

## Deuterium Isotope Effect on the Aquation and Hydrolysis Rates of Aqueous $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]^{+2}$

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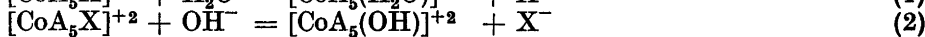
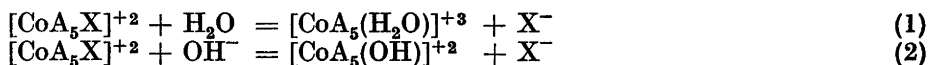
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The hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2}$  and the aquation of this and of  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{+2}$  have been studied in both ordinary and in deuterium containing aqueous systems. The hydrolysis rate in heavy water was some sixty percent of that in ordinary water, an effect due primarily to a lower frequency factor. The aquation rates were similarly lower in deuterium containing systems, and, because of the slow exchange between complex and solvent in acid media, it was possible to observe the four possible aquation rates corresponding to light or heavy complex in light or heavy solvent.

From a consideration of the deuterium effect and also the large entropy of activation, 37 E.U., as well as of other aspects, it is concluded that the hydrolysis proceeds through an acid base pre-equilibrium. For the aquation reaction, an explanation of the deuterium effects is given, involving a "front side" replacement by water, facilitated by hydrogen bond bridges.

The aquation and hydrolysis \*\*\* of complex ions have been rather extensively investigated, but their mechanisms are still a subject for active speculation. The reader is referred to a recent review paper <sup>1</sup> for a summary of the problems involved and a more complete coverage of the literature.

The present investigation relates to the type reactions:



The aquation reaction (1) follows first order kinetics <sup>2-4</sup>, but the mechanism has been considered by some to be  $S_N1$  (rate determining dissociation to a penta-

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\*\*\* Some brief can be made for terming these reactions acid and base hydrolysis, but the older usage will be adhered to here.

coordinated intermediate)<sup>5-7</sup>, and by others, to be  $S_N2$  (bimolecular substitution)<sup>8</sup>. Similarly, although the hydrolysis reaction (2) is second order<sup>9,10</sup>, the mechanism has been supposed to be  $S_N2$  by some investigators<sup>8</sup>, and, by others, to involve an acid-base pre-equilibrium<sup>11,12,13</sup>.

Substitution of deuterium for hydrogen in reacting systems introduces various types of effects in a way that frequently makes it possible to distinguish between various kinetically similar mechanisms<sup>13-15</sup>. The present investigation of the deuterium effect on the rates of aquation and hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{+2}$  was undertaken with this in mind.

### EXPERIMENTAL PROCEDURES

*Preparation of compounds.* The cobalt(III) complexes were kindly supplied by Mr. C. E. Schäffer, who had prepared them by the procedures of S. M. Jørgensen<sup>14</sup>. The compounds were recrystallized, washed with water, alcohol, and ether, and air dried; the  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})\text{Cl}]_2$  was kept under refrigeration.

The preparation of  $[\text{Co}(\text{ND}_3)_5\text{Cl}]\text{Cl}_2$  was as follows. A solution of  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})\text{Cl}]_2$  in 99%  $\text{D}_2\text{O}$  was made alkaline by the addition of metallic sodium, and the resulting solution of  $[\text{Co}(\text{ND}_3)_5(\text{OD})]^{+2}$  was allowed to stand for several hours. It was then acidified with dry hydrogen chloride gas, and digested on a steam bath until the precipitation of  $[\text{Co}(\text{ND}_3)_5\text{Cl}]\text{Cl}_2$  was fairly complete. The product was then washed and air dried. Information about its deuterium content was obtained from a comparison of its infra red spectrum with that for the ordinary complex, using samples of powdered material in *per*-chlorobutadiene. The ordinary and the deuterated complex showed strong bands at 3.00 and 4.14 microns, respectively, as expected for the N-H and the N-D bond<sup>17</sup>. The infra red measurements were made by Mrs. S. Refn through the courtesy of Professor S. Veibel. Some of the  $\text{D}_2\text{O}$  was kindly made available by Professor R. W. Asmussen.

While the above results were quite qualitative, exchange data, to be described below, indicated a deuterium content of 90% for the heavy complex.

*Exchange studies.* Qualitative data on the rates of exchange of deuterium between  $[\text{Co}(\text{ND}_3)_5\text{Cl}]^{+2}$  and  $\text{H}_2\text{O}$  under acid and alkaline conditions, were obtained as follows. For the former, a 0.02 M solution of the complex at pH 3 and at 38° C, was employed. The deuterium content of the solvent was found to rise slowly with time, and corresponded to about 18% exchange after two hours. For the second experiment, a similar solution of complex was employed, but 0.01 M in sodium hydroxide and kept at 18° C. Here exchange appeared to be complete in 1.5 minutes, and corresponded to a deuterium content for the complex of 90%. Anderson *et al.*<sup>11</sup> observed a similar exchange behavior for  $[\text{Co}(\text{NH}_3)_6]^{+2}$ .

The actual deuterium analyses were done by the gradient tube technique<sup>18</sup>, and were carried out at the Carlsberg Laboratory, through the courtesy of Professor Linderstrøm-Lang.

*Aquation runs.* For the aquation rate studies, a solution of the light or heavy complex in light or heavy water ("heavy" denoting about 85 or 90% deuteration) was prepared, and made 0.1 M in nitric acid. A 1 cm absorption cell was filled with the solution, which had been pre-heated to the desired temperature, and the covered cell was then placed in the thermostatted cell holder of a model DU Beckman spectrophotometer. The temperature control, as determined by direct measurements on the solutions in the cells, was good to  $\pm 0.1^\circ$ . Since two or three runs were generally made simultaneously, comparisons between them were not very dependent upon the quality of temperature control.

The course of the reaction was followed by measuring the time variation of the optical density at 550  $m\mu$ , and the data were plotted according to the first order rate law,

$$\log [(D - D^\infty)/(D^\circ - D^\infty)] = - \frac{kt}{2.303} \quad (3)$$

where  $D$  denotes optical density. The appropriate value for  $D^\infty$  was determined from separate extinction coefficient determinations, described below.

**Hydrolysis runs.** The hydrolysis runs were generally carried out as follows. A solution of the chloropentammine complex of the desired concentration was prepared, and its optical density checked. This solution and one of 0.1 M sodium hydroxide were then brought to the desired temperature and equivalent quantities of the two were mixed and immediately placed in a cell waiting in the thermostatted cell block. Due regard was given to the heat of mixing effect; other procedural details were similar to those for the aquation runs.

The rate was measured by following the optical density at 500  $m\mu$ , the data being plotted according to the second order rate law,

$$(D - D^\circ) / (D^\infty - D) = C^\circ kt \quad (4)$$

where  $C^\circ$  denotes the equal concentration of complex and of base.

The procedure for the runs with excess base was quite similar, except that 1 M rather than 0.1 M alkali was employed, and the data were plotted according to (3), the slope of the plot now giving the product of the second order rate constant and the constant concentration of base.

For the hydrolysis of  $[\text{Co}(\text{ND}_3)_5\text{Cl}]^{+2}$  in  $\text{D}_2\text{O}$ , it was only necessary to dissolve ordinary complex in heavy water, since exchange was rapid once the solution was made alkaline.

It might be noted that it appeared desirable to use very pure sodium hydroxide since otherwise irreproducible and generally high rates resulted.

**Determination of extinction coefficients.** In general, it was not possible to determine  $D^\infty$  values from the aquation and hydrolysis rate studies themselves. Some decomposition, with loss of ammonia, would set in before the reactions reached the necessary degree of completion, giving incorrect empirical values of  $D^\infty$ . The only exception was that of hydrolysis in excess base, which was both rapid and first order.

The difficulty was circumvented by employing  $D^\infty$  values calculated from the extinction coefficient separately determined for the assumed product, *i. e.*  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+3}$  or  $[\text{Co}(\text{NH}_3)_5(\text{OH})]^{+2}$ . It was found that the extinction coefficients themselves were subject to an isotope effect, and the complete set of  $\epsilon$  values is given in Table 1.

The complete absorption spectra for complexes in deuterated systems were actually only slightly different, as determined on a Cary recording spectrophotometer. For example, the 550  $m\mu$  peak for  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2}$  was shifted about 5  $m\mu$  toward the blue in the all deuterium system. However, at the wave lengths of 500 and 550  $m\mu$  employed for the rate measurements, significant differences did materialize in some cases, using the DU Beckman spectrophotometer. As might be expected, the isotope shifts were greatest for wave lengths midway between an absorption maximum and minimum, as in the case of the aquopentammine at 550  $m\mu$ , and least when the wave length corresponded to a maximum. (As an aid in orientation, the absorption maxima for  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2}$ ,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+3}$ , and  $[\text{Co}(\text{NH}_3)_5(\text{OH})]^{+2}$  occur at 535, 492, and 500  $m\mu$ , respectively.) In general the presence of deuterium either in solvent or in complex shifted the absorption spectrum towards shorter wave lengths.

The values of  $\epsilon$  in Table 1 were obtained as follows. For the chloro complex, the desired amount of the appropriate form was weighed out, dissolved in 0.1 M nitric acid, and the extinction coefficient calculated from the measured optical density.

Two series of  $\epsilon$  values for the aquopentammine and hydroxypentammine complexes were obtained by starting with a 0.2 M solution of  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})\text{Cl}]_3$ . This was diluted to 0.01 M either with ordinary or with heavy water, and the optical density measured. The solution was then made alkaline with a small excess of concentrated sodium hydroxide solution, giving either  $[\text{Co}(\text{NH}_3)_5\text{OH}]^{+2}$  or  $[\text{Co}(\text{ND}_3)_5(\text{OD})]^{+2}$ , exchange with solvent being rapid under these conditions, and the density again determined, allowance for dilution being made in computing the  $\epsilon$  values. Finally, the solution was acidified with a small excess of concentrated nitric acid, giving  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+3}$  or  $[\text{Co}(\text{ND}_3)_5(\text{D}_2\text{O})]^{+3}$ , and again measured.

Two similar series of measurements were also carried out with a 0.2 M solution of the aquocomplex in heavy water, which had been made alkaline and then reacidified, so that deuterio complex was present.

Table 1. Isotope effect on extinction coefficients.

Complex <sup>a,b</sup>	Substrate <sup>a,c</sup>	Extinction coefficients <sup>d</sup>		
		550 mμ		500 mμ
[Co(NH <sub>3</sub> ) <sub>5</sub> Cl]Cl	H <sub>2</sub> O	46.3, 47.2	46.8	42.2, 42.0
	D <sub>2</sub> O		46.5	42.1
[Co(ND <sub>3</sub> ) <sub>5</sub> Cl]Cl <sub>2</sub>	H <sub>2</sub> O	44.6, 44.8, 46.2	46.5	42.0, 40.2, 41.1
	D <sub>2</sub> O <sup>e</sup>		47.6	41.1
				43.8
[Co(NH <sub>3</sub> ) <sub>5</sub> H <sub>2</sub> O]Cl <sub>2</sub>	H <sub>2</sub> O	21.1, 20.9	21.0	46.9, 47.1
	D <sub>2</sub> O		18.5	47.0
[Co(ND <sub>3</sub> ) <sub>5</sub> H <sub>2</sub> O]Cl <sub>2</sub>	H <sub>2</sub> O		19.2	44.9
[Co(ND <sub>3</sub> ) <sub>5</sub> D <sub>2</sub> O]Cl <sub>2</sub>	D <sub>2</sub> O	19.1, 19.0, 19.4	19.2	44.8
[Co(NH <sub>3</sub> ) <sub>5</sub> OH]Cl <sub>2</sub>	H <sub>2</sub> O			45.3, 45.1, 45.7
[Co(ND <sub>3</sub> ) <sub>5</sub> OD]Cl <sub>2</sub>	D <sub>2</sub> O			45.3
				66.7, 66.9
				66.8
				67.1, 69.2, 69.2
				69.2

a) Where deuterium is indicated, the percent deuteration was ca. 85 %.

b) Only two attainable systems exist for the hydroxypentammine complex because of the rapid exchange with solvent. The complex was ca. 0.01 M in all cases.

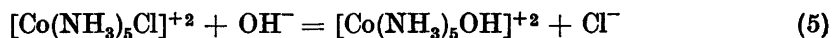
c) Values for the chloro and aquo complex were measured in ca. 0.1 M nitric or hydrochloric acid, while those for the hydroxy complex were for solutions ca. 0.01 M in sodium hydroxide.

d) Individual values represent completely independent determinations.

e) These values are based on run 55 where a reliable determination of  $D^\infty$  was possible.

## EXPERIMENTAL RESULTS

*Comparison of hydrolysis rates as determined spectrophotometrically and titrimetrically.* The spectrophotometric method which was employed for the majority of the rate studies required the use of a calculated  $D^\infty$  value, as discussed in the preceding section. It was therefor considered desirable to verify that the assumed reaction,



was indeed occurring to the practical exclusion of appreciable amounts of other processes and that the spectrophotometric method was not subject to some systematic error.

Two additional methods were therefor employed as a check. The first of these comprised a determination of the rate of consumption of hydroxide ion with time, carried out by first adding excess acid to the sample, to quench the reaction, and then back titrating with base to a thymol blue end point. At the pH of this end point, the aquopentammine complex is not titrated <sup>19</sup>. As shown in Fig. 1, substantial agreement was found between this and the spectrophotometric method. The second check involved a titration for chloride ion, using mercuric nitrate solution as reagent, and nitroprusside ion as indicator, and, again, as shown in Figure 2, satisfactory agreement was obtained.

*Determination of the order of the hydrolysis reaction.* Having established that equation (5) did in fact represent the course of the reaction over its major portion, it was of interest to verify the kinetics. While there is existing evidence

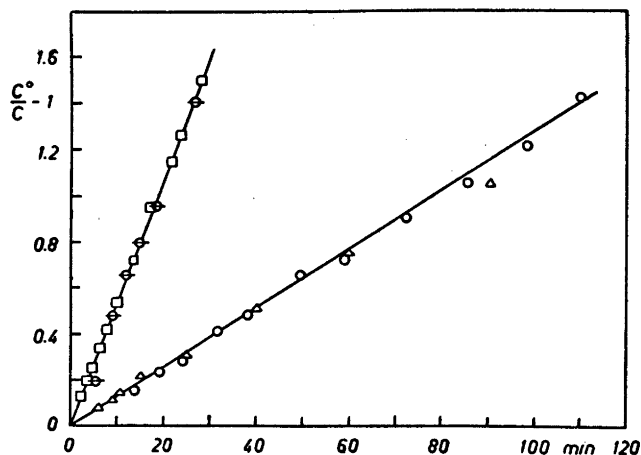


Fig. 1. Hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ ,  $\circ$ -Run 40 (spectrophotometric, at  $3.3^\circ$ );  $\triangle$ -Run 38 (chloride titration, at  $4.0^\circ$ );  $\square$ -Run 42 (spectrophotometric,  $11^\circ$ );  $\oplus$ -Run 29 (hydroxide titration,  $11^\circ$ ).

that the reaction should be second order, some deviations from this kinetics might develop at higher base concentrations if the mechanism were not of the simple  $\text{S}_{\text{N}}2$  type.

The collected results are illustrated in Figs. 2 and 3, and summarized in Table 2. Two series of runs were made. For the first, the starting solutions were made up to be of equal concentration,  $C_0$ , in complex and in base, and it

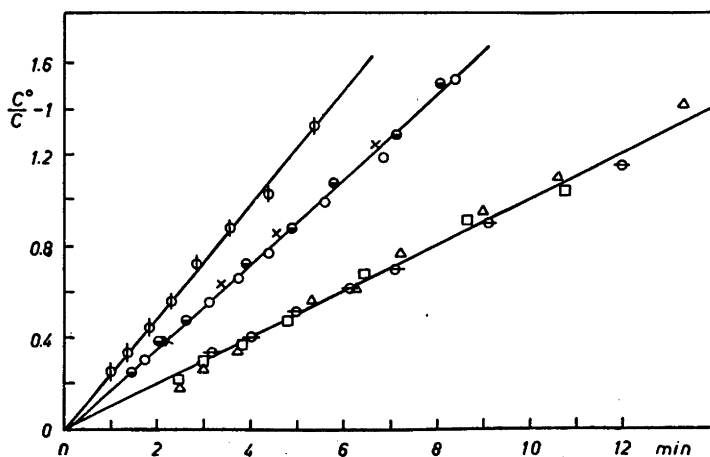


Fig. 2. Hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  at  $18^\circ\text{C}$ .  $\square$ ,  $\oplus$ ,  $\triangle$ -Runs 7, 8, 14,  $C = 0.00650$ ;  $\times$ -Run 37 (chloride titration,  $C = 0.01183$ )  $\circ$ ,  $\ominus$ -Runs 43, 46,  $C = 0.01183$ ;  $\Phi$ -Run 13,  $C = 0.0140$  ( $19^\circ\text{C}$ ).

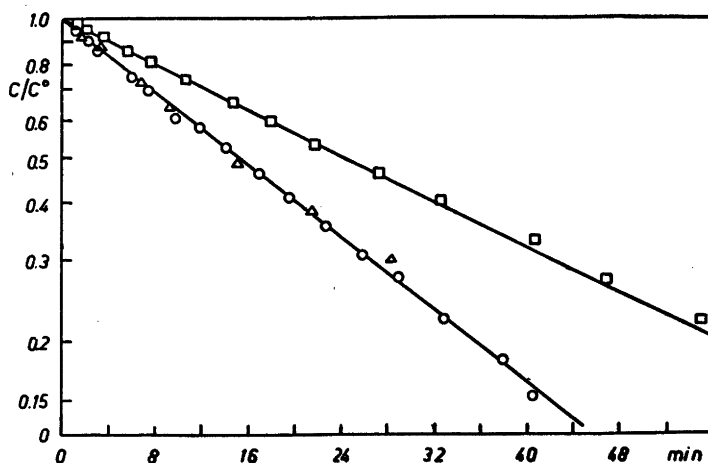


Fig. 3. Hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  at  $2.5^\circ\text{C}$  in excess base. O,  $\Delta$ -Runs 53, 54;  $\square$ -Run 55 ( $[\text{Co}(\text{ND}_3)_5\text{Cl}]\text{Cl}_2$  in  $\text{D}_2\text{O}$ .  $C_{\text{complex}} = 0.0050\text{ M}$ ,  $C_{\text{NaOH}} = 0.0502\text{ M}$ .

is seen that the data obeyed equation (4) and that essentially constant values of  $k_2$ -order were obtained at  $18^\circ$  over a two fold variation in  $C^\circ$ . For the second set, a twenty fold excess of base was employed, and, to keep the velocity

Table 2. Hydrolysis rates for  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Co}(\text{ND}_3)_5\text{Cl}]\text{Cl}_2$ .

Run Nos.	$t^\circ\text{C}$	Concentrations (M)		Rate Law (Equation No.)	Slope of Rate Plot ( $\text{min}^{-1}$ )	$k_2$ -order ( $\text{M}^{-1}\text{min}^{-1}$ )
		Complex	NaOH or NaOD			
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in $\text{H}_2\text{O}$						
47	25.3	0.0118 <sub>s</sub>	0.0118 <sub>s</sub>	4	0.61	51.6
7, 8, 14	18.0	0.00650	0.00650	4	0.100	15.4
37, 43, 46	18.0	0.0118 <sub>s</sub>	0.0118 <sub>s</sub>	4	0.18	15.2
13	19	0.0140	0.0140	4	0.244	17.4 (15) <sup>a</sup>
						Av. 15.2
29, 42	11.0	0.0118 <sub>s</sub>	0.0118 <sub>s</sub>	4	0.053	4.48
38, 40	3.6	0.0118 <sub>s</sub>	0.0118 <sub>s</sub>	4	0.0129	1.09
53, 54	2.5	0.0050	0.0502	3	0.0192	0.91 (1.1) <sup>b</sup>
$[\text{Co}(\text{ND}_3)_5\text{Cl}]\text{Cl}_2$ in $\text{D}_2\text{O}$						
44	18.0	0.0114	0.0118 <sub>s</sub>	6	0.00192	9.2
48	17.6	0.0114	0.0118 <sub>s</sub>	6	0.00155	7.4 (8.0) <sup>c</sup>
						Av. 8.6
55	2.5	0.0050	0.0502	3	0.0124	0.57

a) corrected to  $18^\circ\text{C}$ . b) corrected to  $3.6^\circ\text{C}$ . c) corrected to  $18^\circ\text{C}$ .

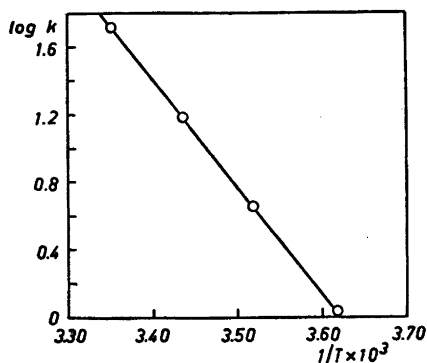


Fig. 4. Temperature dependence of the hydrolysis rate constant for  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .

manageable, a temperature of 2.5°. As seen from Table 2, the second order rate constant computed from the application of equation (3) to the data ( $k_{2\text{-order}} = (\text{slope})/(\text{base})$ ) agreed well with that obtained from data for one fourth the concentration of base and obeying the second order rate law (4).

Between the two series, agreement with second order kinetics is indicated for the range of hydroxide ion concentration from 0.0065 to 0.05 M.

*Temperature dependence of the hydrolysis reaction.* Temperature dependence data have not previously been reported for the hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2}$ , and for this reason the present reaction was studied at several temperatures. The data are included in Table 2, and the plot of  $\log k$  versus  $1/T$  is shown in Fig. 4. The slope corresponds to an activation energy of 28.7 Kcal/mole. This is quite high for so fast a reaction, and the entropy of activation, correspondingly is also high. At 18°, using the molar standard state, it is 37 cal/° mole.

*Hydrolysis rate of  $[\text{Co}(\text{ND}_3)_5\text{Cl}]^{+2}$  in  $\text{D}_2\text{O}$ .* Two hydrolysis runs were made with the deuterated system, under conditions such that the concentrations of complex and of base should have been equal. The rate law (4) was not obeyed, however, and the difficulty was traced to the assumption that the extinction coefficient would be the same as in the non-deuterated system; this led to the examination of isotope effects on  $\epsilon$  values, reported in the preceding section. When the correct values were used, recalculation of the data necessitated the use of the general second order rate equation,

$$\log \frac{b}{a} \left[ \frac{C}{(b-a) + C} \right] = X = \frac{(a-b) kt}{2.303} \quad (6)$$

where  $a$  and  $b$  denote the initial concentrations of complex and of base, and  $C$ , that of the complex at time  $t$ . The data were now found to give linear plots of  $X$  versus  $t$  and the rate constants so calculated are included in Table 2.

In addition, the rate in heavy water was determined under the conditions for first order kinetics, *i. e.* with excess base, at 2.5°, and these results are shown in Fig. 3, and given in Table 2.

Table 3. Rates of aquation of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{++}$  and of  $[\text{Co}(\text{ND}_3)_5\text{Cl}]^{++}$  in ordinary and in heavy water.

Run Nos.	Isotopic Content <sup>a</sup>		Concn. of Complex	<i>t</i> ° C	Half Life (min)
	Complex	Solvent			
20	H	H	0.0201	52	265
52	H	H	0.0137	52	265
56	H	H	0.0119	53.2	253 (262) <sup>b</sup>
					<u>264</u>
50	D	H	0.0133	52	385
57	D	H	0.0123	52.3	365 (378) <sup>c</sup>
					<u>382</u>
21	H	D	0.0195	52	422
51	D	D	0.0140	52	365

a) Where deuterium is indicated, the percent deuteration was ca. 85 to 90.

b) corrected to 52°. c) corrected to 52°.

Note: Runs 20 and 21, Runs 50, 51 and 52, and Runs 56 and 57 were carried out simultaneously in adjacent cells in the spectrophotometer.

The hydrolysis rate in heavy was 56 and 63 % of that in ordinary water, at 18° and 2.5°, respectively. The experimental error was such however, that the difference between these two figures is not an accurate indication of the change in activation energy on deuteration. However, the direction of the variation corresponds to a lesser activation energy for the deuterated system, so that in order to account for the smaller rate, the entropy of activation must also be less positive.

Rates of aquation of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and of  $[\text{Co}(\text{ND}_3)_5\text{Cl}]\text{Cl}_2$  in ordinary and in heavy water. Aquation rates were obtained at 52° C and pH = 1, by the spectrophotometric method, for systems constituted in four different ways. These comprised light or heavy complex dissolved in light or heavy water. The results are presented in Fig. 5 and summarized in Table 3.

The data which were obtained on the rate of exchange of deuterium between  $[\text{Co}(\text{ND}_3)_5\text{Cl}]^{+2}$  and water indicated it to be slow but measurable at 38° and pH = 3 (see Experimental procedures). Although the present runs were made at 52°, the pH was much lower, so some uncertainty existed as to the exchange rate. However, a comparison of runs 20, 52, and 56 with runs 50 and 57 clearly showed that the rates of aquation of the normal and the deuterated complex in ordinary water were different. This would not have been the case had there been exchange. Moreover, the first order plot was obeyed up to more than one half life, so that only a partial exchange could have taken place during this period. It was necessary to establish this point, since the choice of  $\epsilon$  values depended upon whether or not exchange was assumed to have occurred. It should be added that runs 50 and 57 were slower than their counterpart in ordinary water regardless of which set of  $\epsilon$  values was employed.



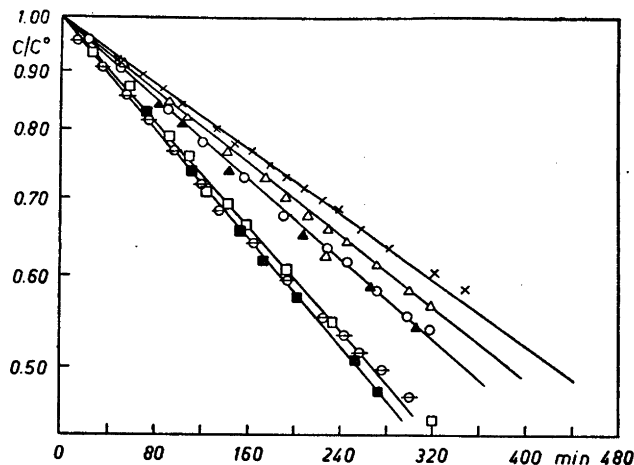


Fig. 5. Aquation of chloropentamminecobalt(III) at 52° C and pH = 1. ○, □, ■ —  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  in  $\text{H}_2\text{O}$ ; △, ▲ —  $[\text{Co}(\text{ND}_3)_5\text{Cl}]\text{Cl}_2$  in  $\text{H}_2\text{O}$ ; × —  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  in  $\text{D}_2\text{O}$ ; ○ —  $[\text{Co}(\text{ND}_3)_5\text{Cl}]\text{Cl}_2$  in  $\text{D}_2\text{O}$ .

If exchange is slow, then the four differently substituted systems were in fact different, and, in principle, four aquation rates should be observable. This appeared to be the case, since half lives of 265, 365, 385, and 422 minutes were found. Comparisons between the last three should only be considered qualitatively, however, since these half lives are subject to an experimental error of perhaps five percent, in spite of precautions taken. The most conservative observation from the data is that the rate was reduced to some 65 percent of the normal value if deuterium was present *either* in the complex or in the solvent, or in both.

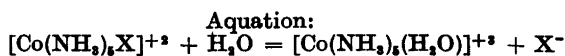
*Aquation and hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ .* A less detailed study was made of the aquation and hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{+2}$  at 48° and 4.5°, respectively. In addition, the aquation rate in heavy water was determined, and found to be 75 % of that in ordinary water. The data are included in Table 4.

Some exploratory data were obtained on the aquation of  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{+2}$  and of  $[\text{Co}(\text{NH}_3)_5(\text{HCO}_3)]^{+2}$ , but the former was found to lose ammonia too rapidly to permit accurate rate studies, and the latter reaction was too fast, even at 0° C.

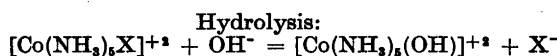
#### DISCUSSION

The rate constants obtained in this investigation are collected in Table 4, together with the available activation energy data, and comparisons with previous results. Where comparisons are possible, our results are in fair agreement with those of previous workers. In addition, from Garrick's value for the aquation rate of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2}$  at 25°, and ours at 52°, we calculate an activation energy of 22.9 Kcal/mole and an activation entropy of  $-9.0$  cal/° mole (or E.U.).

Table 4. Summary of aquation and hydrolysis rate constants.



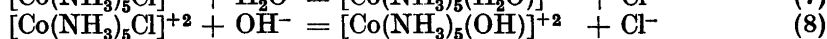
Complex	Solvent	$t^\circ \text{C}$	$k \times 10^3 \text{ (min}^{-1}\text{)}$		$H$ (Kcal)	$S$ (cal/° mole)
			this investig.	previous values		
[Co(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>+2</sup>	H <sub>2</sub> O	25		0.100 <sup>a</sup>	22.9	-9.0
		52	2.53			
[Co(ND <sub>3</sub> ) <sub>5</sub> Cl] <sup>+2</sup>	H <sub>2</sub> O	52	1.81			
[Co(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>+2</sup>	D <sub>2</sub> O	52	1.65			
[Co(ND <sub>3</sub> ) <sub>5</sub> Cl] <sup>+2</sup>	D <sub>2</sub> O	52	1.90			
[Co(NH <sub>3</sub> ) <sub>5</sub> Br] <sup>+2</sup>	H <sub>2</sub> O	48	7.7	7.0 <sup>b</sup>	23.9 <sup>b</sup>	3.2
[Co(NH <sub>3</sub> ) <sub>5</sub> Br] <sup>+2</sup>	D <sub>2</sub> O	48	5.6			



Complex	Solvent	$t^\circ \text{C}$	$k_{2\text{-order}} \text{ (M}^{-1} \text{ min}^{-1}\text{)}$		$H$ (Kcal)	$S$ (cal/° mole)
			this investig.	previous values		
[Co(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>+2</sup>	H <sub>2</sub> O	25		78 <sup>c</sup>	28.7	37
		25.3	51.6			
		18.0	15.2			
		11.0	4.48			
		3.6	1.09			
		2.5	0.91			
[Co(ND <sub>3</sub> ) <sub>5</sub> Cl] <sup>+2</sup>	D <sub>2</sub> O	18.0	8.6			
		2.5	0.57			
[Co(NH <sub>3</sub> ) <sub>5</sub> Br] <sup>+2</sup>	H <sub>2</sub> O	25		360	23.5	23
		15		85		
		4.5	11.8	(15)		

a) Ref.<sup>22</sup>; b) Ref.<sup>9</sup>; c) Ref.<sup>10</sup>; d) Ref.<sup>9</sup>

It is of interest first to compare the aquation and hydrolysis reactions for the all hydrogen system:

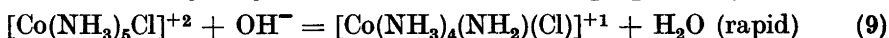


The thermodynamic  $\Delta S_7$  is -26.2 E.U., from data given by Latimer<sup>19</sup>. From J. Bjerrum<sup>20</sup>, the entropy of dissociation of [Co(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sup>+3</sup> is ca. 6 E.U., which, in combination with the entropy of dissociation of water, leads to a value for  $\Delta S_8$  of -1.0. If, as has been argued, both aquation and hydro-

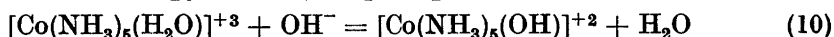
lysis proceed by an  $S_N2$  mechanism<sup>8</sup>, one would expect the entropies of activation to compare similarly with the overall entropies of reaction. This, however, is not the case, *viz.*  $-26.6$  versus  $-9.0$  and  $-1.6$  versus  $37$ .

In particular, it is difficult to account for the 39 E.U. difference between  $\Delta S_8$  and  $\Delta S^\ddagger$  for the hydrolysis reaction, if an  $S_N2$  process, going through a seven coordinated transition state, is truly involved. While there would be *ca.* 12 E.U. favoring this transition state because of the charge effect<sup>21</sup>, there should be  $-8$  E.U. from loss in translational entropy<sup>22</sup>, plus a further negative term reflecting the smaller entropy of a seven coordinated structure as compared to a hexacoordinated one.

An alternative hydrolysis mechanism has been proposed by Garrick<sup>12</sup>:

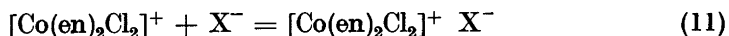


followed by a rate determining step in which the chloride group is replaced by water. The acid base pre-equilibrium (9) must, in fact, exist, and be rapid, in view of our exchange results. Furthermore  $\Delta S_9$ , which would now contribute to the activation entropy, should be quite positive. Thus for



$\Delta S_{10}$  is *ca.* 25 E.U., and  $\Delta S_9$  should be even larger because of the fifteen equivalent positions from which a proton can be removed, in spite of the adverse charge effect. In further support of this mechanism it should be noted that in the case of  $[\text{Co}(\text{CN})_5\text{I}]^{-3}$ , where no acid base pre-equilibrium is possible, work in this laboratory shows the rate of appearance of free  $\text{I}^-$  to be independent of pH.

Actually, the principal evidence that cobalt(III) complexes may react by an  $S_N2$  mechanism lies in the observation by Brown *et al.*<sup>3</sup> that substitution of  $\text{Cl}^-$  by  $\text{N}_3^-$  in *cis*  $[\text{Co}(\text{en})_2\text{Cl}_2]^{+2}$  followed second order kinetics in methanol solution. However, this observation could equally well be explained in terms of the pre-equilibrium



followed by a rate determining exchange of  $\text{X}^-$  for  $\text{Cl}^-$ , whose molecularity is experimentally inaccessible.

Work in this laboratory has shown that the absorption spectrum of  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  in methanol, in the presence of  $\text{N}_3^-$ , shows increased absorption in the near ultra violet, an effect similar to that found by Evans and Nancollas<sup>23</sup> in their study of ion pair formation between  $[\text{Co}(\text{NH}_3)_6]^{+3}$  and halide ions in aqueous media. A similar situation prevailed with  $\text{I}^-$ , which we found also to give second order substitution kinetics in methanol. For  $\text{N}_3^-$  and  $\text{I}^-$ , ion pair formation constants of *ca.* 10 and *ca.* 20 were indicated. That such ion pair formation can indeed be a kinetic precursor to substitution has been shown by Taube and Posey<sup>24</sup>.

Proceeding to the matter of rates in deuterated systems, several effects have been found to contribute to changes in rate when hydrogen is replaced by deuterium. First, there is a general solvent effect, which is small. The solubilities of salts per mole of water are about ten percent less in  $\text{D}_2\text{O}$ <sup>25</sup>, and activity coefficient ratios are nearly invariant<sup>26</sup>. In addition, reactions for which the

only effect on rate should be that of changing solvent environment, show only slight differences in velocity in the two media. Thus the rates of solvolysis of methyl halides were unchanged in  $D_2O^{15}$ .

Interestingly, however, these last authors also reported that the rate of acid hydrolysis of tertiary butyl chloride was some 40 % slower in  $D_2O$ . This, however, they correlated with the high dependence of the reaction upon electrophilic solvation. Thus the rate of this reaction is 340 000 times faster in water than in methanol, while that of methyl bromide is only 27 times faster. Since aquation and hydrolysis reactions for cobalt complexes are generally only about 10 fold slower in alcoholic media than in water, this type of solvent effect should not be important here.

An important effect, in relation to the present studies, arises when an acid base pre-equilibrium exists. A number of acid and base catalyzed reactions have been studied in  $D_2O$ , with the observation that the rates may range from being twice as fast to being twice as slow as in  $H_2O^{25}$ . A bond between deuterium and another atom is generally stronger than the corresponding one with hydrogen, due to the zero point energy effect<sup>27</sup>. Thus the dissociation constants of weak acids and bases are several fold less in  $D_2O$ <sup>13</sup>, and the O—D—O bond in the acetic acid dimer may be somewhat weaker than the corresponding O—H—O bond<sup>28</sup>.

All of the reactions studies in the present investigations were slower in deuterium containing systems, and the differences, being of the order of 30 to 60 %, were greater than to be expected from general solvent effects. The 55 to 60 % decrease in rate of hydrolysis is certainly best explained as arising from the acid base pre-equilibrium postulated above.

The isotope effects on aquation rates require more explanation, however. They do not seem to be accountable for by either an ordinary  $S_N1$  or  $S_N2$  mechanism. In the former case, one would not expect a reduced rate of aquation for the H-complex in  $D_2O$ , and for the latter, the rate for the D-complex in  $H_2O$  should be normal. It seems possible, however, to explain the various aspects of the aquation reaction if one supposes that the ammine complexes are extensively hydrogen bonded with solvent, and that the water molecules so involved play a specific role in directing the course of the reaction. The diagram below illustrates how water molecules might reasonably form bridges between the ammonia groups and the chloride ion in  $[Co(NH_3)_5Cl]^{+2}$ . For purposes of clarity, only two of the four bridges are shown. The second dia-



gram is to scale, assuming  $2.6 \text{ \AA}$  for the N—H—O bond, and tetrahedral angles on the nitrogen and oxygen. The energy of the O—H—Cl interaction is perhaps several kilocalories, judging from the case of *o*-chlorophenol<sup>29</sup>. This

partial solvation of the chloride should aid in its removal during the aquation step, which is pictured as a concerted motion of the chloride outward, and one water molecule inward. Since most of the  $-26$  E.U. entropy for the aquation reaction is ascribable to the charge effect, the more positive entropy of activation,  $-9$  E.U., is explainable if, in the transition state, the Co—Cl distance is only slightly greater than normal. With deuterium present, *either* on the nitrogen or the oxygen, the bridge may be somewhat weaker. Thus replacement of a proton by a deuteron in either the N—H—O or the O—H—Cl position might be expected to give similar results, as is observed.

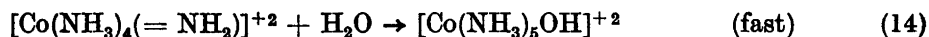
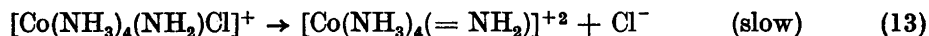
One might expect, however, that if both hydrogens were replaced by deuterium, an even slower rate of aquation should result, in seeming contradiction with our findings. The experiment with D-complex in  $D_2O$ , however, was not conceived with the picture of four equivalent sets of hydrogen bridges in mind, and the percent deuteration was only 85 to 90. Under this circumstance, there was only a minority chance that all *four* of the bridges be deuterated at *both* positions, and the aquation could take place primarily through a singly deuterated bridge.

As final points, the above representation accounts nicely for the stereospecificity of the aquation process, such as Mathieu's observation<sup>30</sup> that  $[Co(en)_2NH_3Br]^{+2}$  underwent mutarotation to the corresponding monoquo species without racemization and with retention of configuration. Also, the explanation previously given<sup>5</sup> for the specific anion effects on the aquation rates of Co(III) acidopentammines would still apply. The observed decrease<sup>6</sup> in the rate of aquation with decreasing number of N—H in cobalt(III) complexes is consistent with the proposed hydrogen bonding picture.

The above conclusions allow a distinction to be made between alternative mechanisms for the hydrolysis reaction. The complete mechanism may be pictured as consisting of reaction (9), followed by either



or



as rate determining steps. Reaction (12), an aquation type step, would not account for the low stereospecificity of hydrolysis reactions. These are generally accompanied by isomerization in contrast to aquation which takes place with retention of configuration. In the alternative sequence proposed, loss in configuration would well occur if there is a pentacoordinated intermediate, stabilized by double bonding to the amide group. It has been suggested, moreover, that such double bonding stabilization may account for the accelerating effect of  $NH_2^-$  and  $OH^-$  groups, relative to other negative groups, on the aquation rates of Co(III) complexes<sup>31</sup>.

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