer-sphere broadening was present.

It should be noted that a similar difficulty has arisen at least twice before in the nickel(II)–dimethyl sulfoxide system. In this case Thomas and Reynolds,[18] and also Blackstaffe and Dwek,[19] neglected the T_{2m} contributions

---

(15) N. Bloembergen, *J. Chem. Phys.*, 27, 595 (1957).

(16) Nonlinear least-squares program, IBM SHARE Library, SDA 3094. All $(T_{2P}')^{-1}$ values were weighted by the reciprocal of the value to give all points equal weighting in the analysis.

(17) Z. Luz and S. Meiboom, *J. Chem. Phys.*, 40, 1066 (1964).

(18) S. Thomas and W. J. Reynolds, *ibid.*, 46, 4164 (1967).

(19) S. Blackstaffe and R. A. Dwek, *Mol. Phys.*, 15, 279 (1968).

Table V. Kinetic Parameters for Water Exchange on Some Nickel(II) Complexes

Complex	k, sec^{-1} (25°)	ΔH^*, kcal mol^{-1}	ΔS^*, eu	Ref
$Ni(OH_2)_6^{2+}$	3.2×10^4	12.1	2.6	7
$Ni(NH_3)_3(OH_2)_3^{2+}$	2.5×10^6	10.2	5.0	4
$Ni(terpy)(OH_2)_3^{2+}$	5.2×10^4	10.7	−1.0	6
$Ni(TRI)(OH_2)_3^{2+}$	3.8×10^4	10.9	−1.9	This work[a]
$Ni(en)(OH_2)_4^{2+}$	4.4×10^5	10.0	10	3
$Ni(en)_2(OH_2)_2^{2+}$	5.4×10^6	9.1	2.6	3
$Ni(dipy)(OH_2)_4^{2+}$	4.9×10^4	12.6	5.1	7
$Ni(dipy)_2(OH_2)_2^{2+}$	6.6×10^4	13.7	9.2	7

[a] The average of the 60- and 100-MHz parameters from fit C, Table IV.

and obtained values of ΔH^* which were too low by 3–3.5 kcal mol^{-1} and ΔS^* too negative by ~14 eu.[20,21]

The original purpose of this study was to determine the effect of a fused-ring tridendate chelate ligand on the water exchange rate. A comparison of results from this and previous work in Table V indicates that $Ni(TRI)(OH_2)_3^{2+}$ is not unusual. The ΔH^* value is certainly not unexpectedly large; therefore, it would seem that no large change in geometry occurs in the transition state for water exchange. This would be consistent with a square-based pyramidal transition state if an SN1 mechanism is assumed.

It may be noted that the variations in ΔH^* and ΔS^* in Table V do not appear to follow any obvious trends. The faster exchange of $Ni(NH_3)_3(OH_2)_3^{2+}$ and $Ni(en)(OH_2)_4^{2+}$ compared to $Ni(terpy)(OH_2)_3^{2+}$ and $Ni(TRI)(OH_2)_3^{2+}$ is largely due to a more favorable ΔS^*. Therefore, simple electron withdrawal by conjugated amines, making Ni–OH$_2$ bond breaking more difficult, does not account for the rate differences. The large difference in ΔH^* for $Ni(terpy)(OH_2)_3^{2+}$ and $Ni(dipy)_2(OH_2)_2^{2+}$ is also noteworthy since these complexes might be expected to be the most similar of all those in Table V.

The results of the study have shown that steric rigidity of the chelating ligand is not a very important kinetic factor for the water exchange rates on nickel(II). However, the factors which do affect these rates remain largely unexplained.

Acknowledgment. The authors wish to acknowledge the financial support of this work by the National Research Council of Canada.

---

(20) N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, 8, 2579 (1969).

(21) N. A. Matwiyoff, private communication.

Interaction between Isothiocyanatopentaaquochromium(III) and Mercury(II). Equilibrium and Kinetics[1a,b]

John N. Armor and Albert Haim*

Contribution from the Departments of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania 16802,
and State University of New York, Stony Brook, New York 11790.
Received August 5, 1970

Abstract: The isothiocyanatopentaaquochromium(III) ion reacts with mercury(II) in aqueous solution to form the binuclear complex $CrNCSHg^{4+}$. From the absorption spectrum of the complex (maxima at 565 and 398 nm with extinction coefficients 21 and 25, respectively) it is deduced that the ligand $HgSCN^+$ lies between NCS^- and NH_3 in the spectrochemical series. The equilibrium quotient for the reaction $CrNCS^{2+} + Hg^{2+} \rightleftarrows CrNCSHg^{4+}$ is $1.66 \times 10^4\ M^{-1}$ at 25° and $[ClO_4^-] = 1.0\ M$. The associated thermodynamic parameters are $\Delta H = -8.0$ kcal/mol and $\Delta S = -7.3$ eu. The relatively high formation quotient is rationalized on the basis of a stable ambidentate arrangement in which the hard and soft ends of thiocyanate are bound to hard and soft acids, respectively. The binuclear ion $CrNCSHg^{4+}$ undergoes aquation to Cr^{3+} and $HgSCN^+$ by a first-order process independent of acidity. The rate constant at 25° and $[ClO_4^-] = 1.0\ M$ is 8.5×10^{-5} sec^{-1} with $\Delta H^{\ddagger} = 20.4$ kcal/mol and $\Delta S^{\ddagger} = -8.5$ eu. Rate comparisons with related spontaneous and mercury(II)-assisted aquations of complexes of the class CrX^{2+} are made. It is suggested that the aquation of $CrNCSHg^{4+}$ proceeds by a dissociative mechanism.

The mercury(II)-induced aquations of halide and pseudohalide complexes of cobalt(III)[2] and chromium(III)[3–7] have been studied extensively. The accepted mechanism for these assisted aquations is (M = Co, Cr; X = Cl, Br, I, CN)

$$MX^{n+} + Hg^{2+} \rightleftarrows MXHg^{(n+2)+} \qquad (1)$$

rapid equilibrium, K

$$MXHg^{(n+2)} + H_2O \longrightarrow MOH_2^{(n+1)+} + HgX^+ \qquad (2)$$

rate determining, k

On the basis of eq 1 and 2, the pseudo-first-order rate coefficient k_p for the disappearance of MX^{n+} [free or complexed with mercury(II)] in the presence of an excess

---

(1) (a) This work was supported in part by the National Science Foundation under Grant No. GP-9669; (b) abstracted in part from the B.S. thesis of J. N. Armor, The Pennsylvania State University, June 1966.

(2) C. Bifano and R. G. Linck, *Inorg. Chem.*, 7, 908 (1968), and references therein.

(3) J. H. Espenson and J. P. Birk, *ibid.*, 4, 527 (1965).

(4) J. H. Espenson and S. R. Hubbard, *ibid.*, 5, 686 (1966).

(5) J. P. Birk and J. H. Espenson, *ibid.*, 7, 991 (1968).

(6) J. P. Birk, *ibid.*, 9, 735 (1970).

(7) S. P. Ferraris and E. L. King, *J. Amer. Chem. Soc.*, 92, 1215 (1970).