The position of the Mo atom was determined by direct methods. All the remaining non-hydrogen atoms were located by structure factor calculations and difference electron density maps. The structure was refined by full-matrix least-square techniques, minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/[\sigma^2(F_o^2) + (pF_o^2)^2]$, where p was set equal to 0.03. Hydrogen atoms were included as fixed contributions at idealized coordinates in the final cycles of refinement. Refinement of the model with anisotropic thermal parameters for Mo, N1, N2, S1, S2, O1, and O2 resulted in $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.074$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.058$. The "goodness of fit" $[\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2} = 1.569$, where n is the number of data (2355) and m is the number of variables (204). Atomic coordinates are given in Table V; anisotropic thermal parameters and values of $|F_o|$ and $|F_c|$ are available as supplementary data.

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Registry No. Mo(hbma)$_2$, 86953-19-7; Mo(hbha)$_2$, 86942-41-8; MoO$_2$(haeH$_2$), 86942-43-0; MoO$_2$(hbpdH$_2$), 84214-36-8; MoO$_2$(acac)$_2$, 17524-05-9; [Et$_4$N][MoO(SC$_6$H$_4$CH$_3$)$_4$], 86942-45-2; [Et$_4$N][Mo(hbma)$_2$], 86953-21-1; [Mo(hbha)$_2$]$^-$, 86953-22-2; [MoO(hae)]$^-$, 86953-23-3; [MoO(hbpd)]$^-$, 86942-46-3; [Et$_4$N][MoO(mae)], 74577-39-2; [Et$_4$N][MoO(mab)], 74577-41-6; Zn(hbpH$_2$), 86942-47-4.

Supplementary Material Available: Listings of thermal parameters and structure factors for [Et$_4$N][Mo(hbma)$_2$] (11 pages). Ordering information is given on any current masthead page.

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Proton Exchange in the Base-Catalyzed Ammoniation of the *trans*-Dichlorotetraamminecobalt(III) Cation

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The ammoniation of the *trans*-[Co(NH$_3$)$_4$Cl$_2$]$^+$ cation to [Co(NH$_3$)$_5$Cl]$^{2+}$, studied in liquid ammonia between −40 and −60 °C, follows the two-step conjugate-base mechanism and gives over 98% stereochemical retention, as shown by ^{15}NH$_3$ labeling. Activation parameters for the overall reaction ($K^{CB}k_2$) are $\Delta H^\ddagger = 59$ kJ mol^{-1} and $\Delta S^\ddagger = -55$ J K^{-1} mol^{-1}. At ammonium perchlorate concentrations below 0.01 mol kg^{-1} deprotonation is rate determining and exhibits general base catalysis, with NH$_3$ and NH$_2^-$ as proton-abstracting bases. Activation parameters for the proton abstraction by NH$_3$ are $\Delta H^\ddagger = 57$ kJ mol^{-1} and $\Delta S^\ddagger = -62$ J K^{-1} mol^{-1}. ^{1}H NMR measurements in N^{2}H$_3$ during ammoniation revealed the loss of one proton in the formation of the pentaammine. The ratio between the rate constants for dissociative elimination of the chloro ligand and proton reentry via the solvent path has an average value of 88. At high ammonium concentrations (>0.1 mol kg^{-1}) acid-dependent reprotonation becomes faster than the elimination of the chloro ligand, thus reverting the reaction to "normal" behavior, exemplified by a relatively fast proton-transfer preequilibrium.

Introduction

Base-catalyzed hydrolysis of cobalt(III) amine complexes can be explained by the two-step conjugate-base (CB) mechanism, consisting of a fast proton-transfer preequilibrium, followed by a rate-determining dissociative elimination of the leaving group.[1,2] Tobe and co-workers found that base hydrolysis and reprotonation are comparable in rate for a number of complexes of the *trans*-[CoL$_4$X$_2$]$^+$ type, where L$_4$ is a four-nitrogen donor set and X is a halide.[3,4]

Our group has been studying base-catalyzed ammoniation reactions of cobalt(III) and rhodium(III) complexes.[5-10] From the results obtained it seems that up to now at least two complexes of the *trans*-[CoL$_4$X$_2$]$^+$ type show limiting behavior in liquid ammonia: the first ammoniation step of the *trans*-[dichloro[(*RS*)-1,9-diamino-3,7-diazanonane]cobalt(III)] cation[10] and of the *trans*-dichlorobis(ethylenediamine)cobalt(III) cation.[7,11]

For liquid ammonia, in contrast to water, the reprotonation reaction is pH dependent. Therefore it should be possible to effect a transition from the limiting (as to proton transfer) to the "normal" case. For the further elucidation of the mechanism of base-catalyzed reactions, we made a search for cobalt(III) complexes showing the behavior indicated. Among a number of *trans*-[CoL$_4$X$_2$]$^+$ systems with apparent rate-determining deprotonation, the only compound that satisfies the conditions set out above is the *trans*-[Co(NH$_3$)$_4$Cl$_2$]$^+$ cation.

We present here the medium dependence of the base-catalyzed ammoniation of this compound, together with a definite proof of the role of proton transfer in the mechanism by NMR isotopic techniques.

Experimental Section

Materials. *trans*-[Co(NH$_3$)$_4$Cl$_2$]Cl was prepared from [Co(NH$_3$)$_4$CO$_3$]$_2$(SO$_4$)·3H$_2$O[12] by the Jörgensen method described by Glemser.[13] The perchlorate was prepared by dissolving the chloride

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rapidly (to prevent hydrolysis) in water, followed by filtering into an ice-cold solution of 30% perchloric acid. The perdeuterated complex was obtained by dissolving the carbonato complex in a minimum amount of ^2H_2O (pH 10 with NaO^2H); after a few minutes at room temperature a double volume of 35% HCl was added; after heating to 60 °C green crystals separated. The degree of exchange was determined with ^1H NMR to be over 95%. Elemental analyses (Co, Cl) revealed the purity to be better than 99%. Potassium perchlorate (Baker Chemicals) was recrystallized from a slightly alkaline aqueous solution and dried by heating at 350 °C for 15 min. Ammonium perchlorate (Fluka) was used without further purification. All solids were dried thoroughly before use and stored in vacuo over sodium hydroxide.

Liquid ammonia was purified and stored as usual.[14] Perdeuterated ammonia was prepared by the reaction of ^2H_2O (Aldrich, 99.8%) with Mg_3N_2[15] in a closed system.[16] Gaseous N^2H_3 obtained in this way was dried over Mg_3N_2 and condensed on potassium. It was then distilled into a stainless steel cylinder, where it was kept over potassium. The degree of deuteration was established by NMR to be better than 98.5%.

Kinetic Measurements. The solutions were made up in a closed stainless steel/glass system under dry nitrogen gas. The reactions were monitored at 320 nm on a Beckman UV 5230 spectrophotometer equipped with a thermostated compartment, containing a thermostated stainless steel measuring cell with quartz windows. The temperature of the solution was kept constant within 0.05 °C by circulating cold nitrogen gas within the compartment and through the walls of the measuring cell separately. The reaction temperature was measured with a platinum resistance thermometer placed in direct contact with the solution. First-order rate constants were obtained from the kinetic runs by a least-squares fitting procedure.[17] The error of the fit was in all cases better than 0.5%. For the isotopically pure systems, no systematic trends were observed in residual absorbances for at least three half-lives.

All kinetic runs were performed at a constant ionic medium of 0.20 mol kg^{-1} ClO_4^-, obtained by the addition of the calculated amount of potassium perchlorate. The ammonium perchlorate concentration was varied between 0.001 and 0.200 mol kg^{-1}; the complex concentration was fixed at 0.001 mol kg^{-1}. The isotope effects were investigated at −40.00 °C and an ammonium perchlorate concentration of 0.010 mol kg^{-1}.

NMR Measurements. The proton exchange was followed on a Bruker WH-90 spectrometer, of which the standard 5-mm ^1H probe and the temperature control were adapted. To minimize the heat leak to the probe, the metal holder of the thermocouple was replaced by a Pt-100 resistance thermometer, in a nonmetallic (Delrin) fitting, placed 1 mm below the bottom of the sample tube. The temperature was regulated with a Cryoson TRL6 unit, equipped with an extra needle valve for an improved adjustment of the flow of the coolant (dry nitrogen). The electronic compartment was protected from moisture by fluxing with dry nitrogen. In this way the temperature was kept constant within 0.2 °C for several hours. Before and after each kinetic run the temperature was measured with a thermocouple, held in a glass capillary in the center of a methanol-filled spinning tube. The temperature gradient in the spinning tube appeared to be less than 0.05 °C.

Solutions were made up in a closed system under dry nitrogen gas by condensing a known volume of N^2H_3 in a NMR tube containing the complex and calculated amounts of ammonium and potassium perchlorate. The stoppered sample tubes were transferred into the NMR probe, which had already been brought to the desired reaction temperature. The extent of proton exchange during the ammoniation of *trans*-$[Co(NH_3)_4Cl_2]ClO_4$ was obtained from the disappearance of the ^1H resonance of a 0.08 mol kg^{-1} solution of the complex. Reactions were followed up to more than 80% completion. For each kinetic run at least 10 data points were collected. The reproducibility of the ^1H integrals is ±3%. The data points could be fitted to a first-order rate law within the same limits. Consequently no secondary isotope effect was observed. The estimated accuracy of the rate constants obtained is 10%.

Stereochemistry. The steric course of ammoniation of *trans*-$[Co(NH_3)_4Cl_2]ClO_4$ was determined by performing the reaction in $^{15}NH_3$. In a high-vacuum glass system, 1000 cm^3 (STP) of $^{15}NH_3$ gas (VEB, Berlin, >99%) was condensed at −75 °C onto 100 mg of the complex. After dissolution of the complex the temperature was raised to −65 °C. The reaction time was 10 min. To prevent the formation of the hexaammine, the liquid $^{15}NH_3$ was distilled off at −45 °C, back into the storage bottle, and the remaining solid product was collected. The ^1H NMR spectrum of this product was recorded on a Brucker WM-250 spectrometer in acidified dimethyl-d_6 sulfoxide.

Results

Kinetic Data. Adaption of the complete conjugate-base reaction scheme[3] for the base-catalyzed ammoniation (reaction 1) to liquid ammonia as solvent, including the two independent

$$\textit{trans-}[Co(NH_3)_4Cl_2]ClO_4 \xrightarrow[ClO_4^-]{NH_3} [Co(NH_3)_5Cl](ClO_4)_2 \tag{1}$$

deprotonation routes that may be expected,[10] leads to eq 2–5.

$$[Co(NH_3)_4Cl_2]ClO_4 + NH_3 \underset{k^0_{-1}}{\overset{k^0_1}{\rightleftharpoons}} [Co(NH_3)_3(NH_2)Cl_2] + NH_4ClO_4 \tag{2}$$

$$[Co(NH_3)_4Cl_2]ClO_4 + KNH_2 \underset{k^1_{-1}}{\overset{k^1_1}{\rightleftharpoons}} [Co(NH_3)_3(NH_2)Cl_2] + KClO_4 + NH_3 \tag{3}$$

$$[Co(NH_3)_3(NH_2)Cl_2] \xrightarrow{k_2} [Co(NH_3)_3(NH_2)Cl]\cdot Cl \tag{4}$$

$$[Co(NH_3)_3(NH_2)Cl]\cdot Cl \xrightarrow[\text{medium}]{\text{reaction}} [Co(NH_3)_5Cl](ClO_4)_2 \tag{5}$$

In formulating these equations the fact is accounted for that in the ionic medium used, ion association with the perchlorate, swamping the chloride, is nearly complete.[14] In the formulation of reaction 4, the dissociative elimination of the leaving Cl^- ligand, this chloride is most probably retained in the second coordination sphere.[6,18] Equation 5 summarizes the rapid irreversible reaction with the ionic medium and the solvent. No direct addition of amide is possible, because it would make the reactions too fast to be measured and lead to polymerization reactions.[19] Therefore the reactions were performed in acidic medium (excess ammonium perchlorate); concentrations of the amide ion (eq 3) were converted to $[NH_4ClO_4]^{-1}$ units. A steady-state treatment leads to a pseudo-first-order rate law with the rate constant k_{obsd} given by eq 6. Constant

$$k_{obsd} = \frac{(12k^0_1 + 12k^1_1[NH_4ClO_4]^{-1})k_2}{k^0_{-1}[NH_4ClO_4] + k^1_{-1} + k_2} \tag{6}$$

medium and solvent terms in eq 6 were omitted. The factor 12 in eq 6 results from the presence of 12 equivalent proton positions.

Figure 1 displays k_{obsd} as a function of the reciprocal ammonium perchlorate concentration (part B). The low $[NH_4ClO_4]^{-1}$ range is plotted on an enlarged scale as part A. No spontaneous ammoniation, analogous to the aquation reaction, is observed. From NMR and UV/vis measurements, *trans*-$[Co(NH_3)_4Cl_2]ClO_4$ and $[Co(NH_3)_5Cl](ClO_4)_2$ appeared to be the only species present. It is obvious that the relation between k_{obsd} and $[NH_4ClO_4]^{-1}$ reduces to linear relations for both high and low $[NH_4ClO_4]^{-1}$ values. For large

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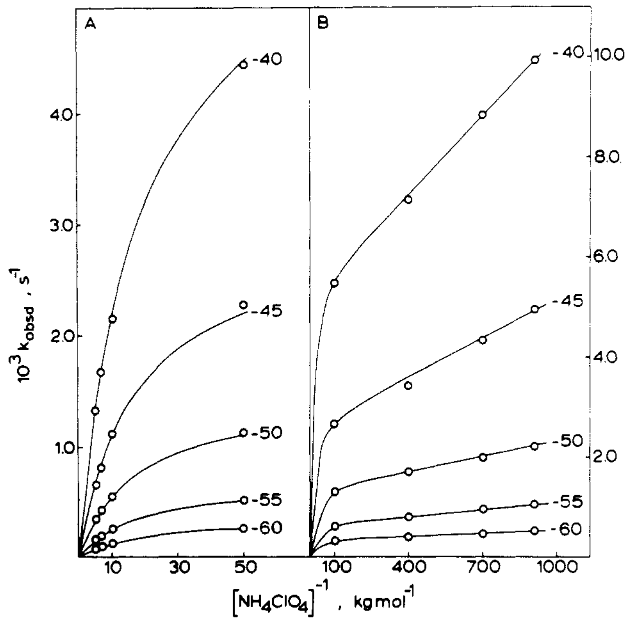

Figure 1. Variation of the observed photometric rate constant of the ammoniation with the reciprocal of the ammonium perchlorate concentration (part B). The data at low $[NH_4ClO_4]^{-1}$ values are plotted on an enlarged scale (part A). Drawn lines are calculated from eq 6 and the parameter values of Table I.

Table I. Kinetic Parameters for the Ammoniation of *trans*-$[Co(NH_3)_4Cl_2]ClO_4$

temp, °C	$10^4 k^0{}_1$, s^{-1}	$10^7 k^1{}_1$, mol kg^{-1} s^{-1}	$10^2 k_2$: $k^0{}_{-1}$, mol kg^{-1}	$10^4 K^{CB} k_2$,[a] mol kg^{-1} s^{-1}	k_2: $k^1{}_{-1}$[a]
−40.00	4.7	4.0	6.2	3.5	73
−45.00	2.28	2.01	6.7	1.8	76
−50.00	1.16	0.75	6.4	0.89	99
−55.00	0.54	0.37	6.3	0.41	92
−60.00	0.277	0.144	5.3	0.18	102
$\Delta H^\ddagger$, kJ mol^{-1}	57 ± 3	67 ± 3		59 ± 3	
$\Delta S^\ddagger$, J K^{-1} mol^{-1}	−62 ± 7	−79 ± 10		−55 ± 10	

[a] Calculated values.

Table II. Comparison of the NMR ^1H–^2H Exchange Rate Constant (k_{ex}) with the Photometric Deprotonation Constant ($k^0{}_1$)

temp, °C	$[NH_4ClO_4]$, mol kg^{-1}	$[ClO_4^-]$, mol kg^{-1}	$10^4 k_{ex}$, s^{-1}	$10^4 k_{ex}{}^{cor}$,[a] s^{-1}	$10^4 k^0{}_1$,[b] s^{-1}
−44.4	1.6	1.7	3.9	2.1	2.4
−50.4	1.0	1.1	2.2	1.2	1.0
−54.3	0.44	1.3	1.7	0.9	0.6
−54.3	0.90	1.0	1.2	0.6	0.6

[a] Corrected for the solvent isotope effect. [b] Calculated from the activation parameters of Table I.

ammonium concentrations, apparently eq 6 reduces to the linear eq 7, where K^{CB} is the conventional apparent acid

$$k_{obsd} = \frac{12k^0{}_1 k_2}{k^0{}_{-1}[NH_4ClO_4]} = K^{CB}k_2[NH_4ClO_4]^{-1} \qquad (7)$$

dissociation constant of the substrate.[8] This is the "normal" case of a rapid preequilibrium, followed by the rate-determining elimination. When low ammonium concentrations are approached, deprotonation becomes rate limiting, leading to eq 8 ($k_2 >> k^1{}_{-1}$, $k^0{}_{-1}[NH_4ClO_4]$). The difference between

$$k_{obsd} = 12k^0{}_1 + 12k^1{}_1[NH_4ClO_4]^{-1} \qquad (8)$$

water and liquid ammonia as media for the base-catalyzed solvolysis is the acid dependence of the reprotonation reaction 2, so that systems as the present one may be "forced" to "normal" behavior (eq 7) by taking a large acid concentration.

The complete set of k_{obsd} vs. $[NH_4ClO_4]$ data was subjected to a three-parameter fit on the basis of eq 6,[20] by use of a Marquardt fitting routine.[21] For all temperatures the mean deviation of the fit was less than 3%. The resulting values of the parameters $k^0{}_1$, $k^1{}_1$ and the ratio k_2:$k^0{}_{-1}$ are presented in Table I. From these the values of $K^{CB}k_2$ and k_2:$k^1{}_{-1}$ can be calculated. Activation parameters were obtained by a weighted least-squares method.[22] No curvature was found; the results are also presented in Table I. The parameter ratio k_2:$k^0{}_{-1}$ is the least accurate (the estimated accuracy is ±10%); the other parameters have accuracies better than 3%. That indeed the complete eq 6 gives a very good fit to the experimental points is illustrated by the drawn lines in Figure 1, which were calculated from the parameter values of Table I.

Isotope Effects. When the ammoniation proceeds by a rate-limiting deprotonation, it obeys all of the requirements for the separate study of a primary and a solvent isotope effect.[4] For the present case isotope effects were studied under optimal conditions (−40.00 °C, $[NH_4ClO_4]$ = 0.010 mol kg^{-1}), where the reaction is reasonably clean from the proton-transfer preequilibrium and one deprotonation route is dominant (proton abstraction by NH_3 according to eq 2, 92% of the overall reaction). As the proton abstraction via the amide presents a complicated set of equilibria, no attempt was made to determine isotope effects for this route. In order to determine the isotope effects, four series of experiments were made, with the resulting observed rate constants (in s^{-1}) given in an obvious notation: $k^H(NH_3) = 5.44 \times 10^{-3}$, $k^D(NH_3) = 2.71 \times 10^{-3}$, $k^H(ND_3) = 1.03 \times 10^{-2}$, $k^D(ND_3) = 4.57 \times 10^{-3}$. The resulting values for the primary isotope effects (k^H:k^D) are 2.0 and 2.3 for NH_3 and ND_3, respectively. The solvent isotope effect ($k(NH_3)$:$k(ND_3)$) has the values of 0.53 and 0.59 for the protonated and perdeuterated complex, respectively.

^{1}H NMR Data on Stereochemistry and Proton Exchange. The product of ammoniation of *trans*-$[Co(NH_3)_4Cl_2]^+$ in liquid $^{15}NH_3$ contained 10% $[Co(NH_3)_4(^{15}NH_3)_2]^{3+}$, as shown by NMR (a doublet ($J(^{15}NH)$ = 70 Hz) around a broad resonance at 3.40 ppm, relative to sodium 3-(trimethylsilyl)propanesulfonate). The main product, identified as $[Co(NH_3)_4(^{15}NH_3)Cl]^{2+}$ from the ^{1}H NMR spectrum,[23] appeared to be more than 98% isomerically pure trans.

^1H–^2H exchange was studied for the nondeuterated complex in N^2H_3. The conjugate-base mechanism outlined above predicts that at large ammonium concentrations ^1H–^2H exchange via the solvent path (eq 2) can be studied free from a subsequent ammoniation. From the NMR spectra it could be settled unambiguously that this condition was met. Table II contains exchange rate constants; the values obtained were corrected for the solvent isotope effect.

Under conditions that deprotonation is rate determining (eq 8) the rate of disappearance of the tetraamine signal, apart from the unknown isotope effect, should be equal to the photometrically determined ammoniation rate. Therefore ^1H–^2H exchange rate constants were also measured under these conditions ($[NH_4ClO_4]$ = 0.002 mol kg^{-1} and $[ClO_4^-]$ = 1.00 mol kg^{-1}) and compared to the photometric values. The

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(20) After dividing numerator and denominator by k_2 and putting $k^1{}_{-1}$ = 0.

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Table III. Disappearance of the ^1H NMR Signal During Ammoniation in N^2H_3[a]

time, s	int[b]	int (cor)[c]	% reaction[d]
3000	98	100	30
3285	95	97	33
3600	96	99	35
3900	96	99	37
4200	94	97	40
4455	95	99	41
4740	94	98	43
5100	94	99	46
5475	91	96	48
5820	92	98	50
6060	92	98	52
6420	90	97	54
6840	92	100	56
7260	89	98	58
7620	86	95	60
7980	88	98	62
9000	88	100	66
9570	83	96	68
10035	83	98	70

[a] Conditions −73.0 ± 0.2 °C; complex concentration 2×10^{-2} mol kg^{-1}; added NaCl, 2×10^{-3} mol kg^{-1}, and NH_4Cl, 9×10^{-2} mol kg^{-1}. [b] Integral (arbitrary units) of the ^1H NMR resonance of tetraammine and pentaammine. [c] Corrected for the ^1H–^2H exchange of the pentaammine. [d] Disappearance of *trans*-$[Co(NH_3)_4Cl_2]^+$.

results were (the photometric values, calculated from eq 8 and the activation parameters of Table I, in parentheses) 3.9 (1.8) $\times 10^{-4}$ s^{-1} at −64.7 °C and 1.2 (0.4) $\times 10^{-4}$ s^{-1} at 73.0 °C. If the isotope effect is close to 2, the agreement is satisfactory.

The interesting fact of the number of protons exchanging during ammoniation of the tetraammine under limiting conditions (eq 8) proved to be difficult to determine accurately, as the ^1H resonances of the tetraammine and the pentaammine partially overlap and the proton-exchange rates of the two cations are comparable. The most reliable results were obtained at low temperature and low acidity in a chloride medium; that was found to slow down the proton exchange of the pentaammine. Even then a correction[24] for the (separately determined) proton loss of the pentaammine was necessary. Representative results are given in Table III. During the ammoniation the value of the integral of the ^1H signal does not decrease significantly (constant at 98 ± 2). This is also evidenced by the statistical F value for a linear descent (1.08), obtained from regression analysis of the entries of Table III; theoretically $F = 4.4$ for 95% probability ($P = 0.95$). Loss of one proton during ammoniation is calculated to involve a 3.3% decrease of the ^1H integral from 30% to 70% reaction. Consequently the experimental result rules out the loss of more than one proton per act of ammoniation.

Discussion

Liquid ammonia provides a unique diagnostic tool for the study of the conjugate-base mechanism under conditions of rate-limiting behavior. The presence of an acid-dependent term ($k^0_{-1}[NH_4ClO_4]$) in the denominator of eq 6 allows reversion from a limiting case, like the *trans*-$[Co(NH_3)_4Cl_2]^+$ cation under discussion, to the "normal" case. This also means that the ratio $k_2:k^0_{-1}$ directly follows from the medium dependence of the observed rate. The implicit definite demonstration of a two-step conjugate-base mechanism proves that ammoniation under rate-limiting conditions is not a concerted process, as claimed for base hydrolysis.[25] In the limiting case of rate-determining deprotonation (eq 8), as expected,[4] general-base catalysis (different routes for NH_3 and NH_2^- as a base) shows up. The stereochemical retention of configuration on ammoniation is completely in line with the picture presented by the aqueous limiting cases.[3]

The postulated role of deprotonation in the reaction mechanism was tested by determining the rate of proton transfer from ^1H–^2H exchange. The necessary higher ionic strength (compared to the photometric measurements) is not expected to influence the rates appreciably, as inferred from an extensive study of ionic strength effects on the analogous reaction of the *trans*-$[Co(en)_2Cl_2]^+$ ion.[26] From the exchange experiments at high acidity we obtained values of k^0_1 that are, after correction for the solvent isotope effect, equal within experimental error to the k^0_1 values obtained photometrically.[27] This direct proof of the mechanism is novel. In addition the agreement between the NMR and the photometric ammoniation rates (k^0_1 values) means that between deprotonation and reprotonation the second coordination sphere rearranges sufficiently to prevent reentry of the abstracted proton, in contrast to what has been found for aqueous solutions by Anderson et al.[28]

The observed primary isotope effects reflect the findings for the base hydrolysis of a macrocyclic cobalt(III) amine, where a small primary isotope effect (1.7 at 13.5 °C) appeared unusual because of the small difference in basicity between the two species competing for the proton.[4] In the present case the expected difference in basicity is orders of magnitude larger ($\Delta pK \simeq 8$),[29] so the small values (2.0 or 2.3) seem to be less unusual. Remarkably the overall isotope effect ($k^{\mathrm{H}}(NH_3):k^{\mathrm{D}}(ND_3)$) is close to 1.

The calculated values of the activation parameters (Table I) for the present case apparently do not offer a reliable criterion for the mechanism, as they are similar for the "normal" and the limiting case. However, $\Delta H^{\neq}$ (59 kJ mol^{-1}) for $K^{\mathrm{CB}}k_2$ is small compared to the values (70–87 kJ mol^{-1}) obtained so far for the limited number of cobalt(III) complexes studied in liquid ammonia.[8] This low $\Delta H^{\neq}$ makes *trans*-$[Co(NH_3)_4Cl_2]^+$ the most reactive complex of the series in liquid ammonia. A similar exceptional sensitivity toward base hydrolysis is shown by the compounds for which proton transfer and base hydrolysis have similar rates.[2–4] Combined with the expected intensitivity of the acid dissociation constant K^{CB}, due to the leveling effect of liquid ammonia,[7,29] this suggests that the explanation of the large values of the ratios $k_2:k^0_{-1}$ and $k_2:k^1_{-1}$ for the ammoniation must involve an exceptionally large value of k_2.[30]

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Registry No. *trans*-$[Co(NH_3)_4Cl_2]^+$, 19173-71-8; NH_3, 7664-41-7; NH_4ClO_4, 7790-98-9; deuterium, 7782-39-0.

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(24) The value of the correction itself is not significantly affected over the region used by the assumption of the number of protons (1–3) exchanged on ammoniation.

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