

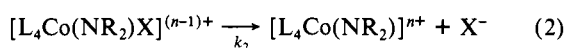
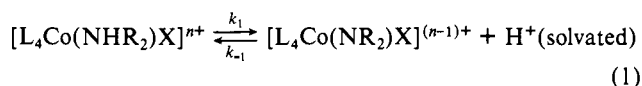
Ammoniation, Acid Dissociation, and Hydrogen Exchange of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and *cis*- and *trans*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ in Liquid Ammonia

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Abstract: An analysis of the medium and concentration dependence of the ammoniations of $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ and *cis*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2](\text{ClO}_4)_2$ in liquid ammonia (under conditions of complete ion-association) has separated the relevant parameters for the acid dissociation preequilibrium (K^{CB}) and the dissociative elimination reaction (k_2) in the conjugate-base mechanism. A comparison of K^{CB} values for the pentaammines $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ ($\text{X} = \text{Cl}^-, \text{N}_3^-, \text{NO}_3^-$), the *cis*-dichlorotetraammine, and the hexaammine leads to the conclusion that the acidity in liquid ammonia of NH_3 coordinated to Co^{3+} is nearly independent of the formal charge of the complex and of the nature and position of the other ligands; this leads to a reformulation of the rate laws. The reactivity pattern for the elimination reaction (k_2) can be explained from *cis* activation of the amido group in the conjugate base. An important contribution to the reactivity of the conjugate base is the large ΔS^\ddagger (in $\text{J K}^{-1} \text{mol}^{-1}$) of k_2 : 75 (*cis*-tetraammine); 46 (*trans*-tetraammine); 143 (pentaammine). The earlier reported mechanism of rate-limiting deprotonation in the *trans*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ complex appears to be due to both an increase in k_2 and a decrease in k_{-1} (reprotonation), compared to the *cis* complex. A ^1H NMR study of ^1H - ^2H exchange in N^2H_3 for the title compounds reveals general base catalysis and a pronounced dependence of the rate constants on the position of the coordinated ammine. Reprotonation by NH_4^+ and deprotonation by the NH_2^- ion are complex processes, involving preassociation. The acidity of NH_3 in liquid ammonia (described by the approximate value of the acid dissociation constant K_a (mol kg^{-1}) at -40°C) depends strongly upon the environment of the molecule: first coordination sphere (Co^{3+}) ($\text{p}K_a = 7$) > second coordination sphere ($\text{p}K_a = 16$) > bulk ($\text{p}K_a = 37$). The consequences for the necessity of assuming intramolecular proton exchange in a conjugate base are discussed.

The now eventually universally agreed upon mechanism for base-catalyzed solvolysis of octahedral cobalt(III) amine complexes is the two-step route via the conjugate base, originally proposed by Garrick,¹ the dissociative conjugate-base mechanism ($\text{S}_{\text{N}}1$ CB or simply CB),^{2,3} This mechanism consists of a generally rapid preequilibrium (eq 1), followed by the dissociative elimination of the leaving group (eq 2) and a rapid capture of a solvent molecule by the five-coordinate intermediate.⁴ A detailed mechanistic



understanding of the reaction is hampered by the fact that the acid dissociation constant ($K^{\text{CB}} = k_1/k_{-1}$) of the reactive amine complexes is very small. The bulk of the mechanistic studies has used aqueous solutions, where⁵ $\text{p}K^{\text{CB}} > 15$. The considerably higher acidic strength of the complexes in liquid ammonia brings the possibility of the experimental evaluation of both K^{CB} and k_2 . Following earlier publications from our laboratory on the evaluation of K^{CB} and k_2 ,^{6,7} we now report a further dissection of the relevant parameters, obtained by a determination of k_1 from ^1H - ^2H exchange measurements. The results obtained for $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and *cis*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ and a comparison with the earlier results⁸ on *trans*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (showing rate-limiting

deprotonation: $k_2 > k_{-1}$) and other pentaammine complexes answer a couple of essential questions about the CB mechanism. Of these, the most important ones are the acidity of geometrically different ammine sites, the relative reactivities of different conjugate bases, and the dependence of K^{CB} and k_2 on the overall ionic charge of the complex. Also the factors leading to a mechanism of rate-limiting deprotonation can now be better assessed. Beside these aspects, ^1H - ^2H exchange of amine complexes up to recently presented an unsolved problem in the absence of the expected⁹ general base catalysis. Preliminary measurements of this exchange in liquid ammonia demonstrated the presence of this type of catalysis.¹⁰ In addition, systems showing rate-limiting deprotonation in liquid ammonia also evidenced to general base catalysis.⁸ In this report, this matter will be taken up again and examined more fully.

Experimental Section

Materials. $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ was prepared and purified as described.¹¹ *cis*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2](\text{ClO}_4)_2$ was prepared according to Werner.¹² The compounds gave satisfactory analysis results. The salts were prepared acid-free by recrystallization from an aqueous borax (1 g/100 mL) solution. The preparation of N^2H_3 has been described.⁸

Kinetics of Ammoniation. The apparatus and data processing were essentially as described previously.⁸ The ionic medium was fixed at 0.20 *m* (mol kg^{-1}) perchlorate; in this medium the cobalt(III) complexes may be considered to be completely ion-associated.^{13,14} The pressure was kept constant at 10 bar. The necessary acid-free conditions of the solution in the reaction cell for the experiments without addition of NH_4ClO_4 are extremely difficult to realize. In these series many runs had to be rejected. A reliable initial criterion proved to be the reproducibility of a series of successive runs from the same stock solution. A further criterion is the obeying of the expected concentration dependence (see the Results

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Table I. Thermodynamic and Activation Parameters for Ammoniation in Liquid Ammonia^a

complex		$k_2 K^{CB}$, m s ⁻¹	$k_2 (K^{CB})^{1/2}$, m ^{1/2} s ⁻¹	K^{CB} , m	k_2 , s ⁻¹
<i>cis</i> -[Co(NH ₃) ₄ Cl] ²⁺	$\Delta H^{(*)}$ ^b	75 ± 2	72 ± 3	6	69
	$\Delta S^{(*)}$ ^c	-32 ± 6	19 ± 13	-102	70
[Co(NH ₃) ₅ Cl] ²⁺	$\Delta H^{(*)}$ ^b	86 ± 2	89 ± 2	-6 (-8) ^d	92 (95) ^d
	$\Delta S^{(*)}$ ^c	-18 ± 8	61 ± 7	-158 (-172) ^d	140 (159) ^d

^a At a constant ionic medium of 0.20 *m* ClO₄⁻; each column in this table gives the values of the activation parameters belonging to the rate or equilibrium constant at the top of the column. ^b In units kJ mol⁻¹. ^c In units J K⁻¹ mol⁻¹. ^d In parentheses, the value from ref 6.

section). The ammoniation of chloropentaamminecobalt(III) was followed photometrically at 532 nm; in the runs with excess ammonium perchlorate, the acid concentration was varied between 10⁻⁴ and 0.04 *m* at a fixed complex concentration of 0.005 *m* in the temperature range -50 to 0 °C (17 independent data points); in the experiments without added acid, the complex concentration was varied between 10⁻³ and 0.02 *m* in the temperature range -45 to -25 °C (51 independent data points). The ammoniation of dichlorotetraamminecobalt(III) to the pentaammine could be studied free from the subsequent ammoniation, as evidenced by the persistence of two isosbestic points in the spectrum, at 408 and 513 nm. The reaction was followed at 610 nm; in one series, the ammonium perchlorate concentration was varied between 10⁻³ and 10⁻² *m* at a fixed complex concentration of 0.005 *m* in the temperature range -50 to -30 °C (23 independent data points). In a second series the complex concentration was varied between 0.005 and 0.020 *m* in the temperature range -70 to -50 °C (24 independent data points). In all cases, a first-order rate law was obeyed within 0.5% for at least 3 half-lives. Temperature accuracy was 0.05 °C.

Kinetics of ¹H-²H Exchange. The exchange was studied by following the ¹H NMR resonances of the complexes, dissolved in N²H₃, as a function of time, employing the apparatus and procedure described.⁸ Temperature accuracy was 0.2 °C. Reactions were followed up to 3 half-lives. For each kinetic run, at least 10 data points were collected. The reproducibility of the ¹H integrals is ±3%. The integral values could be fitted to a first-order rate law within the same limits. Consequently, no secondary isotope effects were observed. The estimated accuracy of the rate constants obtained is 10%. The systems were studied at a fixed complex concentration of 0.15 *m* and varying concentration of N²H₄ClO₄ in a constant ionic medium of 1.00 *m* perchlorate (addition of KClO₄). In the medium employed, [Co(NH₃)₅Cl]²⁺ shows well-resolved singlet resonances at 3.57 (*cis*-NH₃) and 3.14 (*trans*-NH₃) ppm, *cis*-[Co(NH₃)₄Cl]²⁺ at 3.24 (*cis/trans*-NH₃) and 3.76 (*cis/cis*-NH₃) ppm (positions relative to the NH₃ resonance in N²H₃).

Stereochemistry. The steric course of the first step of ammoniation of *cis*-[Co(NH₃)₄Cl]₂(ClO₄) was determined by performing the reaction in ¹⁵NH₃ at -75 °C, as described for the *trans* complex.⁸ The ¹H NMR spectrum of the isolated reaction product was recorded on a Bruker WM-250 spectrometer in acidified dimethyl-*d*₆ sulfoxide. From the ratio of the *cis*- and *trans*-¹⁵NH₃ ¹H resonances, the product appeared to be 60 ± 2% *trans*-[Co(NH₃)₄(¹⁵NH₃)Cl](ClO₄)₂.

Results

Ammoniation. Under conditions of excess added acid (NH₄ClO₄), the ammoniation of *cis*-[Co(NH₃)₄Cl]₂(ClO₄) follows the rate law (eq 3) deduced on the basis of the CB mechanism⁶ (Figure 1). The small intercept, shown in Figure 1, is an as yet unex-

$$k_{\text{obsd}} = k_2 K^{CB} [\text{NH}_4\text{ClO}_4]^{-1} \quad (3)$$

plained artifact of the ammoniation reactions, found for many systems. In reality, the ammoniation rates invariably go to zero at large ammonium concentrations. Equation 3 also holds for the pentaammine, the first compound of which the ammoniation was studied in our group.⁶ We repeated the ammoniation of this complex, as our techniques have improved since then. Activation parameters were obtained by a weighted least-squares analysis on the basis of eq 3 and the Eyring formula. The overall fitting error was ±5%. Within this limit, no curvature was found. The results are in Table I.

The adherence to a first-order rate law exhibited by the reactions performed without addition of acid means that K^{CB} has the same value within the experimental error for the initial and the final ammine complex in the reactions.⁷ The discriminatory power of the experiment with reference to the difference in acidity of amminecobalt(III) complexes involved can be specified as follows: A computer simulation of the change of absorbance with time for the reactions without addition of acid revealed that for each of the steps in the sequence of ammoniations, tetraammine

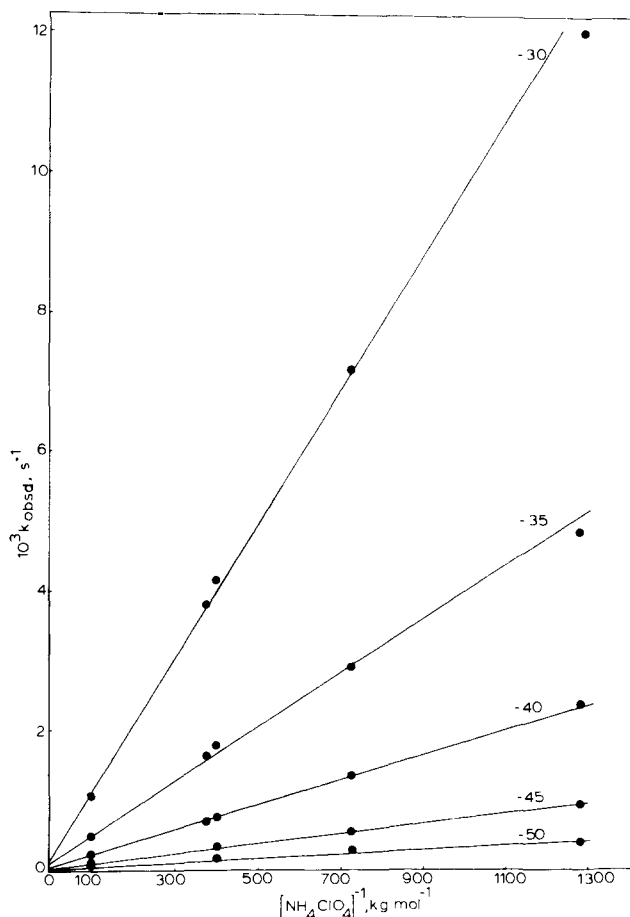


Figure 1. Variation of the observed pseudo-first-order rate constant of ammoniation with the reciprocal of the ammonium perchlorate concentration for *cis*-[Co(NH₃)₄Cl]₂(ClO₄) at constant ionic medium (0.20 *m*).

→ pentaammine → hexammine, there is a qualitative indication of a small increase of K^{CB} with increasing formal charge of the complex. The maximum value of the ratio $K^{CB}(\text{final})/K^{CB}(\text{initial})$ consistent with the spread of the observed kinetic data around a first-order dependence is 2. Within this limit then K^{CB} is the same for the three completely ion-associated complexes *cis*-[Co(NH₃)₄Cl]₂(ClO₄), [Co(NH₃)₅Cl](ClO₄)₂, and [Co(NH₃)₆](ClO₄)₃. Then the observed rate constant in dependence of the complex concentration, [Co]_{tot}, is given by eq 4. For reason of

$$k_{\text{obsd}} = k_2 (K^{CB})^{1/2} [\text{Co}]_{\text{tot}}^{-1/2} \quad (4)$$

conceptual simplicity, this equation involves the assumption that the most acidic proton site also gives the reactive conjugate base. This assumption is in no way self-evident; we will come back to this point later.

Pseudoactivation parameters were obtained by subjecting $k_{\text{obsd}}[\text{Co}]_{\text{tot}}^{1/2}$, i.e., $k_2(K^{CB})^{1/2}$, determined at different complex concentrations and different temperatures, to a weighted least-squares activation analysis on the basis of the Eyring formula. The average fitting error was ±10% for the tetraammine and ±5% for the pentaammine. The results are in Table I. From the values in Table I, activation parameters for k_2 and K^{CB} were calculated. The previously determined⁶ less-accurate values for the pentaammine are not far off (Table I).

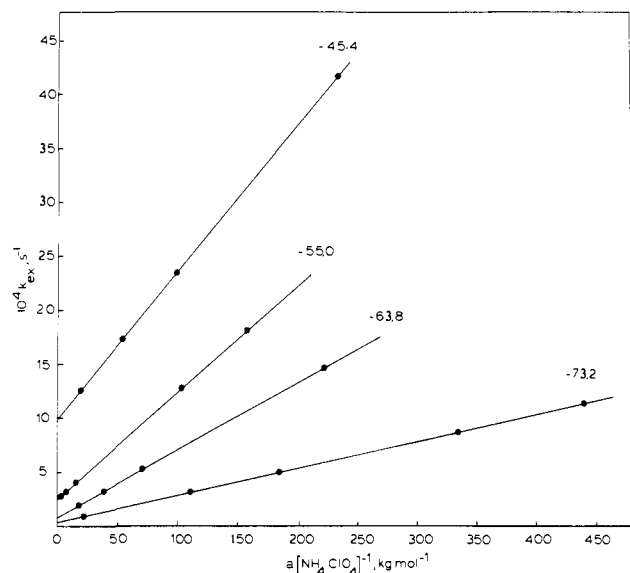


Figure 2. Variation of the observed pseudo-first-order rate constant of ^1H - ^2H exchange in N^2H_3 with the reciprocal concentration of perdeuterated ammonium perchlorate for the *cis*- NH_3 position of $[\text{Co}(\text{N}^2\text{H}_3)_5\text{Cl}](\text{ClO}_4)_2$ at constant ionic medium (1.00 *m*). Values of the scale factor are $a = 10$ (-45.4 °C), 3 (-55.0 °C), 1 (-63.8 °C), $1/3$ (-73.2 °C).

Table II. Kinetic Parameters for ^1H - ^2H Exchange in N^2H_3^a

temp, °C	$10^4 k_1^0$, s^{-1}	$10^5 k_1^1$, m s^{-1}
<i>cis</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (<i>cis/cis</i>)		
-45.3	3.7 ± 0.8	19.3 ± 0.6
-55.0	1.1 ± 0.4	4.1 ± 0.2
-66.4	0.4 ± 0.1	0.63 ± 0.02
-73.7	0.18 ± 0.03	0.107 ± 0.002
<i>cis</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (<i>cis/trans</i>)		
-66.4	17 ± 1	
-73.7	8.1 ± 0.5	
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ (<i>cis</i>)		
-45.4	10 ± 1	14 ± 1
-55.0	2.7 ± 0.2	3.0 ± 0.1
-63.8	1.0 ± 0.2	0.62 ± 0.01
-73.2	0.5 ± 0.2	0.084 ± 0.002

^a At a constant ionic medium of 1.00 *m*.

^1H - ^2H Exchange. Exchange at the *trans* position in the pentaammine proved to be too fast for accurate measurement. In the other cases, the observed exchange rate constants, k_{ex} , at constant temperature and varying acidity, obey¹⁰ eq 5 (Figures 2 and 3). A similar relation has been found for the acid de-

$$k_{\text{ex}} = k_1^0 + k_1^1[\text{NH}_4\text{ClO}_4]^{-1} \quad (5)$$

pendence of the rate-determining deprotonation in the ammoniation of *trans*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$. The parameter values obtained from a weighted least-squares analysis are in Table II. The *cis/trans*- NH_3 (position relative to Cl^-) of *cis*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ behaves exceptionally: k_1^1 is zero within the experimental error. Activation parameters were obtained from a weighted least-squares analysis on the basis of the Eyring formula. No curvature was observed in the $\ln(k/T)$ vs. T^{-1} plots.

Discussion

Acid Dissociation Constants. As stated above, obedience to a first-order rate law in ammoniation reactions without addition of acid means that the difference in K^{CB} between initial and final ammine complex falls outside the discriminatory power of the experiment (a factor of 2 in the K^{CB} values). This holds for the two complexes described in the Results section, but it has also been observed for the azido- and the nitratopentaammine. Consequently, we now have four sets of thermodynamic parameters for K^{CB} that should be approximately identical. The data obtained are (given in parentheses as ΔH° (kJ mol^{-1}), ΔS° (J K^{-1}

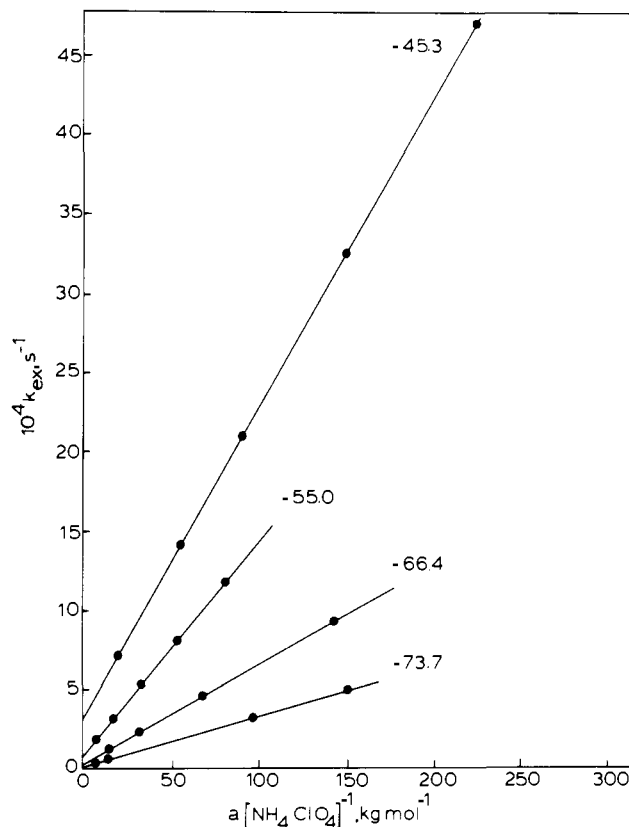


Figure 3. Variation of the observed pseudo-first-order rate constant of ^1H - ^2H exchange in N^2H_3 with the reciprocal concentration of perdeuterated ammonium perchlorate for the *cis/cis*- NH_3 position of *cis*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2](\text{ClO}_4)_2$ at constant ionic medium (1.00 *m*). Value of the scale factor are $a = 10$ (-45.3 °C), 3 (-55.0 °C), 1 (-66.4 °C), $1/3$ (-73.7 °C).

mol^{-1}), as follows: $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ (-6 , -158), *cis*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (6 , -102), $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$ (-4 , -134),¹⁵ $[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{2+}$ (-11 , -164).⁷ The sets show differences. If the mechanistic model is correct, ΔG° values at the reaction temperatures have been proved to be equal within the experimental error. Additional errors in ΔH° and ΔS° will then be introduced by the analysis of the temperature dependence, probably as a result of the widely differing and necessarily limited temperature ranges employed for the systems. An important factor may be curvature in the van't Hoff plot over the entire range, -70 to $+40$ °C, for our weak ammine acids, unnoticeable in the smaller experimentally realized ranges (20–30 °C). If this picture is correct, a compensation effect between ΔH° and ΔS° , evidenced by an isokinetic relationship, should be present.¹⁶ Indeed, the four entries exhibit an isokinetic relationship (correlation coefficient $r = 0.968$) with an isokinetic temperature of 260 K, which is satisfactorily close to the center of the temperature range.

A conclusion from the above is the factual equality of the acid dissociation constants of the hexaammine, the pentaammines (independent of the acido ligand), and the *cis*-tetraammine. It is not reasonable to assume that the *trans*-coordinated NH_3 in the pentaammines, which exchanges its protons orders of magnitude faster than the *cis*- NH_3 ligands (Table II), has a negligible acid dissociation. Then the results suggest that the acidity of ammonia coordinated to Co^{3+} in liquid ammonia is almost independent of the remainder of the complex (nature and position of other ligands and formal charge). This conclusion is in agreement with earlier acid dissociation studies in our laboratory¹⁷ and with the well-known leveling effect of the solvent on acid

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Table III. Activation Parameters and Rate Constants for the Individual Steps of Ammoniation

	k_1^0, s^{-1}	$k_1^1, m s^{-1}$	k_2, s^{-1}	K_0^{CB}, m	$k_{-1}^0, m^{-1} s^{-1}$	k_{-1}^1, s^{-1}	$k_2 K_0^{CB}, m s^{-1}$	$k_2/k_{-1}^0, m$	k_2/k_{-1}^1
<i>cis</i> -[Co(NH ₃) ₄ Cl ₂] ⁺ (<i>cis/cis</i>) ^a									
$\Delta H^{\ddagger b}$	38	67	69	6	32	61	75	37	8
$\Delta S^{\ddagger c}$	-143	-21	75	-122	-21	101	-32	96	-26
$\log k(-40)^d$	-3.3	-3.4	1.1	-7.7	4.4	4.3	-5.8	-3.3	-3.2
<i>cis</i> -[Co(NH ₃) ₄ Cl ₂] ⁺ (<i>cis/trans</i>) ^a									
$\Delta H^{\ddagger b}$	32		69	6	26		75	43	
$\Delta S^{\ddagger c}$	-140		75	-122	-18		-32	93	
$\log k(-40)^d$	-1.8		1.1	-7.7	5.9		-5.8	-4.8	
<i>trans</i> -[Co(NH ₃) ₄ Cl ₂] ⁺ ^e									
$\Delta H^{\ddagger b}$	57	67	53 ^f	6 ^f	51 ^f	61 ^f	59	2	-8
$\Delta S^{\ddagger c}$	-62	-79	46 ^f	-122 ^f	60 ^f	43 ^f	-55	-14	3
$\log k(-40)^d$	-3.3	-6.4	3.2	-7.7	4.4	1.3	-3.4	-1.2	1.9
[Co(NH ₃) ₅ Cl] ²⁺ (<i>cis</i>) ^a									
$\Delta H^{\ddagger b}$	50	68	92	-6	56	74	86	36	18
$\Delta S^{\ddagger c}$	-81	-17	143	-182	101	165	-18	42	-22
$\log k(-40)^d$	-2.7	-3.4	-0.5	-8.2	5.4	4.7	-7.5	-5.9	-5.2

^a Assumed position (relative to Cl⁻) of NH₃ deprotonated in the formation of the reactive base. ^b In units kJ mol⁻¹. ^c In units J K⁻¹ mol⁻¹. ^d Calculated value of rate constant at -40 °C. ^e Reference 8. ^f Calculated from the assumption $K_0^{CB}(\text{trans}) = K_0^{CB}(\text{cis})$.

dissociation.¹⁸ An additional cause will be the state of complete ion association involved.

Dissection into Individual Rate Constants. In view of the conclusion reached in the preceding paragraph, we define K_0^{CB} as the acid dissociation constant for a single proton site of coordinated ammonia in a complex that has n_1 active sites (leading to ammoniation) and n_2 inactive sites. Then the equations describing the acid dependence of the rate constant of ammoniation have to be rewritten: eq 3 to eq 6 and eq 4 to eq 7.¹⁹ The inherent

$$k_{\text{obsd}} = n_1 k_2 K_0^{CB} [\text{NH}_4\text{ClO}_4]^{-1} \quad (6)$$

$$k_{\text{obsd}} = k_1 (n_1 + n_2)^{-1/2} k_2 (K_0^{CB})^{1/2} [\text{Co}]_{\text{tot}}^{-1/2} \quad (7)^{19}$$

assumption on the quality of k_2 for different sites will be justified in the following. Reanalysis of the parameters of Table I on the basis of eq 6 and 7 gives the new values entered in Table III. The assumption of the constancy of K_0^{CB} makes it also possible to calculate K^{CB} and consequently k_2 for the *trans*-[Co(NH₃)₄Cl₂]⁺ by using activation parameters from the *cis* compound. For the *trans*-tetraammine, an experimental split of k_2 and K^{CB} is essentially inaccessible, because the mechanism of ammoniation turns to rate-limiting deprotonation at low acidity.⁸

Now also the reprotonation constants k_{-1}^0 and k_{-1}^1 can be calculated from the relationship $K_0^{CB} = k_1^0/k_{-1}^0 = k_1^1/k_{-1}^1$. The difference in ionic strength between the ammoniation (0.20 *m*) and the exchange experiments (1.00 *m*) is without effect, as demonstrated earlier.²⁰ The values obtained are in Table III. In this table, k_2 values and its combinations for the *cis*-tetraammine are given for the two possibilities, that either the *cis/cis*- or the *cis/trans*-coordinated (relative to Cl⁻) NH₃ gives the reactive conjugate base. Fast intramolecular proton exchange in the conjugate base before the elimination of the leaving group is unlikely.²¹ Inspection of Table III leads to the conclusion that there is no inconsistency in the k_{-1} values (both k_{-1}^0 and k_{-1}^1) obtained, in the sense that the diffusion limit is surpassed. Also the values of k_2/k_{-1} for the pentaammine and the *cis*-tetraammine are as expected for a fast preequilibrium mechanism. Unfortunately no proton-exchange results on *trans*-coordinated NH₃ in [Co(NH₃)₅Cl]²⁺ could be obtained. Extrapolation of the data¹⁰ on the slower exchange in N²H₃ combined with the value of the isotope effect (vide infra) also gives k_{-1} values under the diffusion limit.

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(19) During ammoniation, the factor $(n_1 + n_2)^{-1/2}$ will change to $(n_1 + n_2 + 3)^{-1/2}$; this effect falls well within the experimental error. A similar situation exists for the variation of K^{CB} between complexes having a different number of proton sites.

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All this means that a kinetic analysis cannot decide upon the position of the amido group in the reactive conjugate base. However, the fact that now rate constants (k_2) are available for the elimination reaction 2, for the chloro-pentaammine and both *cis*- and *trans*-dichlorotetraammine, enables an inference from the relative reactivities. The assumption of *trans* activation for the pentaammine is difficult to sustain in view of the observed high reactivity of the *trans*-[Co(NH₃)₃(NH₂)Cl₂] conjugate base that is incapable of this activation. The reactivity order (determined by ΔH^{\ddagger}) of the conjugate bases, *trans*-[Co(NH₃)₃(NH₂)Cl₂] > *cis*-[Co(NH₃)₃(NH₂)Cl₂] > [Co(NH₃)₄(NH₂)Cl]⁺, can most easily be explained within a common *cis* activation mode. The lower reactivity of the pentaammine will then be caused by the higher formal charge. *Cis* activation in general is supported by a considerable accumulation of indirect evidence.²² We may then assume that *cis/cis* deprotonation in the *cis*-tetraammine leads to the reactive base.

Some additional comments will be made: (1) A comparison of *cis*- and *trans*-tetraammine indicates that the *trans* shows limiting behavior ($k_2 > k_{-1}$), because k_2 increases and k_{-1} decreases relative to the *cis* complex. (2) Neither the pentaammine nor the *cis*-tetraammine can go to limiting behavior in the accessible temperature range. (3) There is no obvious relation between activation parameters for deprotonation and the formal charge or the geometry of the complex. (4) Only for the rate constant k_2 do the activation parameters show an isokinetic relationship ($r = 0.992$), with $T_{\text{iso}} = 390$ K. (5) Rate-determining preisomerization of the *cis*-tetraammine conjugate base to the more reactive *trans* counterpart is not completely excluded. Comparison of the steric course of entry of NH₃ (100% *trans*-Cl⁻ for the *trans*⁸ and 60% *trans*-Cl⁻ for the *cis*) fixes the limit of this process to 60% of the total reaction. (6) In an earlier preliminary report,¹⁰ rate constants have been published for ²H-¹H exchange of *cis*-N²H₃ in [Co(N²H₃)₅Cl]²⁺ at -56.5 °C: $k_1^0 = 7 \times 10^{-5} s^{-1}$ and $k_1^1 = 2.1 \times 10^{-5} m s^{-1}$. Combined with the values calculated for -56.5 °C from the parameters in Table III, the observed compound isotope effect⁸ $k^{\text{H}}(\text{NH}_3)/k^{\text{H}}(\text{N}^2\text{H}_3)$ is 0.3 for k_1^0 and 0.9 for k_1^1 . The value 0.3 is in good agreement with the value of 0.26 (-40 °C) reported for k_1^0 of the *trans*-tetraammine.⁸ (7) The fact that the isotope effect is comparatively small will be a result of the large ΔpK_a difference between the partners in the H transfer.²³ For further comments on the magnitude of this effect, we refer to an elaborate discussion in the literature²⁴ and our adaption to reactions in liquid ammonia.⁸

Mechanism of ¹H-²H Exchange. In an early study on hydrogen isotope exchange of cobalt(III) ammine complexes in aqueous

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solution, Block and Gold⁹ realized that the only acceptable mechanism for the exchange is rate-determining H⁺ transfer from the complex ion to a base, demanding in principle general base catalysis. This phenomenon is not generally found for hydrogen exchange in aqueous solution, although it has been reported for [Co(trenen)X]²⁺ (X = Cl⁻, N₃⁻; trenen = 4-(aminoethyl)-1,4,7,10-tetraazadecane) by Sargeson and co-workers.²⁵ General base catalysis is also exhibited by some of the systems showing rate-limiting deprotonation in base hydrolysis.^{26,27} Liquid ammonia clearly exhibits general base catalysis in the exchange, if we ascribe the acid-independent part (k_1^0 of eq 5) to deprotonation by the solvent (NH₃) and the acid-dependent part (k_1^1) to a reaction with the solvent lyate ion, NH₂⁻.

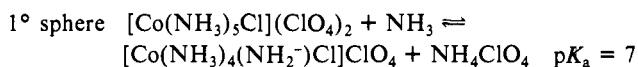
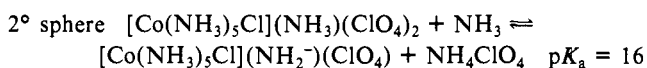
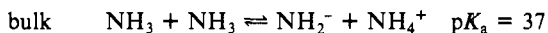
As the acidity of the cobalt(III) ammine complexes may be expected to be intermediate between that of NH₄⁺ and NH₃, and the differences in acidity will be large, reprotonation by NH₄⁺ (k_{-1}^0 route) and deprotonation by NH₂⁻ (k_1^1 route) may be expected to be diffusion-controlled.²⁸ The fact that the actually measured rates are well below this value can be explained for the k_{-1}^0 route by an unfavorable ion-association preequilibrium between NH₄⁺ and the positively charged complex.

The mechanism of deprotonation by NH₂⁻ presents more difficulties. Already from the empirical relation (eq 5), it is clear that k_1^1 derived here is a composite constant. The more, as the deprotonation process, analogous to deprotonation by OH⁻ in H₂O,⁹ will involve preassociation between the ammine complex ion and NH₂⁻. Then

$$k_1^1(\text{obsd}) = k_1^1(\text{real}) K_{\text{os}} K_{\text{auto}} \quad (8)$$

In eq 8, K_{auto} is the autoionization constant of ammonia, K_{os} is the ion-association constant for the complex ion and the amide ion, and $k_1^1(\text{real})$ is the rate constant for proton transfer within the ion pair.

K_{auto} is difficult to determine. It may be expected²⁹ to be as low as 10⁻³⁵ M². $k_1^1(\text{real})$ may be as large as a vibrational frequency (kT/h),³⁰ that is, $\approx 5 \times 10^{12}$ s⁻¹ at -40 °C. This means that for $k_1^1(\text{obsd}) = 3.7 \times 10^{-4}$ m s⁻¹ (pentaammine at -40 °C), K_{os} will be as large as 10¹⁹ m⁻¹. At first sight, this seems incredible. Perhaps a better way of presenting this outcome is a comparison of acid dissociation constants (K_a at -40 °C in units m; i.e., no explicit mention of the solvent concentration in K_a) for NH₃ in the bulk, the first and the second coordination sphere of the [Co(NH₃)₅Cl]²⁺ ion:



Now second-sphere NH₃ seems to bridge the large gulf in acidity between bulk and first-sphere NH₃. The concept of enhancement of the acidity of the ammonia molecule in the second sphere

resembles the explanation given by Block and Gold for the absence of general base catalysis in the proton exchange at [Co(NH₃)₆]³⁺ in aqueous solution: Catalysis by hydroxide ions swamps the catalysis by other bases, because its high hydrogen-bonding power causes its value of the outer-sphere association constant with the hexaammine to exceed that of other bases.⁹ A similar difficulty as the one encountered here has been reported by Grunwald and Fong³¹ for exchange rates at [Pt(NH₃)₆]⁴⁺. There the much smaller surpassing of the diffusion rate limit was met by assuming³¹ rapid intramolecular proton exchange at the conjugate base, [Pt(NH₃)₅NH₂]³⁺. In this case too, increased acidity of second-sphere H₂O may be reverted to for a possible way out and to us seems the more probable explanation.

Reactivity of the Conjugate Base. A knowledge of the individual activation parameters of the generally rate-determining elimination reaction 2 should give more insight into the cause of the extraordinary reactivity of the conjugate base. Because of the constancy of K_0^{CB} , reactivity differences between various complexes stem from k_2 of reaction 2. Earlier reports from our laboratory^{6,7,32} have revealed that for the chloropentaammine, the cause of the reactivity is not so much the expected reduction of ΔH^\ddagger , compared to the spontaneous reaction, but rather the extraordinarily large value of ΔS^\ddagger . For the *cis*-[Co(NH₃)₄Cl₂]⁺ ion, activation parameters for a spontaneous reaction have not been reported. When the equation of *trans*-[Co(NH₃)₄Cl₂]⁺ is compared ($\Delta H^\ddagger = 92$ kJ mol⁻¹; $\Delta S^\ddagger = 10$ J K⁻¹ mol⁻¹),³³ it is striking that the conjugate base shows both a decrease of ΔH^\ddagger and an increase of ΔS^\ddagger (see Table III). Apparently, in contrast to the pentaammine, the tetraammines experience a considerable weakening of the bond to the leaving group in the conjugate base. This is even more conspicuous in the *trans* than in the *cis* isomer.

In earlier publications, one of us has tentatively located the large ΔS^\ddagger value of reaction 2 in the second coordination sphere^{32,34} and explained this phenomenon by a volume increase on activation.³² This was worked out in a volume profile, of which the assumptions concerning dielectric saturation and volume of the intermediate are no longer tenable, as follows from the work of Swaddle and co-workers.^{11,35} However, the general idea of an expansion of the solvation shell of the conjugate base on activation seems to be still worth following up. It fits in with recent conclusions drawn by Sargeson and co-workers⁴ from competition experiments. These authors found that the nucleophile is captured from a region that is better described as an ionic atmosphere in the Debye-Hückel sense than as a definite ion pair.

Unfortunately, activation and reaction volumes for ammoniation reactions in liquid ammonia are difficult to interpret on account of the extensive ionic association.¹⁵ The conclusion must be that the elusive problem of the reactivity of the conjugate base remains largely unsolved.

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Registry No. [Co(NH₃)₅Cl](ClO₄)₂, 15156-18-0; *cis*-[Co(NH₃)₄Cl₂](ClO₄), 96211-53-9; *trans*-[Co(NH₃)₄Cl₂](ClO₄), 26388-79-4; NH₃, 7664-41-7.

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