

Kinetics of Water Proton Exchange of  $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$  in Aqueous Acid

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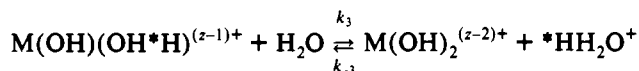
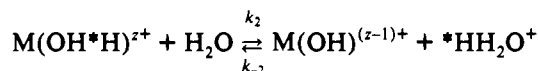
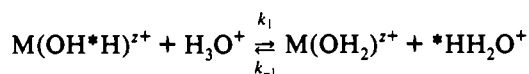
Received August 4, 1992

The solvent water proton transverse ( $R_2$ ) and longitudinal ( $R_1$ ) relaxation rates have been studied for solutions of the organochromium(III) complex  $(\text{H}_2\text{O})_5\text{Cr}(\text{CH}_2\text{CN})^{2+}$  as a function of  $\text{H}^+$  concentration (0.01–0.22 M) and temperature (5–70 °C). The temperature dependence of  $R_2$  is typical of a chemical exchange process which is assigned to exchange of coordinated water protons because of the similarity to the behavior of  $\text{Cr}(\text{OH}_2)_6^{3+}$  and  $(\text{H}_2\text{O})_5\text{Cr}(\text{N}_3)^{2+}$ . The variation of the rate of exchange with  $[\text{H}^+]$  indicates pathways which are first-order ( $k_1$ ) independent ( $k_2$ ) and inverse first order ( $k_3$ ) in  $[\text{H}^+]$ . The rate constants at 25 °C,  $\Delta H^\ddagger$  (kcal mol<sup>-1</sup>), and  $\Delta S^\ddagger$  (cal mol<sup>-1</sup> K) are as follows:  $k_1 = 6.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ,  $3.65 \pm 0.3$ ,  $-24.4 \pm 0.9$ ;  $k_2 = 4.9 \times 10^3 \text{ s}^{-1}$ ,  $8.0 \pm 0.3$ ,  $-14.9 \pm 0.9$ ;  $k_3 = 30 \text{ M s}^{-1}$ ,  $9.7 \pm 0.8$ ,  $-19.4 \pm 2.5$ . The kinetic results are combined with hydrolysis constants to derive further information on protonation–deprotonation kinetics and second hydrolysis constants for aquachromium(III) complexes. The kinetic parameters and general relaxation effects for the organochromium(III) complex are similar to those for  $\text{Cr}(\text{OH}_2)_6^{3+}$  and  $(\text{H}_2\text{O})_5\text{Cr}(\text{N}_3)^{2+}$ .

## Introduction

There have been many NMR studies of the rate of solvent exchange on paramagnetic metal ions because solvent exchange kinetics play a key role in the substitution reactivity of metal complexes. But there have been relatively few studies on the kinetics of proton transfer from such  $\text{M}(\text{OH}_2)_n^{z+}$  systems, although such reactions generate  $\text{M}(\text{OH}_2)_{n-1}(\text{OH})^{(z-1)+}$  which is generally more substitutionally labile than the parent aqua species. The early work of Bloembergen and Morgan<sup>1</sup> and Swift and Stephenson<sup>2</sup> demonstrated that water proton exchange may proceed by the reactions in Scheme I. These reactions can be distinguished by the hydrogen ion dependence of the proton exchange rate. Eyring and co-workers<sup>3</sup> used electric field dissociation relaxation to show that  $k_{-2}$  is near the diffusion control limit and is relatively independent of the type of metal ion. Therefore, determination of  $k_2$  allows one to estimate the hydrolysis constant ( $K_m = k_2/k_{-2}$ ). In addition, the work of Morgan and Bloembergen showed that the relaxation effect of the paramagnetic ion provides characteristic information on its electron spin correlation time which in turn depends on the electronic structure of the species.

## Scheme I



The present study explores the NMR relaxation effect on the solvent water protons of an organochromium(III) species,  $(\text{H}_2\text{O})_5\text{Cr}(\text{CH}_2\text{CN})^{2+}$ . This complex is a representative of a series of organochromium(III) species which have unusual electronic spectra<sup>4</sup> and substitution lability<sup>5</sup> for the water ligand trans to

the organo ligand. The results will be compared to previous work on  $\text{Cr}(\text{OH}_2)_6^{3+}$  and  $(\text{H}_2\text{O})_5\text{Cr}(\text{N}_3)^{2+}$  to determine if the organochromium species causes unusual relaxation effects which might be indicative of unusual electronic properties. The acid dependence of the solvent proton relaxation rate will be used to determine the rate constants in Scheme I, and to estimate the hydrolysis constant for  $(\text{H}_2\text{O})_5\text{Cr}(\text{CH}_2\text{CN})^{2+}$ . The latter cannot be measured directly because of the hydrolytic instability of these species at  $\text{pH} \geq 3$ .

## Results

The measured water proton relaxation rates ( $R_{i\text{obsd}}$ ;  $i = 1$  or  $2$ ) for solutions of  $(\text{H}_2\text{O})_5\text{Cr}(\text{CH}_2\text{CN})^{2+}$  in aqueous perchloric acid have been corrected for pure solvent relaxation ( $R_{i\text{solv}}$ ) and normalized for the chromium(III) concentration according to eq 1, where  $P_m = [(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}]/[\text{H}_2\text{O}]$  is the molar ratio of chromium(III) to solvent water. The number of exchanging sites is introduced below.

$$R_{ip} = \frac{1}{P_m}(R_{i\text{obsd}} - R_{i\text{solv}}) \quad (1)$$

Representative results of the temperature dependence of the solvent proton longitudinal ( $R_{1p}$ ) and transverse ( $R_{2p}$ ) relaxation rates are shown in Figure 1. The temperature dependence of the  $R_{1,2p}$  curves is consistent with the predictions of the theory developed by Swift and Connick,<sup>7</sup> which predicts that  $R_{2p}$  is given by eq 2, where  $r_m$  is the chemical exchange rate,  $R_{2m}$  is the nuclear

$$R_{2p} = nr_m \left\{ \frac{R_{2m}(R_{2m} + r_m) + \Delta\omega_m^2}{(R_{2m} + r_m) + \Delta\omega_m^2} \right\} + R_{20} \quad (2)$$

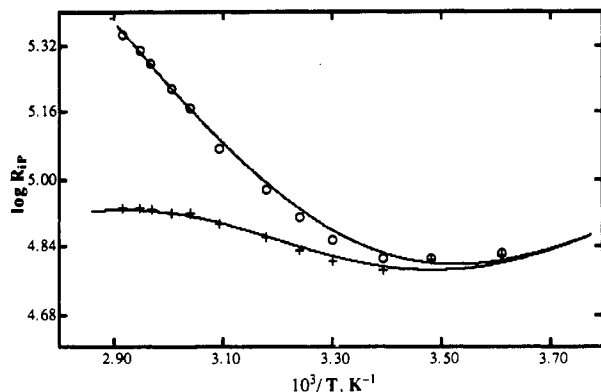
relaxation rate of the coordinated protons,  $\Delta\omega_m$  is the chemical shift difference between coordinated and bulk solvent protons,  $R_{20}$  is the outer-sphere relaxation rate, and  $n$  is the number of water ligands with exchanging hydrogens. For present purposes, it has been assumed that  $n = 5$  (i.e. all the water protons are involved in the exchange process), to be consistent with the earlier studies on aquachromium(III) species. A similar expression<sup>8</sup> applies for  $R_{1p}$  except that the  $\Delta\omega_m$  term is omitted and  $R_{2m}$  and

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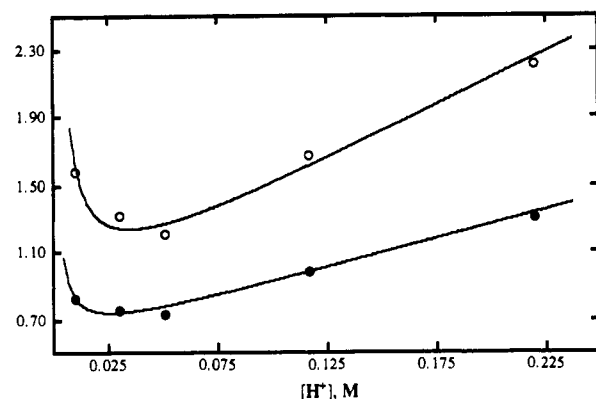
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**Figure 1.** Solvent water proton transverse ( $R_2$ , O) and longitudinal ( $R_1$ , +) relaxation rates for a solution of  $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$  in 0.051 M  $\text{HClO}_4$ .



**Figure 2.** Hydrogen ion dependence of  $10^5 R_{2p}$  for the water protons in solutions of  $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$  at  $50 \pm 1^\circ\text{C}$  (O) and  $30 \pm 1^\circ\text{C}$  (●).

$R_{2O}$  are replaced by  $R_{1m}$  and  $R_{1O}$ . The temperature dependence of these factors is given by the following standard equations<sup>9</sup>

$$r_m = 2.083 \times 10^{10} T \exp(-(\Delta H^* + T\Delta S^*)/RT) \quad (3)$$

$$R_{1m} = [C_{1m}/T] \exp(E_{1m}/RT)$$

$$R_{1O} = [C_{1O}/T] \exp(E_{1O}/RT) \quad (4)$$

$$\Delta\omega_m = -C_w/T$$

where the  $C$ 's are temperature independent constants.

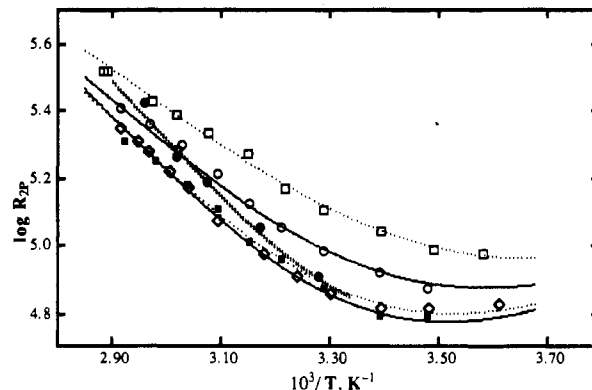
At low temperature, the relaxation rates show the onset of a flat temperature dependence which is typical of outer-sphere relaxation ( $R_{1O}$ ). As the temperature increases, there is a long region in which  $R_{2p}$  increases with increasing temperature as expected for chemical exchange rate ( $r_m$ ) control of the relaxation. For  $R_{1p}$ , this region is shorter and less pronounced because of the onset of control of the relaxation by the inner-sphere relaxation rate ( $R_{1m}$ ). This does not appear with  $R_{2p}$ , either because  $R_{2m}$  is much larger or because the chemical shift difference of the free and coordinated protons ( $\Delta\omega_m$ ) is large enough to provide effective  $R_2$  relaxation through dephasing.

There is an added complication in the system because the chemical exchange process has a dependence of the hydrogen ion concentration as shown in Figure 2. This is consistent with the expectation from the reactions in Scheme I which predict that  $r_m$  is described by the rate law given by eq 5. Therefore the temperature dependence of  $r_m$  will be more complex than described by eq 3, and will depend on the  $\Delta H^*$  and  $\Delta S^*$  values for  $k_1$ ,  $k_2$ , and  $k_3$ , respectively.

**Table I.** Least-Squares Best-Fit Parameters for the Temperature Dependence of the Solvent Water Proton Relaxation Rates in Acidic Solutions of  $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$

parameter <sup>a</sup>	value <sup>b</sup>	parameter <sup>a</sup>	value <sup>b</sup>
$\Delta H_1^*$	$3.65 \pm 0.29$	$\Delta H_3^*$	$9.66 \pm 0.77$
$\Delta S_1^*$	$-24.4 \pm 0.90$	$\Delta S_3^*$	$-19.38 \pm 2.45$
$k_1$ ( $\text{M}^{-1} \text{s}^{-1}$ ), 25 °C	$6.4 \times 10^4$	$k_3$ ( $\text{M s}^{-1}$ ), 25 °C	30
$\Delta H_2^*$	$7.97 \pm 0.28$	$C_m$ ( $\text{s}^{-1} \text{K}$ )	$(3.0 \pm 1.4) \times 10^5$
$\Delta S_2^*$	$-14.9 \pm 0.86$	$E_m$ ( $\text{kcal mol}^{-1}$ )	$2.17 \pm 0.32$
$k_2$ ( $\text{s}^{-1}$ ), 25 °C	$4.9 \times 10^3$	$C_O$ ( $\text{s}^{-1} \text{K}$ )	$(5.47 \pm 0.19) \times 10^4$
		$E_O$ ( $\text{kcal mol}^{-1}$ )	$3.0 \pm 0.3$

<sup>a</sup> The  $\Delta H^*$  and  $\Delta S^*$  values are in  $\text{kcal mol}^{-1}$  and  $\text{cal mol}^{-1} \text{K}^{-1}$  respectively. <sup>b</sup> Errors given are 1 standard deviation.



**Figure 3.** Temperature and  $[\text{H}^+]$  dependence of  $R_{2p}$  for solvent water protons in solutions of  $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$ . The  $\text{H}^+$  concentrations (M) are 0.220 (□), 0.117 (○), 0.051 (◇), and 0.0105 (●).

$$r_m = k_1[\text{H}^+] + k_2 + k_3[\text{H}^+]^{-1} \quad (5)$$

The analysis of the temperature dependence of  $R_{1,2}$  relies first of all on the fact that the  $R_2$  values have a well-defined region where chemical exchange is rate controlling so that the activation parameters  $\Delta H^*$  and  $\Delta S^*$  can be defined using estimated values for the activation energy for the outer-sphere process ( $E_O$ ). Then these activation parameters can be used in the analysis of the  $R_1$  values to obtain  $E_O$  which is assumed to be equal to the activation energy for the  $R_{1m}$  process ( $E_m$ ). Then the  $R_2$  values can be refitted and the process repeated to obtain self-consistency between the parameters. In the final analysis, the  $R_{1p}$  and  $R_{2p}$  data were combined to determine the most self-consistent parameters. This procedure takes advantage of the fact that the  $R_{2p}$  data primarily determine the  $\Delta H^*$  and  $\Delta S^*$  values, while the  $R_{1p}$  data are most sensitive to  $E_O$  and  $E_m$ . As expected, the combined fit did not change the parameters much, but it did reveal that the best overall fit is obtained with  $E_m > E_O$ . The final best-fit parameter values are listed in Table I and shown by the calculated curves in Figure 3. The observed and calculated values are given as supplementary material in Tables S1 and S2.

## Discussion

One purpose of this study is to compare the proton exchange rate from  $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$ ,  $(\text{H}_2\text{O})_5\text{Cr}(\text{N}_3)^{2+}$ , and  $\text{Cr}(\text{OH}_2)_6^{3+}$  in order to assess whether the organochromium(III) species can be viewed as a normal dianionic chromium(III) complex. The kinetic results for these complexes, which are summarized in Table II, reveal that there is nothing particularly unusual about the organochromium(III) complex. The exchange rates and activation parameters are of magnitudes similar to those of the other chromium(III) complexes.

The activation parameters for  $k_1$  are strikingly similar for  $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$  and  $(\text{H}_2\text{O})_5\text{Cr}(\text{N}_3)^{2+}$ . The published value<sup>2</sup> of  $\Delta H_1^*$  for  $\text{Cr}(\text{OH}_2)_6^{3+}$  is surprisingly smaller, since one might expect that the higher positive charge would make protonation

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**Table II.** Comparison of Exchange Rate Parameters for Coordinated Water Protons on Several Chromium(III) Complexes

parameter <sup>a</sup>	(H <sub>2</sub> O) <sub>5</sub> CrCH <sub>2</sub> CN <sup>2+</sup>	(H <sub>2</sub> O) <sub>5</sub> Cr(N <sub>3</sub> ) <sup>2+</sup>	Cr(OH <sub>2</sub> ) <sub>6</sub> <sup>3+</sup>
10 <sup>-4</sup> k <sub>1</sub>	6.4	16 <sup>c</sup>	5 <sup>b</sup> (8) <sup>c</sup>
ΔH <sub>1</sub> <sup>*</sup>	3.7	3.7 <sup>c</sup>	0.5 <sup>b</sup> (3.6) <sup>c</sup>
ΔS <sub>1</sub> <sup>*</sup>	-24.4	-22.4 <sup>c</sup>	-36 <sup>b</sup> (-24.1) <sup>c</sup>
10 <sup>-4</sup> k <sub>2</sub>	0.49	1.3 <sup>c</sup>	7.0 <sup>c</sup> (14) <sup>d</sup>
ΔH <sub>2</sub> <sup>*</sup>	8.0	9.3 <sup>c</sup>	7.5 <sup>c</sup>
ΔS <sub>2</sub> <sup>*</sup>	-15	-8.5 <sup>c</sup>	-11.3 <sup>c</sup>
k <sub>3</sub>	30		42 <sup>c,e</sup> (10 <sup>2</sup> ) <sup>f</sup>

<sup>a</sup> Units as in Table I. <sup>b</sup> Values from ref 2. <sup>c</sup> Values from reanalysis of the data in refs 2 and 6 using the temperature dependence of  $R_{2m}$  and  $R_{20}$  found in this work. <sup>d</sup> Value from ref 3. <sup>e</sup> At 283 K. <sup>f</sup> Estimated at 25 °C using the  $\Delta H_3^*$  in Table I.

more difficult. A reanalysis reveals that the data of Swift and Stephenson<sup>2</sup> are not inconsistent with  $\Delta H_1^* = 3.6$  kcal mol<sup>-1</sup> and  $\Delta S_1^* = -24.1$ , giving  $k_1 = 8 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> at 25 °C. This observation indicates that the  $k_1$  process is kinetically relatively independent of the charge on the metal complex. This is consistent with the published results of Swift and Stephenson, which imply that this path is similar for Ni(OH<sub>2</sub>)<sub>6</sub><sup>2+</sup> and Cr(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup>.

The values of the rate constant for the  $k_2$  path differ by a factor of 2 between the NMR and electric field dissociation methods. This difference is probably due, at least in part, to the ionic strength, which was nearly zero for the electric field dissociation study but in the range of 1 M for the NMR work. For the acid dissociation of Cr(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup>,  $\Delta H_2^\circ$  and  $\Delta S_2^\circ$  are 9.30 kcal mol<sup>-1</sup> and 12.3 cal mol<sup>-1</sup> K<sup>-1</sup> ( $pK = 4.13$  (25 °C),  $\mu = 0.5$  M), respectively.<sup>10</sup> Therefore, if  $k_{-2}$  is a diffusion controlled process with  $\Delta H^* \approx 2$  kcal mol<sup>-1</sup>, then  $k_2$  is predicted to have  $\Delta H^* \approx 7.3$  kcal mol<sup>-1</sup>, in good agreement with the NMR results. The experimental values of  $k_2$  can be combined with the appropriate equilibrium constant ( $pK = 4.29$  at  $\mu = 1.0$ ;<sup>11</sup>  $pK = 3.95$  at  $\mu \approx 0$ <sup>12</sup>) to give  $k_{-2}$  values (M<sup>-1</sup> s<sup>-1</sup>, 25 °C) of  $9.8 \times 10^8$  and  $1.3 \times 10^9$  from the NMR and electric field dissociation studies, respectively.

From the above analysis, it seems reasonable to assume that  $k_{-2} \approx 1 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. This value can be combined with the measured  $k_2$  to estimate the  $pK$  of the chromium(III) complexes. The resulting  $pK$  values are 4.9 and 4.3 for (H<sub>2</sub>O)<sub>5</sub>Cr(N<sub>3</sub>)<sup>2+</sup> and (H<sub>2</sub>O)<sub>5</sub>CrCH<sub>2</sub>CN<sup>2+</sup>, respectively. These values assume that all coordinated water hydrogens are exchanging and would increase by  $\log(5/4) = 0.1$  if the hydrogens of four waters dominate the exchange process, and  $\log(5) = 0.7$  if one set is exchanging faster than the others. The latter would seem to be a possibility, since the protons trans to Cl<sup>-</sup> exchange more rapidly in (H<sub>3</sub>N)<sub>5</sub>CoCl<sup>2+</sup>,<sup>13</sup> although the chemical analogy of the chromium(III) and cobalt(III) systems is certainly questionable.

The  $k_3$  path is apparent in the data of Swift and Stephenson<sup>2</sup> but was ignored in their analysis. Our analysis of their data gives  $k_3 = 42 \pm 4$  M s<sup>-1</sup> at 283 K for Cr(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup> and an estimate of  $k_3 \approx 10^2$  M s<sup>-1</sup> at 25 °C if  $\Delta H_3^*$  is the same as for (H<sub>2</sub>O)<sub>5</sub>CrCH<sub>2</sub>CN<sup>2+</sup>. The  $k_3$  values can be used analogously to the  $k_2$  values to estimate the second ionization constant of these aquachromium(III) species. The estimated  $pK_2$ 's are 7.5 and 7.0 for (H<sub>2</sub>O)<sub>5</sub>CrCH<sub>2</sub>CN<sup>2+</sup> and Cr(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup>, respectively. The latter value is somewhat larger than that of 6.1 obtained by Stünzi and Marty<sup>11</sup> from potentiometric titrations, but is in marked disagreement with the value of 9.7 suggested by Schwarzenbach.<sup>14</sup> The NMR estimate may be slightly low because of uncertainty about the number of exchanging sites, as discussed above, while the potentiometric value could be low because of difficulties in correcting for oligomerization reactions.

Finally, we wish to comment on the general relaxation effects of these chromium(III) complexes. The values of  $R_{2P}$  are of the order of 10<sup>5</sup> for both (H<sub>2</sub>O)<sub>5</sub>Cr(N<sub>3</sub>)<sup>2+</sup> and (H<sub>2</sub>O)<sub>5</sub>CrCH<sub>2</sub>CN<sup>2+</sup> and are about 10 times larger for Cr(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup>. This is consistent with the relaxation by the scalar interaction, controlled by the electron spin relaxation time ( $\tau_e$ )<sup>9</sup> of chromium(III). The lower symmetry of the former two complexes should make this time shorter and thereby reduce the solvent proton  $R_{2P}$  values. The similarity of (H<sub>2</sub>O)<sub>5</sub>Cr(N<sub>3</sub>)<sup>2+</sup> and (H<sub>2</sub>O)<sub>5</sub>CrCH<sub>2</sub>CN<sup>2+</sup> indicates that there is nothing remarkably special about the electron spin properties and therefore the electronic state of the organochromium species.

## Experimental Section

The solutions of (H<sub>2</sub>O)<sub>5</sub>CrCH<sub>2</sub>CN<sup>2+</sup> in aqueous perchloric acid were prepared and purified by ion exchange chromatography as described previously.<sup>5</sup> A stock solution of  $7.51 \times 10^{-3}$  M (H<sub>2</sub>O)<sub>5</sub>CrCH<sub>2</sub>CN<sup>2+</sup> in 0.051 M HClO<sub>4</sub> was adjusted to higher acidity by addition of 1.067 M HClO<sub>4</sub> and to lower acidity by addition of weighed amounts of Na<sub>2</sub>CO<sub>3</sub>. The solutions for NMR measurements were kept under an argon atmosphere in 10 MM tubes sealed with a serum cap.

The NMR relaxation rates were determined by standard 180- $\tau$ -90 ( $R_1$ ) and Carr-Purcell-Meiboom-Gill methods ( $R_2$ ) on a Bruker SXP 4-100 pulsed spectrometer at 89.5 MHz. The instrumentation is fully described elsewhere.<sup>8,15</sup> The temperature was measured in a blank sample tube with a copper-constantan thermocouple before and after each set of measurements. The reported relaxation rates are the average of at least five replicate determinations, with a typical precision of  $\pm 2\%$  for  $R_1$  and  $\pm 5\%$  for  $R_2$ .

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada for funding and Dr. M. J. Sisley for preparation of the (H<sub>2</sub>O)<sub>5</sub>CrCH<sub>2</sub>CN<sup>2+</sup>.

**Supplementary Material Available:** Transverse (Table S1) and longitudinal (Table S2) relaxation rates for solvent protons in solutions of (H<sub>2</sub>O)<sub>5</sub>CrCH<sub>2</sub>CN<sup>2+</sup> in aqueous acid (4 pages). Ordering information is given on any current masthead page.

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