

are not observed (see text and Table II).

- (48) Coordination of the phenol substrate has been suggested by other workers<sup>49</sup> as a requirement for oxidative coupling;<sup>50</sup> this view is supported by evidence for pyridine lability in the initiator.<sup>1,43</sup> The manner of coordination may have some bearing on the product distribution.<sup>13</sup> For example, at relatively low pyridine concentrations, coordination of phenol moieties at adjacent metal centers would produce a high, local concentration of phenol radicals, which might favor C-C coupling to give the quinone, rather than coupling

to phenol, which would give polymer.<sup>13</sup>

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 (50) Formation of phenol radicals could also occur without coordination to the copper center through an outer-sphere electron-transfer process mediated by the oxygen atom of the initiator.<sup>24</sup>

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## Studies on the Base Hydrolysis of $\text{Co}(\text{NH}_3)_5\text{X}^{(3-n)+}$ Complexes

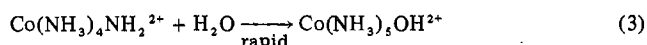
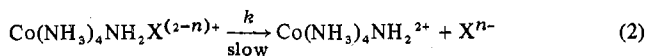
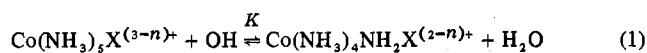
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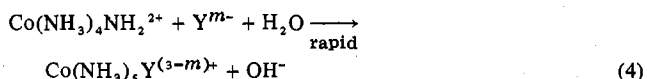
The product ratios  $[\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}]/[\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}]$  were determined in aqueous solutions of sodium azide at various temperatures and ionic strengths for the base hydrolysis of  $\text{Co}(\text{NH}_3)_5\text{X}^{(3-n)+}$  ( $\text{X}^{n-} = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-, \text{Me}_2\text{SO}$ ) complexes. The results showed that the  $\text{S}_{\text{N}}1\text{cB}$  mechanism involving the five-coordinate  $\text{Co}(\text{NH}_3)_4\text{NH}_2^{2+}$  intermediate was inadequate to explain the product ratios obtained. The observed results can be adequately explained by an interchange mechanism of the conjugate base  $\text{Co}(\text{NH}_3)_4\text{NH}_2\text{X}^{(2-n)+}$  contributing significantly to the observed overall reaction. The temperature dependence of the product ratio indicated that the cobalt(III)-ligand bonds to the leaving and incoming ligands in the activated complexes were essentially completely broken for practical purposes in the interchange mechanism. Alternate mechanisms were considered.

### Introduction

The  $\text{S}_{\text{N}}1\text{cB}$  mechanism shown in reactions 1-3 seems to be



presently accepted as the mechanism for the base hydrolysis of various pentaammine complexes of cobalt(III) with the five-coordinate, trigonal-bipyramidal  $\text{Co}(\text{NH}_3)_4\text{NH}_2^{2+}$  complex as the intermediate.<sup>1</sup> When a nucleophile  $\text{Y}^{m-}$  which can compete with water is added to the reaction mixture initially, the intermediate can also react with this nucleophile to form a second product (reaction 4) in a competition reaction



with water for the intermediate. Certainly the general features of these base hydrolyses and competition reactions are explained by this mechanism and by this one intermediate. However, as it has already been pointed out,<sup>2</sup> an important experimental fact is not explained by this mechanism: the fact is that all starting complexes, or substrates  $\text{Co}(\text{NH}_3)_5\text{X}^{(3-n)+}$ , do not form the products  $\text{Co}(\text{NH}_3)_5\text{Y}^{(3-m)+}$  and  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$  in the same ratio for the same concentration of a given  $\text{Y}^{m-}$  as is required for the common intermediate  $\text{Co}(\text{NH}_3)_4\text{NH}_2^{2+}$  of the  $\text{S}_{\text{N}}1\text{cB}$  mechanism. The intermediate  $\text{Co}(\text{NH}_3)_4\text{NH}_2^{2+}$  will react with a nucleophile such as  $\text{N}_3^-$  in competition with  $\text{H}_2\text{O}$  in the same way whether it came from, say,  $\text{Co}(\text{NH}_3)_5\text{NO}_3^{2+}$  or  $\text{Co}(\text{NH}_3)_5(\text{Me}_2\text{SO})^{3+}$ . But if the product ratio is dependent on the nature of the leaving group, then the intermediate in the hydrolysis is not solely the one pictured for the  $\text{S}_{\text{N}}1\text{cB}$  mechanism.

The  $\text{S}_{\text{N}}2$  and  $\text{S}_{\text{N}}2\text{cB}$  mechanisms for the base hydrolyses of these pentaammine complexes were examined<sup>1d</sup> and rejected. However, an interchange mechanism for the conjugate base was not examined. Thus, the leaving group of the

conjugate base may leave the first coordination shell by an interchange reaction with the competing incoming ligands as well as, or instead of, by the dissociation mechanism which produces the  $\text{Co}(\text{NH}_3)_4\text{NH}_2^{2+}$  intermediate.

Here we report on the  $[\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}]/[\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}]$  product ratios formed when the substrates  $\text{Co}(\text{NH}_3)_5\text{X}^{(3-n)+}$  ( $\text{X}^{n-} = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-, \text{Me}_2\text{SO}$ ) are hydrolyzed in aqueous basic  $\text{NaN}_3$  media. The results show that the product ratios obtained from the various substrates (except possibly  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  and  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ ) are not all equal.

### Experimental Section

**Chemicals.** Concentrated reagent grade acids were diluted and standardized by the usual methods. The complexes  $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$  were prepared from the chloride and bromide salts, respectively, by dissolving in water, adding concentrated perchloric acid, cooling in ice, and recrystallizing from water with sodium perchlorate until pure.<sup>3,4</sup> The complex  $[\text{Co}(\text{NH}_3)_5\text{OH}_2](\text{ClO}_4)_3$  was obtained by dissolving the nitrate salt in water, adding concentrated perchloric acid, cooling in ice, and then recrystallizing from water with sodium perchlorate.<sup>5</sup> The complex  $[\text{Co}(\text{NH}_3)_5\text{NO}_3](\text{ClO}_4)_2$  was prepared by heating  $[\text{Co}(\text{NH}_3)_5\text{O}(\text{H}_2)](\text{NO}_3)_3$  at 80 °C as described,<sup>6</sup> dissolving in water, adding concentrated perchloric acid, cooling in ice, and recrystallizing from water with sodium perchlorate until pure. The complexes  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{ClO}_4)_2$ <sup>7</sup> and  $[\text{Co}(\text{NH}_3)_5\text{Me}_2\text{SO}](\text{ClO}_4)_3$ <sup>8</sup> were prepared as described and were recrystallized from water with perchloric acid until pure. The purity of the complexes was checked by comparing the wavelength maxima and corresponding extinction coefficients with literature values. The purity of the chloro, bromo, nitrate, azido, and  $\text{Me}_2\text{SO}$  complexes was also checked by conversion to the aquo complex by both acid and base hydrolyses where possible (nitrous acid oxidation in acid medium for the azido complex) and determination of the amount of the aquo complex formed. All complexes were better than 98% pure.

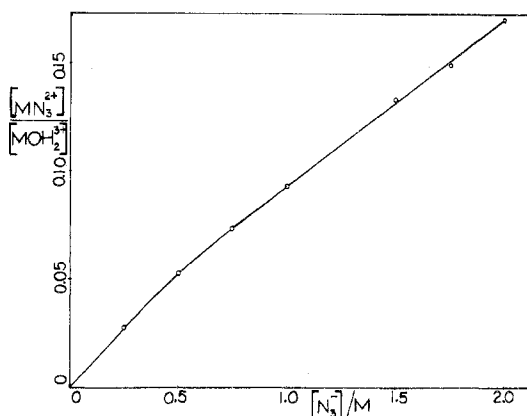
The wavelengths (molar extinction coefficients), in nm ( $\text{M}^{-1} \text{cm}^{-1}$ ), respectively, used were the following:  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$  490 (48.0), 508.5 (45.0);  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  532 (50.4), 508.5 (45.0);  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$  550 (57.7);  $\text{Co}(\text{NH}_3)_5\text{NO}_3^{2+}$  500 (57.4);  $\text{Co}(\text{NH}_3)_5\text{Me}_2\text{SO}^{3+}$  515 (62.3);  $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$  518 (266).

**Procedure.** Usually 0.100 to 0.150 mmol of the desired complex was dissolved in a few milliliters of water,  $\text{NaN}_3$  solution was added to give the desired  $\text{N}_3^-$  concentration for the final volume, and the

**Table I.** Variation of the Percentage  $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$  and of the Product Ratio Obtained from the Base Hydrolysis of 0.0100 M  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  in 0.125 M NaOH

$[\text{N}_3^-]/\text{M}$	$\mu/\text{M}$	% $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ <sup>a</sup>	Product ratio <sup>b</sup>
0.500	1.00	4.6	0.0482
1.00	1.00	8.5	0.0929
0.500	1.50	4.2	0.0439
1.50	1.50	11.8	0.134
0.500	2.00	4.2	0.0439
1.00	2.00	8.1	0.0881
1.50	2.00	11.2	0.126
2.00	2.00	14.5	0.170

<sup>a</sup> Approximately 2% relative error, not absolute error. <sup>b</sup> Approximately 3% error.

**Figure 1.** A plot of the product ratio against  $[\text{N}_3^-]$  at variable ionic strength  $\mu = [\text{N}_3^-]$ .

solution was thermostated at the selected temperature. A predetermined volume of a standard NaOH solution at the same temperature was injected rapidly into the magnetically stirred first solution so as to give 0.125 M  $\text{OH}^-$  for the reaction mixture. After reaction periods of approximately 30 min at 0 °C, 5 min at 25 °C, and 3 min at 40 °C, the reaction mixture was diluted with cold water to stop the reaction and to decrease the ionic strength to less than 0.5 M. The reaction mixture was acidified with perchloric acid, and approximately 1.0–1.5 mL of cold, wet Dowex 50W-X4, 200–400 mesh, resin was added to adsorb the products. The resulting mixture was quantitatively transferred to a column of the same resin in hydrogen form and washed thoroughly with water. The azido complex was eluted with 2 M  $\text{HClO}_4$  to separate it from the aquo complex followed by 3 M  $\text{HClO}_4$  to reduce the volume of eluent containing the azido complex. The aquo complex was eluted with 4 M  $\text{HCl}$ . The eluents containing the individual complexes were collected at 0 °C. The quantities of azido and aquo complexes formed were determined spectrophotometrically. The recovery was always 98% or better.

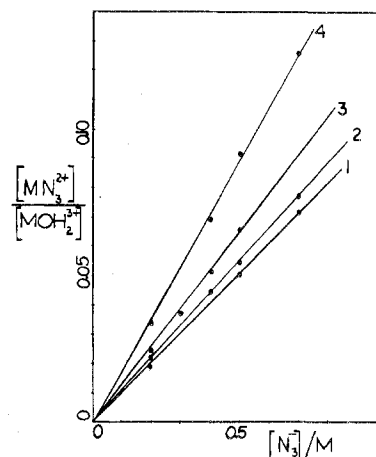
Blank experiments showed that  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{ClO}_4)_2$  placed on the column was quantitatively recovered when eluted with 2 and 3 M  $\text{HClO}_4$  as described above if the column was protected from light and if recovery was completed within about 2–3 h.

### Results and Discussion

The percentages of  $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$  formed and the values of the product ratio  $[\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}]/[\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}]$  obtained in the base hydrolysis of  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  at various azide concentrations and at various ionic strengths,  $\mu$ , are given in Table I. It is readily seen that the product ratio is proportional to the azide concentration at constant ionic strength and that the product ratio is not greatly dependent on ionic strength at  $\mu \geq 1.0$  M. If the products are being formed from  $\text{N}_3^-$  and  $\text{H}_2\text{O}$  competing in an ion pair such as  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}, \text{N}_3^-$  or  $\text{Co}(\text{NH}_3)_4\text{NH}_2^{2+}, \text{N}_3^-$ , the maximum extent of ion-pair formation is far from being achieved at 2.0 M  $\text{N}_3^-$ . If formation constants for ion pairs of divalent  $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$  ions are as large as indicated by Burnett,<sup>9</sup> some trace of saturation with respect to ion-pair formation should be ap-

**Table II.** Dependence of the Product Ratio Obtained in the Base Hydrolysis of  $\text{Co}(\text{NH}_3)_5\text{X}^{(3-n)+}$  Complexes on  $\text{NaN}_3$  Concentration at 25 °C and 0.70 M Ionic Strength

Complex	$[\text{N}_3^-]/\text{M}$	Product ratio	Slope
$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	0.000	0.0000	$0.103 \pm 0.006$
	0.200	0.0194	
	0.500	0.0504	
	0.700	0.0718	
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	0.200	0.0225	$0.111 \pm 0.001$
	0.400	0.0449	
	0.500	0.0548	
	0.700	0.0776	
$\text{Co}(\text{NH}_3)_5\text{NO}_3^{2+}$	0.200	0.0246	$0.132 \pm 0.001$
	0.300	0.0373	
	0.400	0.0515	
	0.500	0.0661	
$\text{Co}(\text{NH}_3)_5(\text{Me}_2\text{SO})^{3+}$	0.200	0.0341	$0.182 \pm 0.011$
	0.400	0.0695	
	0.500	0.0917	
	0.700	0.1261	

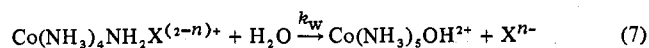
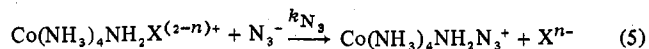
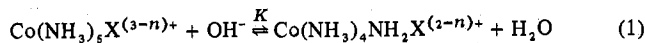
**Figure 2.** Plots of the product ratio against  $[\text{N}_3^-]$  at  $\mu = 0.70$  M for different substrates: 1,  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ ; 2,  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ ; 3,  $\text{Co}(\text{NH}_3)_5\text{NO}_3^{2+}$ ; 4,  $\text{Co}(\text{NH}_3)_5(\text{Me}_2\text{SO})^{3+}$ .

parent by approximately 1 M  $\text{NaN}_3$  if not at lower concentrations. However, saturation effects from ion-pair formation would not be expected for monovalent cations such as  $\text{Co}(\text{NH}_3)_4\text{NH}_2\text{X}^+$  if it were a reactive species.

Figure 1 shows that the values of the product ratio obtained in the base hydrolysis of  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  depend nonlinearly on the sodium azide concentration when  $\mu = [\text{N}_3^-]$  and is variable. However, the nonlinearity is most pronounced below  $\mu \approx 0.75$  M and essentially disappears above this ionic strength. Again, this type of dependence is not what is expected when ion pairing occurs to a significant degree as is expected for  $\text{Co}(\text{NH}_3)_4\text{NH}_2^{2+}, \text{N}_3^-$  or  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}, \text{N}_3^-$  acting as precursor complexes leading to products through formation of activated complexes. This result is in agreement with an earlier study<sup>2</sup> which concluded that the ion pair  $\text{Co}(\text{NH}_3)_5\text{X}^{(3-n)+}, \text{NCS}^-$  was not the reactive species from which the products were formed in an elementary step.

The product ratios obtained in aqueous basic  $\text{NaN}_3$  solutions in the base hydrolysis of  $\text{Co}(\text{NH}_3)_5\text{X}^{(3-n)+}$  ( $\text{X}^n = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-, \text{Me}_2\text{SO}$ ) are given in Table II and plotted in Figure 2. Also given in Table II are the least-squares slopes and their standard deviations of the straight lines obtained by plotting the product ratios against the  $\text{N}_3^-$  concentration using the origin as a point since the product ratio is zero at zero added  $\text{N}_3^-$ . Except possibly for the chloro and bromo complexes, the plots are different from one another and show that all the base hydrolyses do not go through only the  $\text{Co}(\text{NH}_3)_4\text{NH}_2^{2+}$  intermediate. If all the base hydrolyses went only through the

one  $\text{Co}(\text{NH}_3)_4\text{NH}_2^{2+}$  intermediate, all of the data in Table II would fit one straight-line plot through the origin. Since the dimethyl sulfoxide and nitrate complexes manifestly give plots different from one another and from the halo complexes, some or all of these complexes have significant contributions from base hydrolysis mechanisms other than  $\text{S}_{\text{N}}1\text{cB}$ . A mechanism which is consistent with all of the data is shown in reactions 1 and 5-7. In this mechanism the conjugate base



can replace the  $\text{X}^{n-}$  ligand by  $\text{N}_3^-$  or  $\text{H}_2\text{O}$  ligands using interchange reactions instead of using a D mechanism. That an interchange mechanism can contribute to base hydrolysis should not be too surprising since the interchange mechanism is widely accepted for aquation (acid hydrolysis) of these complexes and since Reynolds and Barber<sup>10</sup> have quantitatively disproven the D mechanism for aquation of  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  in some water-organic solvent media. The experimental results do not allow a conclusion as to the percentage of the products formed in each mechanistic pathway.

A contribution from an interchange mechanism can account for the dependence of the product ratio on the nature of the leaving group since the leaving group is present in the activated complex of an interchange path. An interchange mechanism is also consistent with the rest of the experimental data. For example, the product ratio is given by equation 8, and it is

$$[\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}]/[\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}] = (k_{\text{N}_3}/k_{\text{w}})[\text{N}_3^-] \quad (8)$$

readily seen that the product ratio is proportional to the azide concentration at constant ionic strength (as it is for the  $\text{S}_{\text{N}}1\text{cB}$  mechanism) and that the proportionality constant is dependent on ionic strength in a manner determined by the ionic strength dependence of the rate constants. The rate constant  $k_{\text{w}}$  is not expected to be sensitive to ionic strength changes. Whether  $k_{\text{N}_3}$  is sensitive to such changes depends on the extent of interaction between the conjugate base  $\text{Co}(\text{NH}_3)_4\text{NH}_2\text{X}^{(2-n)+}$  and  $\text{N}_3^-$ . If the reactants in the activated complex closely resemble the separated reactants (as Langford<sup>11</sup> has shown they do for aquation and anation), then the rate constant  $k_{\text{N}_3}$  may not be very dependent on ionic strength.

Since the activated complexes in the interchange mechanism contain the leaving and entering ligands, it remains to show

Table III. Percentage  $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$  Formed at Different Temperatures in the Base Hydrolyses of  $\text{Co}(\text{NH}_3)_5\text{X}^{(3-n)+}$  Complexes at  $[\text{N}_3^-] = \mu = 1.00 \text{ M}$

T, °C	$\text{X}^{n-}$			
	$\text{Cl}^-$	$\text{Br}^-$	$\text{NO}_3^-$	$\text{Me}_2\text{SO}$
0	$11.2 \pm 0.7^a$	$9.7 \pm 0.2$	$11.1 \pm 0.4$	$14.5 \pm 0.5$
25	$8.5 \pm 0.2$	$8.8 \pm 0.4$	$10.6 \pm 0.5$	$12.8 \pm 0.5$
40	$8.5 \pm 0.2$	$8.6 \pm 0.2$	$10.0 \pm 0.3$	$13.2 \pm 0.5$

<sup>a</sup> All errors are standard deviations of a single measurement.

whether or not there exist any bonds of significant strength between the central metal and these ligands. If there are, it is not expected that all the bonds would have the same strength. Consequently, if the base hydrolyses are conducted over a temperature range, the product ratios of one or more of the substrates should vary with temperature. The results of the temperature studies are given in Table III. It is seen that there was no effect of temperature on the percentage of  $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$  formed with the possible exception of the change from 0 to 25 °C for  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ . Because of the difference in bond energies between cobalt(III) and the six ligands  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{Me}_2\text{SO}$ ,  $\text{N}_3^-$ , and  $\text{H}_2\text{O}$ , it is improbable that all of the cobalt(III)-ligand bonds in the activated complexes are of appreciable but equal strengths. It is much more reasonable to regard all six bonds as being completely broken for all practical purposes in the activated complex. Consequently, the contributing interchange mechanism for base hydrolysis can be classed as an  $\text{I}_{\text{d}}$  mechanism for the conjugate base.

Registry No.  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ , 14970-14-0;  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ , 14970-15-1;  $\text{Co}(\text{NH}_3)_5\text{NO}_3^{2+}$ , 15077-47-1;  $\text{Co}(\text{NH}_3)_5(\text{Me}_2\text{SO})^{3+}$ , 44915-85-7.

## References and Notes

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