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# Interpretation of Kinetic Data for the Reaction of Azide with Aquapentaamminechromium(III) and the Reverse (Aquation) Reaction

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The reaction of azide with $Cr(NH_3)_5H_2O^{3+}$ (pH 2.5–4.5) yields the azido complex $Cr(NH_3)_5N_3^{2+}$, which over extended run periods undergoes further substitution. First-order rate constants for the formation of $Cr(NH_3)_5N_3^{2+}$, $k_{obsd}$, give a dependence on total azide, $[N_3^-]_T$, of the form $k_{obsd}/[N_3^-]_T = (k_1K_a + k_2[H^+])/(K_a + [H^+])$, where $K_a$ is the acid dissociation constant for $HN_3$ and $k_1$ and $k_2$ are rate constants for the reactions of $Cr(NH_3)_5H_2O^{3+}$ with $N_3^-$ and $HN_3$, respectively. At 50 °C and $I = 1.0$ M ($NaClO_4$), $K_a = 5.0 \times 10^{-5}$ M corresponding to $pK_a = 4.3$ ($\Delta H = 2.6$ kcal mol$^{-1}$, $\Delta S = -11.8$ cal K$^{-1}$ mol$^{-1}$), $k_1 = 3.2 \times 10^{-4}$ M$^{-1}$ s$^{-1}$, and $k_2 = 5.5 \times 10^{-6}$ M$^{-1}$ s$^{-1}$. The interpretation differs from that of a previous study in which a pathway involving reaction of $Cr(NH_3)_5OH^{2+}$ with $N_3^-$ was implicated with no consideration of the reaction $Cr(NH_3)_5H_2O^{3+} + HN_3$. A brief study has also been made of the kinetics of the aquation of $Cr(NH_3)_5N_3^{2+}$, which conforms to the rate law $k_{obsd} = k_{aq} + k_H[H^+]$, with $k_{aq} = 1.39 \times 10^{-6}$ s$^{-1}$ and $k_H = 4.2 \times 10^{-5}$ M$^{-1}$ s$^{-1}$ at 50 °C. Activation parameters have been determined for $k_1$, $k_2$, $k_{aq}$, and $k_H$, and updated values for the Br$^-$ anation of $Cr(NH_3)_5H_2O^{3+}$ are also presented. A comparison of existing data for substitution on $Cr(NH_3)_5H_2O^{3+}$ is made.

Investigations on substitution reactions of $Cr(NH_3)_5H_2O^{3+}$ are more detailed and require more care than those of $Co(NH_3)_5H_2O^{3+}$ because of competing $NH_3$-loss processes,[1] and full kinetic studies of the anation of $Cr(NH_3)_5H_2O^{3+}$ with simple anions such as nitrate, sulfate, fluoride, and formate have yet to be reported.[2]  As more information becomes available, it is clear that $NH_3$-loss processes for Cr(III) complexes $Cr(NH_3)_5X^{n+}$ fall into at least two different categories. The first is with X a small oxyanion (nitrate,[3] sulfate,[1] and carboxylates $RCO_2^-$[4] but not phosphate[5] or selenate[6]). Cis labilization is believed to be featured in such reactions since loss of more than one $NH_3$ is observed,[1,3] and transient chelation of an uncoordinated O atom is the most likely explanation. Similarly, with glycinate[7] and oxalate,[8] rate-determining formation of the monodentate complex is followed by rapid (and permanent) chelation involving $NH_3$ loss. A second category of reaction with X = F$^-$, OH$^-$, (and $N_3^-$) has been reported, where loss of $NH_3$ is a consequence of the nature of the bonding Cr–X. Although it is not clear whether cis or trans products predominate in such reactions,[2] in a recent definitive study with X = F$^-$ both appear to be formed.[9]

An earlier study by Banerjea and Sarkar[10] on the conversion of $Cr(NH_3)_5H_2O^{3+}$ (orange) to $Cr(NH_3)_5N_3^{2+}$ (red) also reported formation of low-charged (green) complexes resulting from the replacement of $NH_3$'s by $N_3^-$. We confirm that it is possible to monitor the kinetics of the primary process (1)

$$Cr(NH_3)_5H_2O^{3+} + N_3^- \rightarrow Cr(NH_3)_5N_3^{2+} + H_2O \quad (1)$$
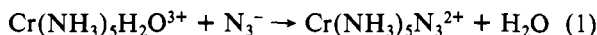
and that in the latter stages of the reactions there is green coloration. However, we differ in interpretation of the kinetics, which previously included consideration of the reactions of $Cr(NH_3)_5H_2O^{3+}$ and $Cr(NH_3)_5OH^{2+}$ with $N_3^-$ but no contribution from reactions of $HN_3$. We are interested in evaluating further the kinetics of (1) and comparing the results

**Table I.** Acid Dissociation Constants, $K_a$, for $NH_3$, $I = 1.0$ M ($NaClO_4$)

| temp, °C | $10^5K_a$, M | temp, °C | $10^5K_a$, M |
|---|---|---|---|
| 22 | 3.39 ± 0.08 | 50 | 5.01 ± 0.18 |
| 25 | 3.63$^a$ | 60 | 5.62 ± 0.32 |
| 40 | 4.36 ± 0.15 | | |

$^a$ Literature value from ref 14.

with earlier data for substitution reactions involving $Cr(NH_3)_5H_2O^{3+}$.

## Experimental Section

**Reactants.** The nitrate salt of aquapentaamminechromium(III), $[Cr(NH_3)_5H_2O](NO_3)_3 \cdot NH_4NO_3$, was converted into the perchlorate salt, $[Cr(NH_3)_5(H_2O)](ClO_4)_3$, as previously described.[5] A sample of azidopentaamminechromium(III) perchlorate, $[Cr(NH_3)_5N_3](ClO_4)_2$, was prepared from the latter.[11] Relevant details of spectra in 0.10 M $HClO_4$, $\lambda_{max}$/nm ($\epsilon$/M$^{-1}$ cm$^{-1}$), are for $Cr(NH_3)_5H_2O^{3+}$ 481 (35.4) and 361 (30.8) and for $Cr(NH_3)_5N_3^{2+}$ 500 (144) (Figure 1), in agreement with literature values.[5,12] Analar grade sodium azide ($NaN_3$), sodium perchlorate ($NaClO_4 \cdot H_2O$), and sodium bromide were used without further purification. Lithium perchlorate, prepared from $Li_2CO_3$ (BDH, Laboratory Reagent) and perchloric acid (BDH, AnalaR), was recrystallized three times. Solutions of $NaClO_4$ and $LiClO_4$ were standardized by passing them down an Amberlite IR 120(H) resin column and titrating the liberated H$^+$ with NaOH.

**Determination of Acid Dissociation Constant for $HN_3$.** The pHs of nine solutions, made up with varying concentrations of $NaN_3$ and $HN_3$ (assumed to be equal to the amount of $HClO_4$ added), were measured at 22, 40, 50, and 60 °C on a Radiometer (PHM62) pH meter calibrated with solutions at $I = 1.0$ M ($NaClO_4$). A Russell (Type CWR/322) special stem combination glass electrode was used, with the KCl component replaced by NaCl to enable measurements in $ClO_4^-$ solutions. This was immersed in solution in a 1-cm optical cell, the temperature of which was rapidly adjusted with a digitial temperature controller. To avoid loss of $HN_3$ (bp 37 °C), the cell was closed with a rubber seal holding the electrode. No effective loss of $HN_3$ was demonstrated for a series of measurements by returning to the initial temperature (22 °C) when an identical reading was obtained. Solutions investigated were in the pH range of 2.8–4.6. Equation 2 was used to calculate acid dissociation p$K_a$ values, and

$$pH = pK_a + \log ([NaN_3]/[HN_3]) \quad (2)$$

hence $K_a$ as listed in Table I.  Values determined spectrophotometrically,[13] by a procedure based on the different absorbances of

(1) Ramasami, T.; Wharton, R. K.; Sykes, A. G. *Inorg. Chem.* **1975**, *14*, 359.
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(8) Nor, O.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1973**, 1232.
(9) Kirk, A. O.; Glover, S. G. *Inorg. Chem.* **1983**, *22*, 176.
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(12) Linhard, M.; Siebert, H.; Weigel, M. *Z. Anorg. Allg. Chem.* **1955**, *278*, 240.
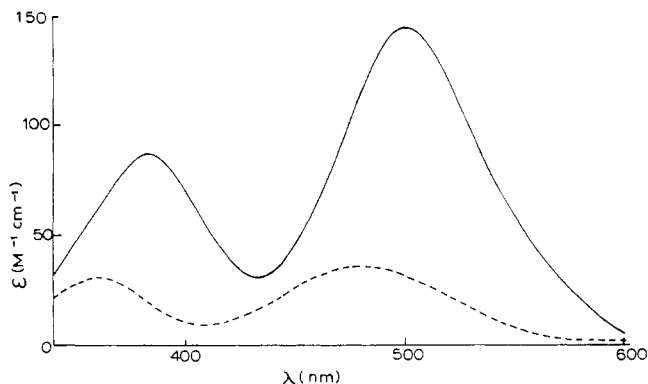(13) Burns, E. A.; Chang, F. D. *J. Phys. Chem.* **1959**, *63*, 1314.

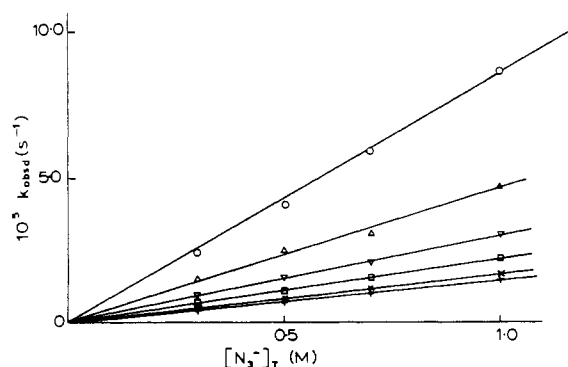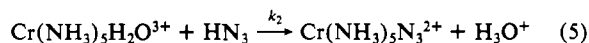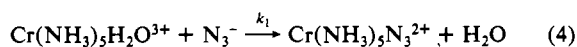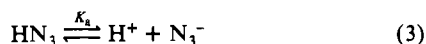**Figure 1.** UV–visible spectra for $Cr(NH_3)_5N_3^{2+}$ (—) and $Cr(NH_3)_5H_2O^{3+}$ (- - -) in 0.1 M $HClO_4$.



**Figure 2.** Dependence of first-order rate constants, $k_{obsd}$, on total azide concentration, $[HN_3] + [N_3^-]$, for the anation of $Cr(NH_3)_5H_2O^{3+}$ with $10^4[H^+]$ (M) = 1.51 (+), 3.39 (×), 6.03 (□), 9.55 (▽), 14.5 (▲), and 17.4 (○) at 50 °C, $I$ = 1.0 M ($NaClO_4$).

$N_3^-$ and $HN_3$ in the region 228–242 nm, were in satisfactory agreement with those listed. From the temperature dependence of log $K_a$ against $1/T$, $\Delta H$ = 2.61 ± 0.08 kcal mol$^{-1}$ and $\Delta S$ = −11.6 ± 0.3 cal K$^{-1}$ mol$^{-1}$, to be compared with literature values,[14] $I \rightarrow 0$, of $\Delta H$ = 3.8 kcal mol$^{-1}$ and $\Delta S$ = −8.6 cal K$^{-1}$ mol$^{-1}$.

**Buffering of Solutions.** For the anation studies azide served as the buffer. Solid $NaN_3$ was added to solutions of $NaClO_4$ (or $LiClO_4$), $HClO_4$, and $Cr(NH_3)_5H_2O^{3+}$ as required. The pH of duplicate-run solutions was checked at 22 °C and then converted to the higher temperature, 40, 50, or 60 °C (as relevant to the kinetic runs), by means of (2).

**Kinetic Studies.** Run solutions filled a 1 cm path length optical cell, and Teflon stoppers were put in place with no residual air gap. For the anation reaction azide with in large excess of the complex. Absorbance changes at 500 nm were recorded on a Pye-Unicam SP8000 complete with automatic cell changer, and plots of ln ($A_\infty$ − $A_t$) against time were with calculated $A_\infty$ values from the known spectrum of $Cr(NH_3)_5N_3^{2+}$. Such plots were linear to 35–75% completion only, due to further reactions involving loss of $NH_3$ ligands. The slope of the linear section gave first-order rate constants $k_{obsd}$. A reaction scheme (eq 3–5) is considered here. This gives the de-

$$HN_3 \xrightleftharpoons{K_a} H^+ + N_3^- \tag{3}$$

$$Cr(NH_3)_5H_2O^{3+} + N_3^- \xrightarrow{k_1} Cr(NH_3)_5N_3^{2+} + H_2O \tag{4}$$

$$Cr(NH_3)_5H_2O^{3+} + HN_3 \xrightarrow{k_2} Cr(NH_3)_5N_3^{2+} + H_3O^+ \tag{5}$$

pendence (6), where $[N_3^-]_T$ is the total azide present as $N_3^-$ and $HN_3$.

$$\frac{k_{obsd}}{[N_3^-]_T} = \frac{k_1K_a + k_2[H^+]}{K_a + [H^+]} \tag{6}$$

The aquation of $Cr(NH_3)_5N_3^{2+}$ was studied at 50 and 55 °C with $[H^+]$ = 0.02–0.08 M. Reactions were monitored at 300 nm, and plots of ln ($A_t$ − $A_\infty$) against time were linear to at least 50% completion,
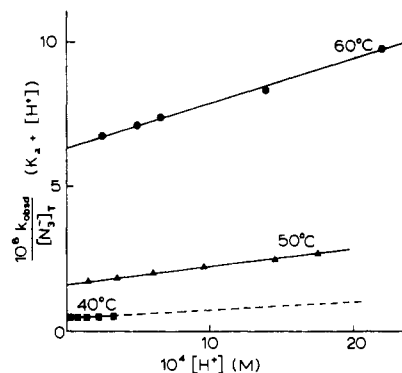
(14) Boughton, J. H.; Keller, R. N. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2851.



**Figure 3.** Dependence of $k_{obsd}$ on $[H^+]$, demonstrating the applicability of eq 6 for the azide anation of $Cr(NH_3)_5H_2O^{3+}$, $I$ = 1.0 M ($NaClO_4$).



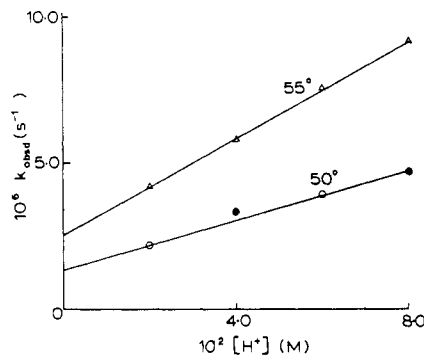**Figure 4.** Dependence of first-order rate constants, $k_{obsd}$, for the aquation of $Cr(NH_3)_5N_3^{2-}$ on $[H^+]$: (△ and ○) $I$ = 1.0 M ($NaClO_4$); (●) $I$ = 1.0 M ($LiClO_4$).
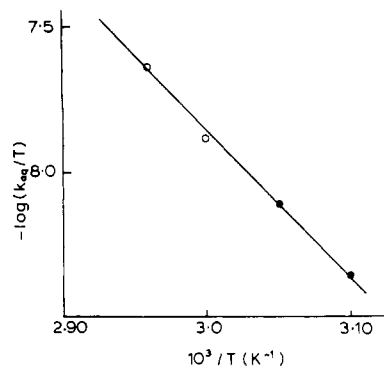


**Figure 5.** Activation plot for the aquation of $Cr(NH_3)_5N_3^{2+}$ with the inclusion of new data (●) alongside previous data (○) reported in ref 15, $I$ = 1.0 M ($NaClO_4$).

the extent of most studies. Supplementary runs on the Br$^-$ anation of $Cr(NH_3)_5H_2O^{3+}$ were monitored at 265 nm, when plots were linear to 80% completion.

Ionic strengths were adjusted to a value $I$ = 1.0 M ($NaClO_4$), and use of $LiClO_4$ demonstrated that there was no effect of $Na^+$ or $Li^+$ on $k_{obsd}$.

**Treatment of Data.** A nonlinear least-squares program with $1/y^2$ weighting was used to fit data to (6) and obtain activation parameters for $k_1$ and $k_2$. Elsewhere least-squares programs were used.

## Results

First-order rate constants $k_{obsd}$ for the anation process are listed in Table II. Figure 2 illustrates the linear dependence of $k_{obsd}$ on $[N_3^-]_T$ at 50 °C, pH 2.53–3.60, with no evidence for positive intercepts at $[N_3^-]_T$ = 0 corresponding to contributions from the reverse reactions. The slopes give second-order rate constants, $k_{obsd}/[N_3^-]_T$. A good fit to (6) is obtained, which is illustrated by plotting $k_{obsd}(K_a + [H^+])/[N_3^-]_T$ against $[H^+]$ (Figure 3). The intercepts and slopes correspond to $k_1K_a$ (hence $k_1$) and $k_2$, respectively. At 50 °C

**Table II.** First-Order Rate Constants for the Azide Anation of $Cr(NH_3)_5H_2O^{3+}$ ($\sim 2.0 \times 10^{-3}$ M), $I = 1.0$ M ($NaClO_4$)

| temp, °C | $10^4[H^+]$, M | $[N_3^-]_T$, M | $10^5 k_{obsd}$, $s^{-1}$ |
|---|---|---|---|
| 40.0 | 0.34 | 0.40 | 2.38 |
| | | 0.60 | 3.6 |
| | | 0.80 | 4.8 |
| | | 1.00 | 6.4 |
| | 0.68 | 0.40 | $1.82^a$ |
| | | 0.60 | 2.69 |
| | | 0.80 | $3.2^a$ |
| | | 1.00 | 4.4 |
| | 1.26 | 0.40 | 1.21 |
| | | 0.60 | 1.81 |
| | | 0.80 | 2.34 |
| | | 1.00 | 2.77 |
| | 2.14 | 0.40 | 0.78 |
| | | 0.80 | 1.65 |
| | | 1.00 | 1.97 |
| | 3.16 | 0.40 | 0.60 |
| | | 0.60 | 0.91 |
| | | 0.80 | 1.20 |
| | | 1.00 | 1.47 |
| 50.0 | 1.51 | 0.30 | 2.39 |
| | | 0.50 | 4.1 |
| | | 0.70 | 5.9 |
| | | 1.00 | 8.7 |
| | 3.39 | 0.30 | 1.47 |
| | | 0.50 | 2.51 |
| | | 0.70 | 3.0 |
| | | 1.00 | 4.7 |
| | 6.03 | 0.30 | 0.92 |
| | | 0.50 | 1.60 |
| | | 0.70 | 2.08 |
| | | 1.00 | 3.06 |
| | 9.55 | 0.30 | 0.67 |
| | | 0.50 | 1.02 |
| | | 0.70 | 1.54 |
| | | 1.00 | 2.28 |
| | 14.5 | 0.30 | 0.53 |
| | | 0.50 | 0.82 |
| | | 0.70 | 1.10 |
| | | 1.00 | 1.62 |
| | 17.4 | 0.30 | 0.40 |
| | | 0.50 | 0.80 |
| | | 0.70 | 1.08 |
| | | 1.00 | 1.59 |
| 60.0 | 2.45 | 0.30 | 6.7 |
| | | 0.50 | 11.0 |
| | | 0.70 | 16.5 |
| | | 1.00 | 21.7 |
| | 4.90 | 0.30 | 3.7 |
| | | 0.50 | 6.7 |
| | | 0.70 | 8.8 |
| | | 1.00 | 13.1 |
| | 6.61 | 0.30 | 3.2 |
| | | 0.50 | 5.3 |
| | | 0.70 | 7.5 |
| | | 1.00 | $10.0^b$ |
| | 13.8 | 0.30 | 1.62 |
| | | 0.50 | 3.0 |
| | | 0.70 | 3.9 |
| | | 1.00 | $5.8^b$ |
| | 21.9 | 0.30 | 1.31 |
| | | 0.50 | 2.23 |
| | | 0.70 | 3.3 |
| | | 1.00 | 4.2 |

$^a$ $I$ adjusted with $LiClO_4$. $^b$ [Cr(III)] = $2.6 \times 10^{-3}$ M.

$k_1 = 3.2 \times 10^{-4}$ $M^{-1}$ $s^{-1}$ and $k_2 = 6.1 \times 10^{-6}$ $M^{-1}$ $s^{-1}$, and from the temperature dependence and plots of log $(k/T)$ against $1/T$ (Eyring equation), activation parameters are $\Delta H_1^* = 23.0 \pm 0.4$ kcal $mol^{-1}$, $\Delta S_1^* = -3.6 \pm 1.2$ cal $K^{-1}$ $mol^{-1}$, $\Delta H_2^* = 26.1 \pm 2.2$ kcal $mol^{-1}$, and $\Delta S_2^* = -2.0 \pm 0.7$ cal $K^{-1}$ $mol^{-1}$. Rate constants, $k_{obsd}$, for the aquation of $Cr(NH_3)_5N_3^{2+}$ at 50 and 55 °C (Table III) conform to the dependence (Figure 4)

$$k_{obsd} = k_{aq} + k_H[H^+] \tag{7}$$

**Table III.** First-Order Rate Constants for the Aquation of $Cr(NH_3)_5N_3^{2+}$ ($\sim 4.0 \times 10^{-4}$ M), $I = 1.0$ M ($NaClO_4$)

| temp, °C | $10^2[H^+]$, M | $10^6 k_{obsd}$, $s^{-1}$ |
|---|---|---|
| 50.0 | 2.0 | 2.1 |
| | 4.0 | $3.3^a$ |
| | 6.0 | 3.9 |
| | 8.0 | $4.7^a$ |
| 55.0 | 2.0 | 4.2 |
| | 4.0 | 5.8 |
| | 6.0 | 7.6 |
| | 8.0 | 9.2 |

$^a$ $I$ adjusted with $LiClO_4$.

**Table IV.** Equilibration Rate Constants for the Reaction of $Br^-$ with $Cr(NH_3)_5H_2O^{3+}$ at $[H^+] = 0.10$ M and $I = 1.0$ M ($LiClO_4$) as a Supplement to Existing Data[21]

| At 40 °C | |
|---|---|
| $[Br^-]$, M | 0.10, 0.30, 0.40, 0.50, 0.60 |
| $10^3 k_{eq}$, $s^{-1}$ | 0.45, 0.52, 0.53, 0.56, 0.56 |

| At 60 °C | |
|---|---|
| $[Br^-]$, M | 0.2, 0.35, 0.5, 0.6, 0.8 |
| $10^3 k_{eq}$, $s^{-1}$ | 3.5, 3.7, 3.9, 4.1, 4.4 |

with $k_{aq} = (1.4 \pm 0.2) \times 10^{-6}$ $s^{-1}$ and $k_H = (4.2 \pm 0.4) \times 10^{-5}$ $M^{-1}$ $s^{-1}$ at 50 °C. By combination of the data at 50 and 55 °C with literature values at 60 and 65 °C,[15] $I = 1.0$ M ($NaClO_4$), activation parameters $\Delta H^*$ (kcal $mol^{-1}$) and $\Delta S^*$ (cal $K^{-1}$ $mol^{-1}$) are respectively 23.8 ± 0.2 and 11.6 ± 0.2 (for $k_{aq}$) and 20.1 ± 2.2 and -16.5 ± 3.6 (for $k_H$).

Runs in which the ionic strength was adjusted with $LiClO_4$ instead of $NaClO_4$ were in excellent agreement (see Tables II and III). The supplementary runs on the $Br^-$ anation are listed in Table IV.

## Discussion

Anation of $Cr(NH_3)_5H_2O^{3+}$ proceeds by two dominant kinetic pathways at pH 2.5–4.5, here assigned to the reaction of $Cr(NH_3)_5H_2O^{3+}$ with $N_3^-$ ($k_1$) and $Cr(NH_3)_5H_2O^{2+}$ with $HN_3$ ($k_2$). Previous interpretation has been in terms of reaction of $N_3^-$ with $Cr(NH_3)_5H_2O^{3+}$ and $Cr(NH_3)_5OH^{2+}$, with no contributions from reaction paths involving $HN_3$, which at 50 °C and pH ≤4.3 is the dominant form of azide. It would be unusual if $HN_3$ did not participate since a path $k_H$ depending on $[H^+]$ and corresponding to the aquation of $HN_3$ is involved in the aquation of $Cr(NH_3)_5N_3^{2+}$. As a general rule, replacement of a negative ligand by a negative ion does not occur directly and certainly would not be expected for an interchange mechanism in which the two ions involved are in close proximity. Thus in the reaction of $Co(NH_3)_5NO_3^{2+}$ with $NCS^-$ it has been demonstrated that the reaction proceeds with intermediate formation of $Co(NH_3)_5H_2O^{3+}$.[16] There are no grounds for supposing that in the present study the $OH^-$ in $Cr(NH_3)_5OH^{2+}$ would be a good leaving group. A reaction path involving $Cr(NH_3)_5OH^{2+}$ would moreover have to be very favorable for there to be a significant contribution, since the $pK_a$ of $5.2^{17}$ for $Cr(NH_3)_5H_2O^{3+}$ indicates that $Cr(NH_3)_5OH^{2+}$ is a minority species at pH ≤4.5. It is apparent also in other studies involving $N_3^-$,[18] $F^-$,[19] and $SO_4^{2-}$ ligands[20] that protonation is similarly effective in both the forward and the reverse reactions. The interpretation now adopted with $K_a$ for $HN_3$ incorporated in the rate law (6) gives at 50 °C

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Table V. Summary of Rate Constants ($k_f$) and Activation Parameters for the Replacement of $H_2O$ in $[Cr(NH)_5H_2O]^{3+}$ with Different Incoming Ligands X, $I$ = 1.0 M (Standard Deviations in Parentheses)

| X | $10^4 k_f$ (50 °C), $M^{-1} s^{-1}$ | $\Delta H_f^{\ddagger}$, kcal mol$^{-1}$ | $\Delta S_f^{\ddagger}$, cal K$^{-1}$ mol$^{-1}$ | ref |
|---|---|---|---|---|
| $N_3^-$ | 3.2 | 23.0 (0.4) | -3.6 (1.2) | this work |
| $NCS^-$ | 4.2 | 24.4 | 3.0 | 21, 22 |
| $CCl_3CO_2^-$ | 1.81 | 25.2 | 2.2 | 21 |
| $CF_3CO_2^-$ | 1.37 | | | 21 |
| $Cl^-$ | 0.69 | 25.6 | 2.0 | 21 |
| $Br^-$ | 3.7 | 26.5 (2.5)$^a$ | 7.7 (7.7)$^a$ | this work |
| $NH_3^+CH_2CO_2^-$ | 7.8 | 25.3 | 5.6 | 7 |
| $HC_2O_4^-$ | 6.5 | 26.7 | 9.4 | 8 |
| $H_2PO_4^-$ | 2.59 | 25.0 | -1.2 | 5 |
| $H_2PO_2^-$ | 1.14 | 28.7 | 12.3 | b |
| $H_2O$ | 13.7$^c$ | 23.2 | 0 | 25 |
| $H_3PO_4$ | 0.46 | 25.0 | 2.3 | 5 |
| $H_3PO_2$ | 0.45 | 28.7 | 14.9 | b |
| $C_2O_4^{2-}$ | 29.1 | 24.9 | 7.8 | 8 |

$^a$ From data at 40, 50, and 60 °C; previous values $\Delta H^{\ddagger}$ = 21.9 kcal mol$^{-1}$, $\Delta S^{\ddagger}$ = -4.0 cal K$^{-1}$ mol$^{-1}$.[21] $^b$ Martinez, M.; Ferrer, M. *Inorg. Chim. Acta* 1983. $^c$ First-order rate constant.

an $N_3^-$ anation rate constant $k_1$ (3.4 × 10$^{-4}$ M$^{-1}$ s$^{-1}$) and an overall equilibrium constant $k_1/k_{aq}$, here represented as $K_{IS}K_{OS}$, of 229 M$^{-1}$, not too dissimilar from values for the corresponding NCS$^-$ reaction.[21,22] Similar $N_3^-$ and NCS$^-$ behavior has been observed previously in other comparable studies involving Co(NH$_3$)$_5$H$_2$O$^{3+}$.[23] If Cr(NH$_3$)$_5$OH$^{2+}$ plays any significant role, it is more likely to be alongside that of Cr(NH$_3$)$_5$N$_3^{2+}$ in providing a possible pathway for NH$_3$ loss (OH$^-$ and/or $N_3^-$ labilization), leading to the more extensive substitution by azide and the green coloration that is observed toward the end of kinetic runs.

The mechanistic assignment for substitution of Cr-(NH$_3$)$_5$H$_2$O$^{3+}$ continues to be of interest, and indeed concern.[5,24] Table V is an updated summary of second-order rate constants $k_f$ (=$K_{OS}k_{an}$)[21] for the formation of Cr(NH$_3$)$_5$X$^{n+}$, including $k_1$ and $k_2$ (and activation parameters) from this study. For the ten X ligands having a 1- charge a narrow ((0.69-7.82) × 10$^{-4}$ M$^{-1}$ s$^{-1}$) range of rate constants is observed. With the inclusion of supplementary runs for equilibration of Br$^-$ with Cr(NH$_3$)$_5$H$_2$O$^{3+}$, and recomputation of activation parameters, we are now able to specify $\Delta H^{\ddagger}$ values in a narrow range (23.0-26.7 kcal mol$^{-1}$) for all but one of these reactions. This contrasts with the marked trend in aquation rate constants, $k_{aq}$, of (0.11-102) × 10$^{-4}$ s$^{-1}$ and the systematic trend in $\Delta H^{\ddagger}$ values of 18.3-24.3 kcal mol$^{-1}$ (Table VI), indicating some dependence on bond breaking. The slope of the plot of log $k_{aq}$ against log $K_{IS}K_{OS}$ remains in the range 0.70-0.90, the exact value depending on the position of the Br$^-$ point.[5] A different procedure was used by Monsted[24] to evaluate $K_{IS}K_{OS}$ (0.019 M$^{-1}$), but this does not give a value in agreement with the kinetically determined $K_{IS}K_{OS}$ of 0.30 M$^{-1}$. Since the volume of activation of -5.8 cm$^3$ mol$^{-1}$ for H$_2$O exchange on Cr(NH$_3$)$_5$H$_2$O$^{3+}$ favors more an I$_a$ process,[25]

Table VI. Summary of Rate Constants and Activation Parameters for Aquation of Cr(III) Complexes Cr(NH$_3$)$_5$X$^{n+}$, $I$ = 1.0 M (Standard Deviations in Parentheses)

| ligand X | $10^4 k_{aq}$ (50 °C), $s^{-1}$ | $\Delta H_{aq}^{\ddagger}$, kcal mol$^{-1}$ | $\Delta S_{aq}^{\ddagger}$, cal K$^{-1}$ mol$^{-1}$ | ref |
|---|---|---|---|---|
| $N_3^-$ | 0.014 | 23.8 (0.2) | -11.6 (0.2) | this work |
| $NCS^-$ | 0.011 | 24.3 | -8.0 | a |
| $CCl_3CO_2^-$ | 0.51 | 21.5 | -11.3 | 4 |
| $CF_3CO_2^-$ | 0.50 | 20.2 | -13.9 | b |
| DMF | 1.79 | 20.2 | -13.5 | 2 |
| $Cl^-$ | 1.75 | 20.7 | -11 | c |
| $Br^-$ | 12.5 | 19.0 (0.4) | -13.2 (1.3) | 21, d |
| $I^-$ | 102 | 18.3 | 10.8 | 21 |

$^a$ Adamson, A. W.; Wilkins, R. G. *J. Am. Chem. Soc.* 1954, 76, 3379. $^b$ Davies, R.; Evans, G. B.; Jordan, R. B. *Inorg. Chem.* 1969, 8, 2025. $^c$ Duffy, N. V.; Earley, J. E. *J. Am. Chem. Soc.* 1967, 89, 272. $^d$ From data at 40, 50, and 60 °C; previous values $\Delta H_{aq}^{\ddagger}$ = 20.9 kcal mol$^{-1}$, $\Delta S_{aq}^{\ddagger}$ = -7.2 cal K$^{-1}$ mol$^{-1}$.[21]

Table VII. Summary of Outer-Sphere Association Constants (50 °C) Obtained from Kinetic Studies, $I$ = 1.0 M (LiClO$_4$)

| | $K_{OS}$, M$^{-1}$ | ref | | $K_{OS}$, M$^{-1}$ | ref |
|---|---|---|---|---|---|
| $H_3PO_4$ | 0.32 | 5 | $H_2PO_2^-$ | 0.33 | 6 |
| $H_3PO_2$ | 0.13 | 6 | $HC_2O_4^-$ | 1.16 | 8 |
| $NH_3^+CH_2CO_2^-$ | 0.55 | 7 | $C_2O_4^{2-}$ | 4.5 | 8 |
| $H_2PO_4^-$ | 1.8 | 5 | | | |

intermediate I$_a$ and I$_d$ behavior remains the most acceptable interpretation of all the data currently available.

No evidence was obtained in the present study (Figure 2) for positive intercepts indicating equilibrium kinetics. This observation is supported by the $K_{IS}K_{OS}$ of 229 M$^{-1}$ determined from forward and back rate constants ($k_1/k_{aq}$). Also there was no evidence for downward curvature with increasing [N$_3^-$]$_T$, suggesting significant outer-sphere association of N$_3^-$ to Cr(NH$_3$)$_5$H$_2$O$^{3+}$ ($K_{OS}$ ≤0.1 M$^{-1}$). It is of considerable interest that the instances in which $K_{OS}$ has been determined from the kinetics are with incoming groups containing O atoms capable of H bonding to the NH$_3$ ligands (Table VII). The values listed are consistent with calculations based on an electrostatic model,[26] although this model does not explain why, with other incoming groups of similar charge, $K_{OS}$ is at a lower level. Moreover, the careful work by Ferrer has demonstrated that whereas H$_2$PO$_4^-$ associates with Cr(NH$_3$)$_5$H$_2$O$^{3+}$ ($K_{OS}$ = 1.8 M$^{-1}$),[5] with Co(NH$_3$)$_5$H$_2$O$^{3+}$, under identical conditions, no ion pairing is detectable ($K_{OS}$ ≤ 0.10 M$^{-1}$).[27] This difference in behavior of 3d$^3$ and 3d$^6$ ions suggests that one reason Co(NH$_3$)$_5$H$_2$O$^{3+}$ and the Ni$^{2+}$ and Co$^{2+}$ aqua ions exhibit I$_d$ behavior is that $K_{OS}$ is at a much lower level due to the higher t$_{2g}$ orbital occupancy, thus making an I$_a$ process more difficult.

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(22) Van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* 1979, 18, 1520.
(23) See e.g.: Haim, A. *Inorg. Chem.* 1970, 9, 426.
(24) Monsted, L. *Acta Chem. Scand., Ser. A* 1978, 32A, 377.
(25) Swaddle, T. W.; Stranks, D. R. *J. Am. Chem. Soc.* 1972, 94, 8357.
(26) See e.g.: Kustin, K.; Swinehart, J. H. *Prog. Inorg. Chem.* 1970, 13, 135.
(27) Coronas, J. M.; Vicente, R.; Ferrer, M. *Inorg. Chim. Acta* 1981, 49, 259.